SPONS' ENCYCLOPÆDIA

OF THE

INDUSTRIAL ARTS, MANUFACTURES

AND

COMMERCIAL PRODUCTS.

DIVISION I.

CONTAINING

ACIDS, ALCOHOL, ALKALIES, ALLOYS, ALUM, ARSENIC, ASPHALT,
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ENCYCLOPÆDIA

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INDUSTRIAL ARTS, MANUFACTURES, AND COMMERCIAL PRODUCTS.

ACID. (Fr., *Acide;* Ger., *Säure.*)

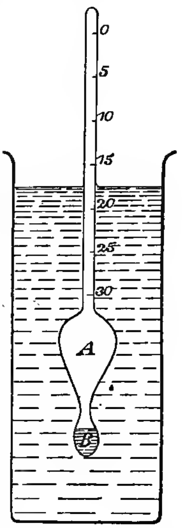
The term "*acid*" (Latin, *acidus*, sour) is applied in chemistry to a very large and important class of compounds, possessing certain distinctive properties. The most characteristic of these is the power of uniting with alkalies or bases to form *salts* which have neither acid nor alkaline properties. Every acid, in the strictest sense of the word, contains hydrogen. The difference between an acid and a salt will be readily seen by regarding an acid as a salt containing one or more atoms of hydrogen as its base, and having the power, when brought into contact with basic substances, under favourable conditions, of giving up all or part of its hydrogen, and taking up an equivalent quantity of the base in its stead. In the fewest words possible, an acid is a *salt of hydrogen*, or a compound in which the hydrogen may be readily replaced by a base or metal, so as to form a salt. There are other characteristics which, though not essential, are common to a large number of acids; they are (1), sourness of taste; (2), solubility in water; (3), the power of reddening blue organic colouring matters, such as litmus, &c.; and (4), that of decomposing carbonates with evolution of carbon dioxide. These secondary characteristics are extremely variable. The sourness from which the acids derive their name, and which was considered by the older chemists to be their most distinctive feature, is exceedingly intense in some, as sulphuric and acetic acids; in others, as benzoic acid, the acidity is so feeble as to be almost imperceptible, whilst others again excite no sensation of acidity when applied to the tongue. The same variableness is extended to the solubility of acids in water. All acids, however, possess in a greater or less degree the power of reddening tincture of litmus, just as all alkalies, on the other hand, restore to the reddened litmus its blue colour; this reaction with litmus forms the simplest test for acidity and alkalinity in liquid bodies.

By the chemist, then, the word "acid" is restricted to the so-called salt of hydrogen; and to him it has no reference whatever to the sourness of the substance, so long as it fulfils the primary condition that its hydrogen is replaceable by a base or metal. It is unfortunate that a name which not only fails to convey a correct impression to the uninitiated, but conveys a distinctly erroneous one, should have been extended to a class of bodies whose right to that name is based solely upon their fulfilment of the above condition.

The acids as a class are of very high importance in the arts and manufactures. The most important from a manufacturing point of view are sulphuric, hydrochloric, nitric, acetic, tartaric, citric, and oxalic; but a large number of others are manufactured and consumed, on a small scale, in the chemical industries of this country, of which acids a few of the best known only will be considered in the following articles.

ACIDIMETRY.—This is the name given to the processes employed for the determination of the strength of acids, or of the amount of *free acid* contained in a given weight or volume of an acid liquid. In the processes herein described it must be understood that the liquid under examination is in a state of tolerable purity, i. e. freedom from foreign matter, which would tend to give rise to inaccurate results. Thus, if a sample of nitric acid contained a small quantity of hydrochloric acid, the latter would be estimated as nitric acid and would apparently increase the result, whereas it should be diminished by the amount of hydrochloric acid present. It will thus be seen that unless the sample operated upon be absolutely free from other acids, only approximate results can be obtained. It is possible to estimate with some degree of accuracy the strength of an acid solution by the temperature at which it boils, or by its specific gravity. The latter means is, indeed, most commonly employed in manufacturing operations to test the strength of commercial acids. It has been ascertained that the specific gravity of an acid solution almost invariably bears a uniform relation to its strength, or degree of dilution; it is clear that if the density of absolutely pure sulphuric acid be 1·845, water being represented by 1, that a mixture of this with water in equal proportions would have a density exactly equal to the mean of those figures, and that according as acid or water predominated the density of the mixture would be higher or lower. In order to determine the density of such a mixture, and thereby its strength, or the amount of free acid which it contains, recourse is had to the small but exceedingly useful instrument known as the "hydrometer." We shall proceed to describe the principle on which this instrument depends, together with the two best-known forms and the mode of using. When a solid body is immersed in water, it is buoyed up by a pressure or force equivalent to the weight of a volume of water equal in bulk to the body immersed. In the same way, if it be plunged into a liquid of greater or less density than water, the pressure of the surrounding liquid, and the consequent buoyancy of the body, are also greater or less in proportion; and from the difference obtained by observing the depths to which the body sinks, first in the liquid under examination, and then in pure water, by means of a graduated scale attached to the sinking body, the density of the heavier or lighter liquid may be easily calculated, that of water representing unity. Most hydrometers are constructed on the same plan, and only differ from one another in the mode of graduation. They consist usually of a light glass tube, having an oval bulb A, Fig. 1, blown on the lower end. Below this bulb, which contains air, is another small bulb, B, weighted with shot or quicksilver in sufficient quantity to cause the tube to sink to a convenient depth in a liquid of the required density. Inside the tube is fixed a paper scale, the graduation of which is arbitrary. The hydrometer in common use in this country for testing the density of acids and other liquids heavier than water is that known as "Twaddell's." In this instrument the density of pure distilled water is represented by 0°, and the scale is graduated in such a manner that the specific gravity of the liquid may be calculated by multiplying the number of degrees registered on the scale by 5, and adding the product to 1000; thus the density of a liquid testing 100° Twaddell would be 100 × 5 + 1000 = 1500, or 1·500. The reading is made by placing the instrument in the liquid and observing the figure registered on the scale at the surface. Baumé's hydrometer is the form in use on the Continent; in shape it is exactly similar to the preceding, but the stem is graduated differently. It may be used for liquids either heavier or lighter than water, the graduation in one case being slightly different from the other. As this graduation is entirely arbitrary, in order to ascertain from the number of degrees registered the actual density of the liquid tested the following tables may be conveniently referred to:—

I.



FOR LIQUIDS LIGHTER THAN WATER.

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
10	1·000	23	·918	36	·849	49	·789
11	·993	24	·913	37	·844	50	·785
12	·986	25	·907	38	·839	51	·781
13	·980	26	·901	39	·834	52	·777
14	·973	27	·896	40	·830	53	·773
15	·967	28	·890	41	·825	54	·768
16	·960	29	·885	42	·820	55	·764
17	·954	30	·880	43	·816	56	·760
18	·948	31	·874	44	811	57	·759
19	·942	32	·869	45	·807	58	·753
20	·936	33	·864	46	·802	59	·749
21	·930	34	·859	47	·798	60	·745
22	·924	35	·854	48	·794		

FOR LIQUIDS HEAVIER THAN WATER.

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
0	1·000	8	1·056	16	1·118	24	1·188
1	1·007	9	1·063	17	1·126	25	1·197
2	1·013	10	1·070	18	1·134	26	1·206
3	1·020	11	1·078	19	1·143	27	1·216
4	1·027	12	1·086	20	1·152	28	1·226
5	1·034	13	1·094	21	1·160	29	1·236
6	1·041	14	1·101	22	1·169	30	1·246
7	1·048	15	1·109	23	1·178	31	1·256

FOR LIQUIDS HEAVIER THAN WATER—*continued.*

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
32	1·267	44	1·407	55	1·567	66	1·767
33	1·277	45	1·421	56	1·583	67	1·788
34	1·288	46	1·434	57	1·600	68	1·809
35	1·299	47	1·448	58	1·617	69	1·831
36	1·310	48	1·462	59	1·634	70	1·854
37	1·322	49	1·476	60	1·652	71	1·877
38	1·333	50	1·490	61	1·670	72	1·900
39	1·345	51	1·505	62	1·689	73	1·924
40	1·357	52	1·520	63	1·708	74	1·949
41	1·369	53	1·535	64	1·727	75	1·974
42	1·382	54	1·551	65	1·747	76	2·000
43	1·395						

The tables given below represent the actual percentages of real sulphuric, nitric, and hydrochloric acids corresponding to the various densities of their aqueous mixtures.

FOR SULPHURIC ACID. TEMPERATURE, 15° (60° F.).

Specific Gravity.	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.	Per cent.
1·8426	100	1·734	80	1·501	60	1·306	40	1·144	20
1·842	99	1·722	79	1·490	59	1·2976	39	1·136	19
1·8106	98	1·710	78	1·480	58	1·289	38	1·129	18
1·840	97	1·698	77	1·469	57	1·281	37	1·121	17
1·8384	96	1·686	76	1·4586	56	1·272	36	1·1136	16
1·8376	95	1·675	75	1·448	55	1·264	35	1·106	15
1·8356	94	1·663	74	1·438	54	1·256	34	1·098	14
1·834	93	1·651	73	1·428	53	1·2476	33	1·091	13
1·831	92	1·639	72	1·418	52	1·239	32	1·083	12
1·827	91	1·627	71	1·408	51	1·231	31	1·0756	11
1·822	90	1·615	70	1·398	50	1·223	30	1·068	10
1·816	89	1·604	69	1·3886	49	1·215	29	1·061	9
1·809	88	1·592	68	1·379	48	1·2066	28	1·0536	8
1·802	87	1·580	67	1·370	47	1·198	27	1·0464	7
1·794	86	1·568	66	1·361	46	1·190	26	1·039	6
1·786	85	1·557	65	1·351	45	1·182	25	1·032	5
1·777	84	1·545	64	1·342	44	1·174	24	1·0256	4
1·767	83	1·531	63	1·333	43	1·167	23	1·019	3
1·756	82	1·523	62	1·324	42	1·159	22	1·013	2
1·745	81	1·512	61	1·315	41	1·1516	21	1·0064	1

FOR HYDROCHLORIC ACID. TEMPERATURE, 15° (60° F.).

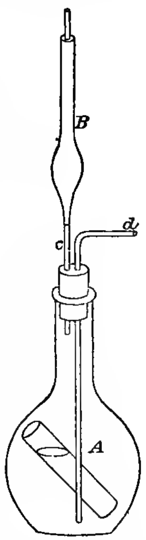
Specific Gravity.	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.	Per cent.
1·2000	40·777	1·1515	30·582	1·1000	20·388	1·0497	10·194
1·1982	40·369	1·1494	30·174	1·0980	19·980	1·0477	9·786
1·1964	39·961	1·1473	29·767	1·0960	19·572	1·0457	9·379
1·1946	39·554	1·1452	29·359	1·0939	19·165	1·0437	8·971
1·1928	39·146	1·1431	28·951	1·0919	18·757	1·0417	8·563
1·1910	38·738	1·1410	28·544	1·0899	18·349	1·0397	8·155
1·1893	38·330	1·1389	28·136	1·0879	17·941	1·0377	7·747
1·1875	37·923	1·1369	27·728	1·0859	17·534	1·0357	7·340
1·1857	37·516	1·1349	27·321	1·0838	17·126	1·0337	6·932
1·1846	37·108	1·1328	26·913	1·0818	16·718	1·0318	6·524
1·1822	36·700	1·1308	26·505	1·0798	16·310	1·0298	6·116
1·1802	36·292	1·1287	26·098	1·0778	15·902	1·0279	5·709
1·1782	35·884	1·1267	25·690	1·0758	15·494	1·0259	5·301
1·1762	35·476	1·1247	25·282	1·0738	15·087	1·0239	4·893
1·1741	35·068	1·1226	24·874	1·0718	14·679	1·0220	4·486
1·1721	34·660	1·1206	24·466	1·0697	14·271	1·0200	4·078
1·1701	34·252	1·1185	24·058	1·0677	13·863	1·0180	3·670
1·1681	33·845	1·1164	23·650	1·0657	13·456	1·0160	3·262
1·1661	33·437	1·1143	23·242	1·0637	13·049	1·0140	2·854
1·1641	33·029	1·1123	22·834	1·0617	12·641	1·0120	2·447
1·1620	32·621	1·1102	22·426	1·0597	12·233	1·0100	2·039
1·1599	32·213	1·1082	22·019	1·0577	11·825	1·0080	1·631
1·1578	31·805	1·1061	21·611	1·0557	11·418	1·0060	1·124
1·1557	31·398	1·1041	21·203	1·0537	11·010	1·0040	0·816
1·1536	30·990	1·1020	20·796	1·0517	10·602	1·0020	0·408

FOR NITRIC ACID. TEMPERATURE, 15° (60° F.).

Specific Gravity.	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.	Per cent.
1·530	100·00	1·456	79·00	1·363	58·00	1·225	36·00
1·529	99·52	1·451	77·66	1·358	57·00	1·218	35·00
1·523	97·89	1·445	76·00	1·353	56·10	1·211	33·86
1·520	97·00	1·442	75·00	1·346	55·00	1·198	32·00
1·516	96·00	1·438	74·01	1·341	54·00	1·192	31·00
1·514	95·27	1·435	73·00	1·339	53·81	1·185	30·00
1·509	94·00	1·432	72·39	1·335	53·00	1·179	29·00
1·506	93·01	1·429	71·24	1·331	52·33	1·172	28·00
1·503	92·00	1·423	69·96	1·323	50·99	1·166	27·00
1·499	91·00	1·419	69·20	1·317	49·97	1·157	25·71
1·495	90·00	1·414	68·00	1·312	49·00	1·138	23·00
1·494	89·56	1·410	67·00	1·304	48·00	1·120	20·00
1·488	88·00	1·405	66·00	1·298	47·18	1·105	17·47
1·486	87·45	1·400	65·07	1·295	46·64	1·089	15·00
1·482	86·17	1·395	64·00	1·284	45·00	1·077	13·00
1·478	85·00	1·393	63·59	1·274	43·53	1·067	11·41
1·474	84·00	1·386	62·00	1·264	42·00	1·045	7·22
1·470	83·00	1·381	61·21	1·257	41·00	1·022	4·00
1·467	82·00	1·374	60·00	1·251	40·00	1·010	2·00
1·463	80·96	1·372	59·59	1·244	39·00	0·999	0·00
1·460	80·00	1·368	58·88	1·237	37·95		

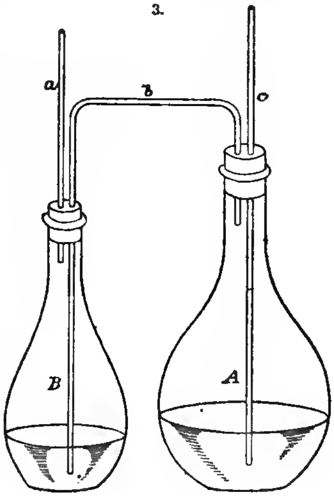
The use of the hydrometer in acidimetrical operations constitutes the simplest and roughest test employed. When any degree of accuracy is required, the operator must have recourse to the more elaborate and lengthy processes of chemical analysis. A description of these in full would be out of place in a work like the present, and we shall content ourselves with noticing briefly the most popular methods in use in the laboratory. One of these, and perhaps the simplest, depends upon the weight of carbonic acid gas evolved from bicarbonate of soda by a known quantity of acid. The apparatus required is shewn in Fig. 2, and may be readily constructed by the operator himself. It consists of a wide-mouthed flask A, furnished with a tightly-fitting cork, through which pass two glass tubes *c* and *d*. The tube *c* terminates in a bulb B, which is filled with chloride of calcium; the bent tube *d* reaches nearly to the bottom of the flask. A carefully weighed quantity of pure bicarbonate of soda is introduced into the flask and covered with distilled water. This done, a small glass test-tube containing a known volume of the acid to be examined (which must not be sufficient to decompose the whole of the alkali) is carefully lowered into the flask, in the position shown in the figure. The flask is then corked up, and accurately weighed on a delicate balance. After this, the acid in the test-tube is run out upon the alkali by causing the tube to slip into a horizontal position. By this means, a part of the alkali, equivalent to the amount of real acid in the liquid, is decomposed, the carbonic acid gas evolved escaping through the bulb-tube B; any moisture which may be carried upwards mechanically is absorbed by the chloride of calcium, the affinity of which substance for water is well known. When the whole of the acid has been neutralized, and the disengagement of gas has ceased, air is sucked through the tube B in order to withdraw any gas remaining in the flask and tubes. When perfectly cool, the whole apparatus is re-weighed. The difference between the two weighings represents the weight of carbonic acid expelled, and from this the amount of real acid in the volume of liquid operated upon may readily be calculated by multiplying it by the combining weight of the acid and dividing the product by 44, the combining weight of carbonic acid gas. Thus, suppose the weight of the apparatus before the experiment be 32·355 gram., and after the experiment 31·785 gram., the less in weight, ·570 gram., represents the amount of gas evolved from the bicarbonate of soda by the acid (say sulphuric acid). Then, $\frac{\cdot570 \times 98}{44} = 1\cdot27$ gram. of real sulphuric acid, the amount contained in the volume of liquid taken for experiment. The same method applies to the estimation of any acid which decomposes carbonates, the combining weight of such acid being substituted for that of sulphuric acid used in the above example.

2.



Another application of the same principle is a method devised by Fresenius and Will. The apparatus is shown in Fig. 3, and consists of two small flasks, A and B, A being slightly the larger. These are furnished with tightly fitting corks, through each of which pass the glass tubes *a*, *b*, and *c*, arranged as shown in the figure. The flask B is half filled with concentrated sulphuric acid, and in the other is placed the acid to be tested, accurately measured, and, if necessary, diluted with water. A test tube is now introduced into the flask A, in the same manner as described in the previous case; this tube contains bicarbonate of soda, in quantity more than sufficient to neutralize the whole of the acid contained in the sample. After carefully weighing the apparatus, the acid and alkali are allowed to mix; carbonic acid is evolved, passes through the sulphuric acid in the other flask, being thereby thoroughly dried, and escapes through the tube *a*. All effervescence having ceased, air is drawn through the two flasks by sucking at the extremity of the tube *a*, to remove any traces of carbonic acid remaining behind. When quite cool, the apparatus is reweighed, the loss representing the amount of carbonic acid disengaged from the alkali. The calculation to find the total quantity of acid in the volume of liquid employed is, of course, the same as in the preceding example.

3.



The estimation of acids by volumetric analysis is the exact converse of the method used in alkalimetry, since it depends upon the volume of an alkaline solution of known strength required to neutralize a given volume of the acid under examination. For a description of this process, the reader is referred to the article on "Alkalimetry."

Works for reference:—Fresenius' 'Quantitative Analysis'; Sutton's 'Volumetric Analysis.'

ACETIC ACID. (Fr., *Acide acétique;* Ger., *Essigsäure*). Formula of the hydrated acid $C_2H_4O_2$; of the anhydrous $C_4H_6O_3$. Specific gravity of the hydrated acid 1·064; of the anhydrous, according to Gerhardt, 1·073. Boiling points 104° (219° F.) and 137° (278° F.) respectively.

Pure acetic acid is a thin colourless liquid, with a pungent odour, which becomes suffocating without a liberal admixture of air. The purest acid solidifies below 15° (60° F.), forming large colourless crystals of prismatic or tabular form. In this, its "glacial" state, it does not redden litmus, requiring the addition of water for the development of acidity. It may, however, be kept in a closed vessel, if perfectly at rest, down to 12° in a liquid form, but upon the slightest agitation the whole body of acid immediately solidifies. Its vapour is exceedingly inflammable, burning with a bright blue flame and forming carbonic acid and water. Passed through a red-hot tube the greater part of the acid remains unchanged, but a portion is split up into free carbon and combustible gases, with acetone, napthalin, benzol, and hydrate of phenyl.

Readily miscible with water in all proportions, the specific gravity of the solution is, however, irregular, and forms only an uncertain test of strength. As will be noted from the following table given by Mohr ('Ann. der Chem. und Phar.' xxxi. 227), the density increases with the increased percentage of acid up to a certain point, but upon the further addition of acid falls away.

Per cent. of Acid.	Specific Gravity.	Per cent. of Acid.	Specific Gravity.	Per cent. of Acid.	Specific Gravity.	Per cent. of Acid.	Specific Gravity.	Per cent. of Acid.	Specific Gravity.
100	1·0635	80	1·0735	60	1·067	40	1·051	20	1·027
99	1·0655	79	1·0735	59	1·066	39	1·050	19	1·026
98	1·0670	78	1·0732	58	1·066	38	1·049	18	1·025
97	1·0680	77	1·0732	57	1·065	37	1·048	17	1·024
96	1·0690	76	1·0730	56	1·064	36	1·047	16	1·023
95	1·0700	75	1·0720	55	1·064	35	1·046	15	1·022
94	1·0706	74	1·0720	54	1·063	34	1·045	14	1·020
93	1·0708	73	1·0720	53	1·063	33	1·044	13	1·018
92	1·0716	72	1·0710	52	1·062	32	1·042	12	1·017
91	1·0721	71	1·0710	51	1·061	31	1·041	11	1·016
90	1·0730	70	1·0700	50	1·060	30	1·040	10	1·015
89	1·0730	69	1·0700	49	1·059	29	1·039	9	1·013
88	1·0730	68	1·0700	48	1·058	28	1·038	8	1·012
87	1·0730	67	1·0690	47	1·056	27	1·036	7	1·010
86	1·0730	66	1·0690	46	1·055	26	1·035	6	1·008
85	1·0730	65	1·0680	45	1·055	25	1·034	5	1·007
84	1·0730	64	1·0680	44	1·054	24	1·033	4	1·005
83	1·0730	63	1·0680	43	1·053	23	1·032	3	1·004
82	1·0730	62	1·0670	42	1·052	22	1·031	2	1·002
81	1·0732	61	1·0670	41	1·051	21	1·029	1	1·001

Acetic is one of the most powerful of acids, raising blisters if dropped upon the skin, and blackening organic substances after the manner of sulphuric acid. Owing to a peculiar and complex constitution, the crude acid (pyroligneous or commercial, i. e. the acid obtained by distilling acetate of lime with sulphuric or hydrochloric acid) is exceedingly uncertain in its action, a sample registering (say) 6° Tw. often producing as good results as one at 9°. The hydrated acid is a powerful solvent of various organic bodies, camphor, resins, essential oils, phosphorus, &c., and it is this and its ready combination with various bases, forming a series of well-known salts, that are its most valuable properties. These salts are remarkable for being all soluble in water; they may be formed by the direct action of the acid upon an oxide, or by the indirect means of double decomposition between an acetate and a salt of the base required. It should be noted that on account of its solvent power over copper and lead, acetic acid ought to be carefully tested for these substances, which the vessels used in the various processes of manufacture are liable to contaminate it with.

The anhydrous acid has been but little examined, and is, as yet at least, of comparatively small importance. It is a heavy, mobile liquid, colourless, and strongly refracting, with a powerful ethereal odour. Poured into water it does not readily dissolve, but falls to the bottom in oily drops, and is gradually converted into the hydrated acid.

The manufacture and use of acetic acid, as its name implies (Lat. *acetum* = vinegar), are of great antiquity. Moses speaks (Numbers vi. 3) of "vinegar of wine," "vinegar of strong drink," and from the testimony of several ancient writers it is evident that the properties and uses of the acid were well ascertained. Perhaps the oldest record proving this is the noteworthy allusion in the Book of Proverbs to the action of vinegar upon nitre. It is the product of the oxidation or destructive distillation of various organic bodies, and exists in nature in considerable quantities, in the juices of many plants, especially trees, and in animal secretions. Until a comparatively recent date, however, its chief source was the distillation of acetate of copper—verdigris.

Acetic acid in its various forms occupies a very prominent place in the arts, manufactures, and commerce. It is extensively used in the treatment of gums, caoutchouc, and various albuminous substances, in the manufacture of paints and varnishes, and as a drug. In a diluto state, and in its well-known form of vinegar (which is simply a weak solution of the acid contaminated with certain vegetable impurities), it is largely employed in culinary arts and the manufacture of pickles, &c. The crude pyroligneous acid, prepared by the distillation of wood, is, from its admixture with creasote and other hydrocarbons, a valuable antiputrescent, and as such is used in the preservation of timber—also flesh. The distilled vinegar (wine or malt vinegar deprived by distillation of colouring and other non-volatile bodies) is used in medicine to relieve nervous headache, fainting fits, and sickness. Smelling salts are usually sulphate of potassium mixed with a little glacial acetic acid. Finally, it forms a series of salts, or "acetates," of special value in calico printing, dyeing, and other branches of industry.

METHODS OF PREPARATION AND MANUFACTURE.—The anhydrous acid may be dismissed without further notice, beyond simply stating that it may be prepared by the action of acetyl chloride upon potassium or sodium acetate, or by heating one of these acetates with benzoyl chloride.

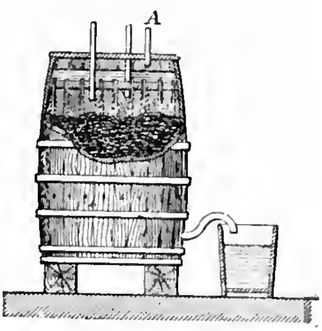
For the production of the ordinary hydrated acid, three processes are employed—(*a*), acetous fermentation, chiefly carried on for the production of vinegar; (*b*), the dry distillation of wood, whereby the impure or pyroligneous acid is obtained, and, by subsequent processes, the acetates of lime, iron, soda, &c.; (*c*), the distillation of various metallic acetates with sulphuric or hydrochloric acid, yielding the pure acetic acid of commerce.

By acetous fermentation is meant the oxidation of dilute alcohol, or various liquids containing alcohol, in the presence of yeast, or almost any azotized matter liable to decay. Not that the presence of these putrescible substances or "ferments" is necessary to bring about the change, for by the simple action of the air, or by various oxidizing agents—chromic, nitric, or hypochlorous acids &c.—alcohol may be converted into acetic acid; but the change is effected much more rapidly and effectually in the presence of a ferment, along with an abundant supply of air. The nature and action of these ferments are as yet only imperfectly understood. According to Pasteur the formation of acetic acid from alcohol depends upon the presence of a fungus—the *Mycoderma aceti*—which, like platinum black, has the power of absorbing oxygen within its pores and brings it into peculiarly intimate contact with the alcohol. His experiments go to show that this fungus (yeast-plant) can be sown on the surface of the liquid by introducing a small portion of another alcoholic liquid already in a state of fermentation, that it requires nutrition, subsisting upon the albuminous matters and mineral salts which alcoholic liquors usually contain, and that if these be absent the mycoderm remains barren for lack of food, and no acetification can take place. According to Mayer's experiments (see 'Ann. Chem. Pharm.' clvii. 227) the salt most necessary to the yeast-plant is the acid phosphate of potash, since if this salt be excluded the fermentative process is checked. At the same time the presence of other substances seems necessary, if not to produce fermentation, at least to maintain the mycoderm in proper condition, the salts of ammonium and magnesium, or nitrogenous organic bodies similar in constitution to ammonia, pepsin, or the diastase of beer. Differing from these theories as to the nature and work of the mycoderm, Liebig and other eminent chemists regard the process of fermentation as one of the simplest alcoholic oxidation, and certainly wood shavings which have been used for many years in the manufacture of vinegar have been examined under the microscope without finding a trace of fungus upon them.

The "souring" of wine is an everyday and natural illustration of the process of acetous fermentation, strong wines souring more readily than weak because they contain less vegetable matter in proportion to absolute alcohol.

During acetous fermentation a substance called aldehyde—a lower compound of alcohol and oxygen—is probably always formed. Aldehyde is an exceedingly unstable body, and to prevent loss of acetic acid through its volatilization it is advisable to bring the ferment and alcohol together with as free admixture of air as possible, that a rapid and more perfect oxidation may be ensured. The German, or "quick vinegar" process, effects this in the following manner. A vessel is prepared of the description shown in Fig. 4, varying in size from 13 ft. high and 15 ft. in diameter to 8 ft. high and 6 ft. in diameter, a large size being preferred. This "tun" (*essigbilder*, or vinegar "generator" or "graduator") is carefully hooped, and set up on any convenient platform. A cover, fitting loosely on the top, keeps out dust and dirt, and about 12 in. below this is a fixed shelf, perforated with a great number of small holes and two or three larger ones. In the small holes are suspended pieces of thread or string, kept in their place by knots at the upper end. In the larger holes are fitted short glass or wooden tubes which go through the cover and serve as vents. About 18 in. from the bottom of the generator is fixed a second perforated shelf or false bottom, and some few inches above this the sides of the tub are pierced with holes 1¼ in. in diameter which admit the necessary supply of air. Below the false bottom is an exit pipe for the liquid, preferably curving upwards when it reaches the outside until close upon the level of the air-holes. Finally, the generator is filled from the false bottom to within a short distance of the top shelf with shavings, chips of beech wood, or charcoal. The latter is preferable, as presenting a greater surface for oxidation than any other substance, but it requires frequent renewal,—not admitting of being cleansed. If shavings or chips are employed, they should be boiled in water and dried in a close oven before being used. Before passing the alcoholic liquors into the generator, the shavings, and the vessel itself, are "soured" with hot strong vinegar to accelerate the subsequent oxidation. The alcoholic liquors, usually consisting of 50 gallons of brandy of 60 per cent. and 37 gallons of beer with about $\frac{1}{1000}$th of ferment, are now introduced into the generator through a funnel in the cover shown at A, Fig. 4. The liquors percolate slowly through the shavings, chips, or charcoal, meet an ascending current of air, and undergo oxidation. Flowing over through the exit siphon they are returned once more to traverse the generator, or are transferred to a second similar apparatus,—the latter being the preferable plan. By this "quick" process, practised largely in Germany, France, and England, as much as 150 gallons of vinegar can be manufactured per diem in 10 tuns of the description shown in the drawing. The liquors should be as clear as possible—free from suspended organic substances—or else the chips or shavings become rapidly choked, and unless these are constantly cleaned by boiling in water, or renewed, equal distribution of the liquors is impossible. No pyroligneous acid, with admixture of tarry matters and oils, should be present, as they prevent oxidation.

4.



The nitrogenous organic substances having promoted the acetification of the alcohol, settle out and then assume a new form; they are known as "mother of vinegar." Treated with potash this "mother," a white gelatinous mass, loses its nitrogen, pure cellulose being left.

Further details of the process, and modifications of it—such as Ham's—concern rather the manufacturer of vinegar than of acetic acid, and these, together with further details relating to acetous fermentation, will be dealt with at length in a separate article upon vinegar.

It should be noted that simple oxidation of alcohol—by the carefully regulated action of air or an oxidizing agent—produces *pure* acetic acid, but in the ordinary acetous fermentation, where certain vegetable bodies are present, the acid is yielded in the form of *vinegar* by admixture with various organic impurities.

PYROLIGNEOUS ACID (LAT. *Acidum pyrolignosum*; GER. *Holzsäure* or *Holz-essig*; FR. *Acide pyroligneux*). The impure or pyroligneous acid is obtained by the dry distillation of wood in close ovens. From the first distillation it is a dark, yellowish-brown liquid of varying strength, possessing an unpleasant clinging odour from the tarry compounds and various resinous matters with which it is more or less impregnated. The manufacture is carried on extensively in various parts of this country, in France, Germany, and Belgium, for the production not only of the pyroligneous acid, but also for the sake of the naphthas, charcoal, and various tar compounds which are obtained. Indeed the process is one in which *all* the products are utilized in a remarkable degree—from the cutting of the timber down to all the final issues.

Inasmuch as the item of carriage is an important consideration—owing to the bulk of several of the products, and to the necessity for a cheap and ample supply of timber isolating the works, and banishing them, as a rule, from the great centres of industry—it is advisable for the manufacturer to select a site for his works within easy and convenient range of his staple raw material (wood), and not far removed from rail or water communication. Isolation from works of a similar character is necessary to prevent enhancement of the cost of the timber through undue competition. An ample supply of water for condensing purposes is also an essential, and if the source of the water be so situated that hand-labour and fuel can be saved by the employment of water-machinery, it is a considerable advantage. The questions of isolation and ample supply of timber within easy range are too often lost sight of, the omission entailing serious loss in a trade where the turn over is comparatively small, and the saving of labour and prevention of competition important items. It should be appreciated that an ordinarily sized works, of say eight ovens, consuming 40 to 50 tons of wood per week, absorb over 100 acres of coppice in the year, and a coppice can only be advantageously cut once in every twenty years.

Large timber—indeed, as will be seen hereafter, almost any woody substance, except such as are decayed—may be used for distillation; but, except perhaps in the case of beech, it is usual to take the "lop," or smaller branches, or "coppice" wood (small timber grown for the purpose). These coppices, which are generally a mixture of various woods (hazel, oak, beech, maple, &c.), occupy an immense acreage in many parts of the country, are sold by the landowner to the manufacturer at prices varying from 3*l.* to 15*l.* per acre, and are "cut" about every sixteen years. Sometimes younger growths are taken—some manufacturers maintain that they can get good yields from a seven or eight years' growth—but it is beyond doubt that the coppice does not reach its prime till it is about eighteen years old. The amount of water in the wood is an important consideration in distilling, second only to that of the constitution of the woody fibre itself, inasmuch as it both takes up a portion of the heat, entailing a loss of fuel, and weakens the products of distillation. It will be readily apparent that the amount of water is greater in twigs and young shoots than in the more solid stem. It is also greater at the flow of the sap than when growth is less rapid, and hence, other things being equal, it is better to fell at the latter time.

With regard to the respective amounts of water in different woods, the following table of Schübler and Hartig is worthy of note:—

Hornbeam	contains..	18·6	per cent. of water.
Willow	„	26·0	„ „
Sycamore	„	27·0	„ „
Mountain Ash	„	28·3	„ „
Ash	„	28·7	„ „
Birch	„	30·8	„ „
Oak	„	34·7	„ „
White Fir	„	37·1	„ „
Horse Chestnut	„	38·2	„ „
Pine	„	39·7	„ „
Red Beech	„	39·7	„ „
Alder	„	41·6	„ „
Elm	„	44·5	„ „
Red Fir	„	45·2	„ „
Lime	„	47·1	„ „
Italian Poplar	„	48·2	„ „
Larch	„	48·6	„ „
White Poplar	„	50·6	„ „

The samples tested were in all cases freshly cut wood. As all kinds of timber are hygroscopic, the action of the air in abstracting the moisture is to a certain extent neutralized. Probably wood for distilling purposes, stacked in the yard or kept in the open, does not lose on an average more than one-third of its water.

Roots of trees may be distilled with very fair results, but are liable to the great evil of dry rot, and are expensive to prepare and pack in the ovens. In the proper sizing of these and of large logs dynamite might be advantageously substituted for the gunpowder which is often employed.

Different woods of course give different yields of the various products; broadly speaking, perhaps, the charcoal—due regard being paid to its after uses—determines the quality of timber selected rather than any other consideration. If this product is destined for the manufacture of gunpowder, alder, willow, or dogwood is chosen; if for tin-plating and heating purposes, the heavier woods, oak and beech; if for crayons, willow; if for absorbing purposes, a dense wood—box or lignum-vitæ. If it be desired to obtain chiefly a good yield of pyroligneous acid, birch, thorn, and apple are the most esteemed. Firs, and other resinous trees, give good yields of the tar compounds and naphthas, but are not very extensively employed. As the most generally useful wood, giving good yields of all products—charcoal, acid, naphtha, and tar—oak holds the first place, and beech the second. The gunpowder woods give poor yields.

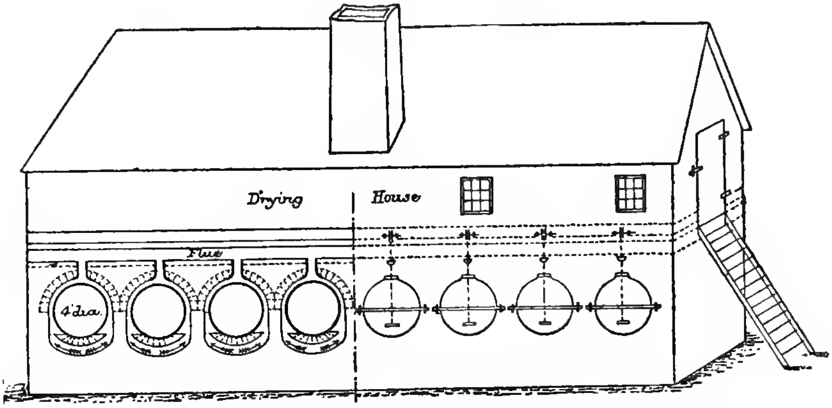
When the wood is cut it is "peeled"—that is the bark taken off—and allowed usually to lie in the coppice until required for distillation, the bark being stacked for sale to the tanners. Sometimes the timber is removed and stacked at the works, but this twice shifting entails unnecessary expense, and should be only resorted to in cases of enforced removal. The cutting and peeling are done either by day work or "on piece," at very varying rates. It may be estimated roughly that the bark pays for the preparation of the timber, and the cost of drawing to the ovens and cutting up may be averaged at 7*s.* per ton.

The average yield of timber may be taken at 15 tons per acre, and the average cost delivered to the ovens at 13*s.* per ton. The yield and weight of bark varies very much with the quality of timber and the wetness or dryness of the season, but may be averaged at 2 tons per acre.

For removal, the timber is packed into "cords," of which there are several descriptions. The "government," or "crown," cord is 27 ft. 4 in. × 2 ft. 2 in. × 2 ft. 2 in., containing 128 cub. ft., but two other cords are largely used, one 8 ft. long by 4 ft. wide and 4 ft. high, and the other 16½ ft. long by 2 ft. 2 in. high, and made up of pieces cut 2 ft. 2 in. long. The weights of these cords vary from 14 to 25 cwt. The short pieces, 2 ft. 2 in. long, are almost invariably preferred in Wales, and timber used there is, as a rule, much smaller than in other parts of the country. The length of time that the timber is allowed to lie or to remain stacked varies with different circumstances, but it should not be put into the ovens green, or else a large amount of moisture has to be dealt with in distillation, and the labour and fuel costs are proportionately increased. It is also essential that there shall be no dry rot or "taint" present. In South Wales, where stacking in the yard is common, this last point is too little regarded.

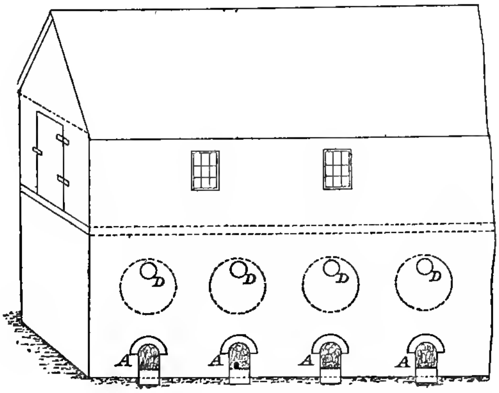
The ovens are cylindrical or square, of cast or wrought iron, and of varying dimensions, according to the experience and judgment of the individual manufacturer. A convenient and very general form is shown in Figs. 5, 6, and 7; Fig. 5 showing the front elevation and section of the ovens crossways, Fig. 6 the back, Fig. 7 the section of an oven lengthways. The ovens here are in the form of cast-iron cylinders, 9 ft. long, 4 ft. in diameter, and 1¼ in. thick, set horizontally in brickwork, side by side, and forming any convenient range. A good-sized works will have eight such cylinders. The house shown in elevation and section, and built on the top of the range of ovens, is for drying the acetate of lime, the production of which usually forms a continuous process with that of wood distillation. For a further description of this, see under "Acetate of Lime." One end of the cylinder, where the charge of wood is introduced and withdrawn, is closed by a strong cast-iron door, working on a hinge at the side (or preferably, and as in Fig. 5, at the top), and secured by a crossbar. For convenience sake this door may be hauled up by a chain and pulley set in the brickwork above. From the other or fire end of the cylinder issues a pipe, 9 or even 10 in. in diameter, which carries off all the gaseous products of distillation. Each cylinder is heated by a separate fire, shown at A, Fig. 6. The products of combustion pass through the pigeon-holed arch, circulate round the oven into flues which run under the

5.



drying floor, and finally escape up the stalk. The fireplaces should be 5 ft. long and 20 in. wide. In some works two or more cylinders are set to one fire, and occasionally the flues are in no way divided, but the flames allowed to intermingle. Both these plans are, however, open to serious objections, the slight economy of fuel and brickwork which they effect being more than counterbalanced by the difficulty of repairing a cylinder when it is laid off. Moreover, if the flues are properly arranged, and the drying floor is carefully constructed, the loss of heat up the chimney is comparatively slight. Some manufacturers prefer the cylinder ends projecting 2 or 3 in. from the brickwork, but it is very doubtful if any benefit accrues from such setting, and there is a distinct loss of heat from radiation. It is better to let the fire end of the cylinder stand in about 5 in., as shown in the drawings, allowing for a 4½-in. brick wall to be built up and around the exit pipe. At B, Fig. 7, is shown an arrangement for drawing the charcoal as whole as possible, consisting of a sheet of stout iron fitting the interior of the cylinder transversely, but only reaching about half-way up. When the cylinder is charged, this diaphragm is set back to the fire end, but when the operation is completed, and the door raised, the workman draws it towards him by means of a rod lying on the bottom of the cylinder, and with it the whole of the charcoal residue.

6.



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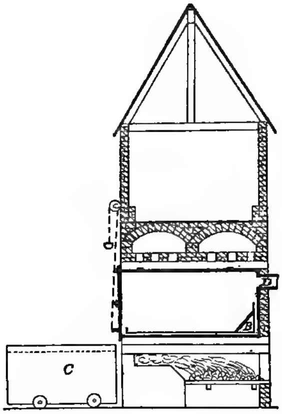
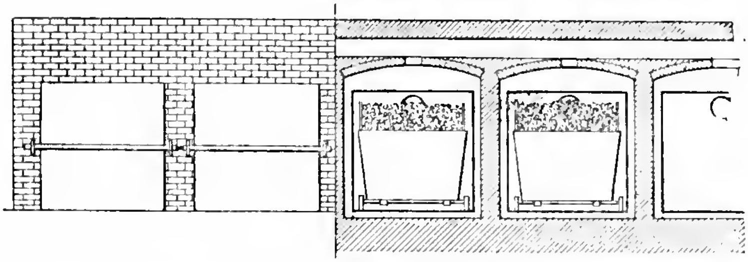


The charge of wood, cut into suitable lengths, is thrown in until the cylinder is as full as possible. With ordinarily dry wood a charge will weigh about 24 cwt.; if the pieces are crooked they should be sawn up, that no room may be wasted. The door is now lowered down, secured by the crossbar, and carefully plastered round with a loam or clay luting, so as to prevent either ingress of air or egress of the products of distillation. At first the fire should be kept under, to dry the charge, but after about two or three hours driven hard to effect perfect decomposition of the wood and the separation of all volatile constituents. The rate at which the fire is driven must of course depend upon the time allowed to work off the batch. If a large turn-out is necessary, carbonization may be effected in twelve or thirteen hours, but a slower process, say sixteen hours, gives better results. Not only is a slowly charred wood better in quality, but the amount of uncondensable gases is reduced. During carbonization the following changes are effected. First, all extraneous moisture is driven off; then, as the temperature is raised, and decomposition of the wood takes place, acetic acid and water; then the tar and volatile oils; and, finally, carbonic oxide, carbonic acid, and marsh gas. In the cylinder is left charcoal, retaining, piece by piece, the shape of the original wood. When the run of liquid from the condenser ceases, and the exit pipe from the cylinder becomes cool, it is known that the distillation is complete. The fire is allowed to die down, the door opened, and the charcoal raked out, by means of the diaphragm above described, into deep, iron waggons, shown at C, Fig. 7, and run away to cool. The waggons are fitted with a sheet-iron cover, which is luted down with clay to prevent absolute combustion of the charcoal by the air. To effect this purpose, a little water is occasionally sprinkled over the charge when raked out into the waggon, but, as a rule, this is unnecessary. In the case of some old-fashioned plants, the charcoal is raked into a luted box, sunk in the ground underneath the cylinder door, but it need hardly be pointed out that this plan creates an unnecessary amount of "smalls" and dust.

To economize fuel in the distilling operation, and prevent nuisance, some of our best manufacturers are now beginning to adopt the very excellent plan of bringing the waste gases back from the end of the condensers, returning them into or under the fires, and burning them. The advantages of this plan are apparent—it is only surprising that it is not more generally adopted.

In the Forest of Dean, and some other parts of the country, instead of cast-iron cylinders, wrought-iron ovens, set in somewhat similar fashion, are used. This arrangement, without the drying house—which is the same as in Figs. 5, 6. and 7—is shown in Figs. 8, 9, and 10. Figs. 8 and 9 give the elevation of back and front, partly in section, and Fig. 10 the longitudinal section of an oven. It will be noticed that the charge is introduced and withdrawn in small sheet-iron waggons. By this arrangement labour is saved, and the removal of the charge effected with a minimum of breakage. The waggons are piled up about 18 in. above the sides. These ovens are usually about 8 ft. long by 5 ft. square, and the charge is contained in two waggons. It would, however, be an improvement on the usual plan to have only one, longer, waggon, as the charge would thereby be more speedily withdrawn and covered up. The fire is sometimes allowed to play direct upon the oven after about 2 ft. from the arch, up to which point a 4½-in. casing gives protection; sometimes the oven is set "naked," and occasionally a 4½-in. casing is carried all round. The heat and products of combustion pass up the sides, along an arched flue formed on the top of the oven, from thence into a series of flues forming the bed of the drying house, and finally escape up the chimney.

8.



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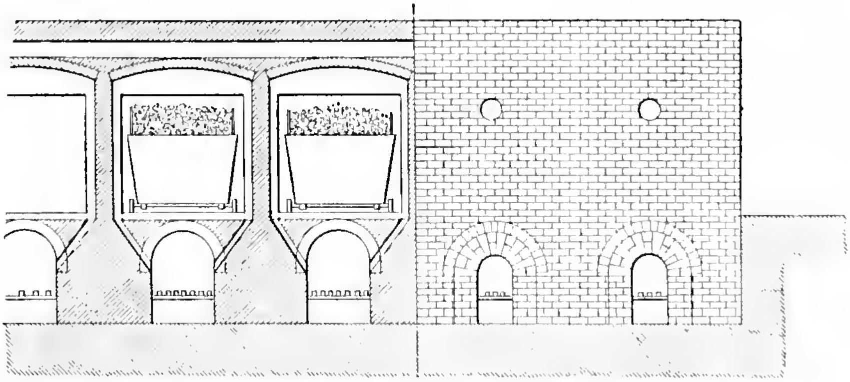

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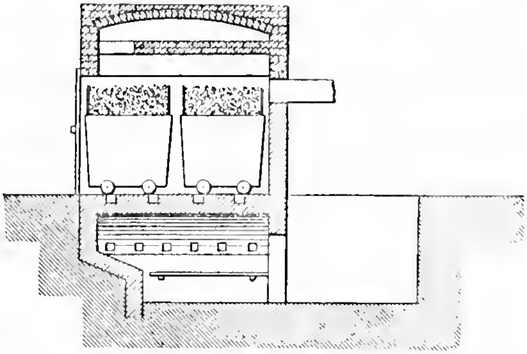
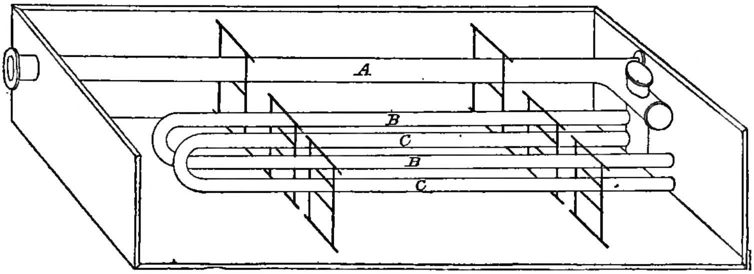


Each of these two systems of distilling—in cast-iron cylinders and wrought-iron boxes—has its stanch upholders, and it would be difficult to assign to either the pre-eminence. As a general rule, it may be laid down that the Welsh ovens are the best for the small timber which is generally distilled there, and the cast-iron cylinders more suitable for the heavier cuts preferred in other parts of the country. The disadvantages of the cylinders are, a liability to crack, and a somewhat larger consumption of fuel through the thickness of the plate. On the other hand, the wrought-iron oven is apt to leak at the joints and doors, to warp with the heat, and is more appreciably acted upon by the acid products of distillation—especially when cooling down. With judicious and careful patching, a cylinder, even when cracked, may be worked for eight or nine years with only the necessary renewal of the door and lighter parts.

Occasionally, yet another style of oven is used, made of sheet iron, and divided into compartments, into each of which a charge of wood is lowered through a hole in the top. The compartments rest upon a movable framework, and are brought in turn under the door to receive the charge. By this plan only one opening is necessary, but the warping and general wear and tear present formidable objections.

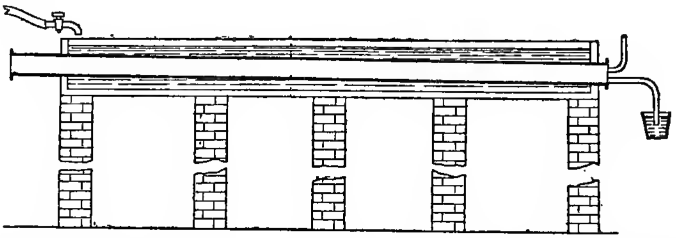
From the retort, of whatever description it may be, the gases pass along the exit pipe shown at D in Figs. 6 and 7 into the condensers. These are of various forms. A most effectual one is shown in plan in the general arrangement of works set forth in Plate I., and in perspective in Fig. 11. At the rear of the ovens a large tank is built, the same length as the range of furnaces, about 14 ft. wide and 3 ft. 6 in. deep. The exit pipe from each oven or cylinder is carried straight through the side of the tank and continued to the opposite side, at its full size of 9 or 10 in. as the case may be (see A, Fig. 11). It then turns sharply back, and is branched into two copper pipes B and C, one above the other. These copper pipes should not be less than 5 in. in diameter. They run back to the oven side of the tank, and are once more returned sharply, passing finally through the side of the tank farthest from the ovens, and dipping about 2 in. into a spout, which carries over the condensed products to a suitable receiver. The uncondensed gases are conducted away by a small pipe, after the manner shown in Fig. 13. The whole tank is kept full of water, a continual flow of which, on and off, must be secured by any convenient arrangement. The copper pipes must also have a considerable fall, to prevent their being choked by the deposit of tar, &c. This tarry deposit, from its clinging and heavy nature, is difficult to deal with, and the one great objection to this form of condenser is that it cannot be readily and speedily cleaned out.

11.



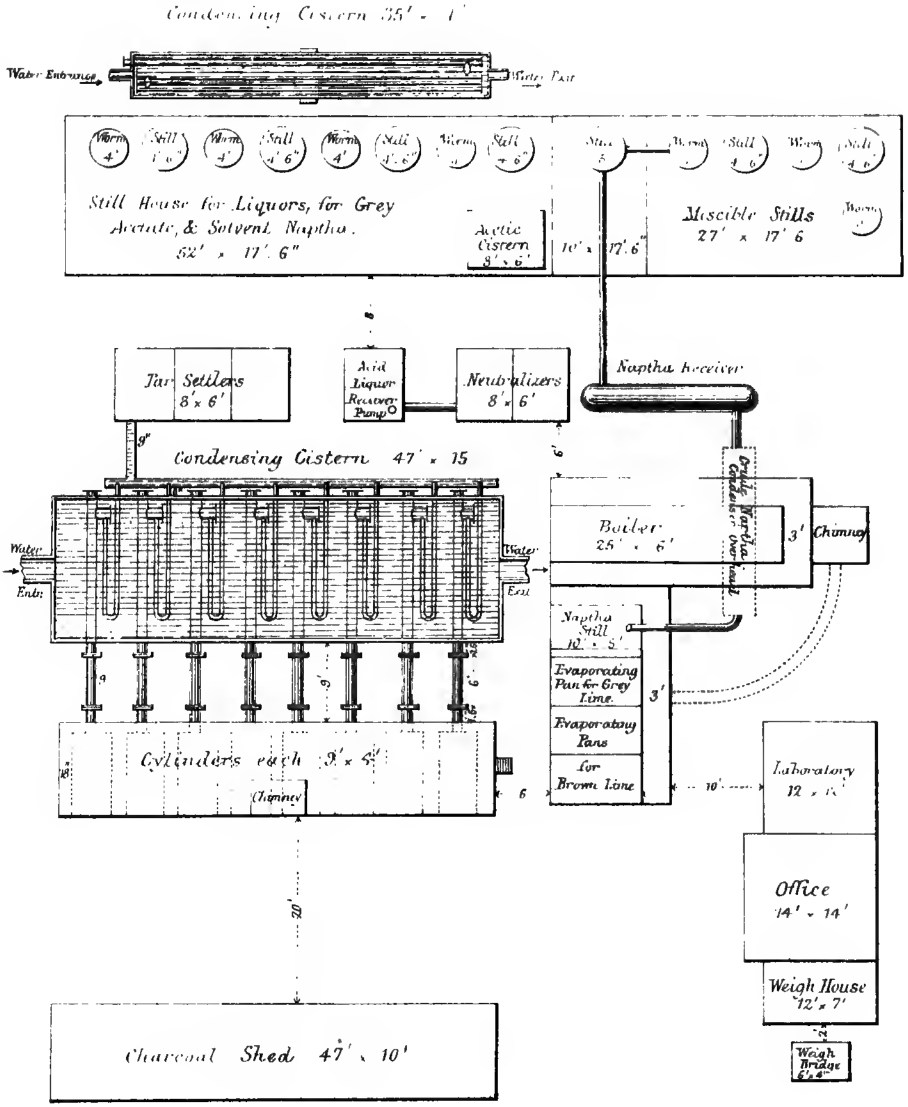
Another very simple condenser is shown in Fig. 12, which will readily explain itself. The cast-iron exit pipe from each cylinder is carried through a separate tank, or long box, about 30 ft. long by 3 ft. square, and dips into a spout at the end through a reduced pipe. The tank is kept full of constantly renewed water. Condensation by this method is not very perfect, and the great length of pipe renders proper cleaning out difficult. The uncondensed gases are carried off by a small pipe.

12.



The plan which seems the most convenient, but which is not very largely used, is shown in Fig. 13. The exit pipe from the ovens, reduced in size to about 6 in., is connected with a range of pipes, preferably of copper, set zigzag fashion in an upright, strong, wood framework. By means of an overhead pipe, which is perforated on its under side, a constant flow of water is precipitated over the whole range along which the gaseous and half-condensed products of distillation are passing, and falls into a tank in which the framework is set. A small pipe carries off the uncondensable gases to be consumed in the retort fire. All the ends of the condenser pipes should be closed by blank flanges, so that there may be no difficulty in cleaning out the tarry deposit. Whatever form of condenser is used, the exit pipe from the oven should be connected with it by means of

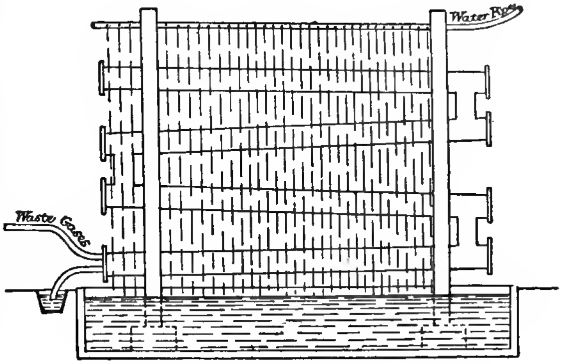
GENERAL ARRANGEMENT OF WOOD DISTILLING WORKS.



E.&F.N. Spon, London & New York.

a short length, as shown in Plate I., so that the apparatus can be readily and quickly disconnected. For economy's sake, two ovens are sometimes made to work through one set of condensing pipes, but much better, and more certain, results are obtained when each oven has its separate condenser.

13.



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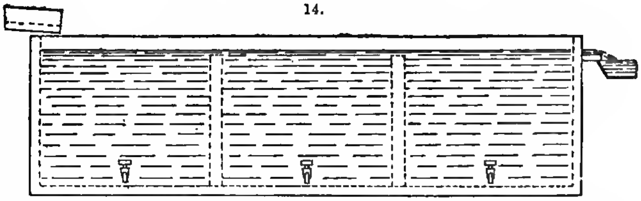


The condensed products consist of water, pyroligneous acid, ammonia, tar, naphtha, and various oils and resinous matter; the uncondensable gases, returned to the fireplace or allowed to pass off into the air, consist of carbonic oxide, carbonic acid, marsh, and olefiant gases. The former are delivered into a tank, where the tar settles to the bottom and is drawn off by stop-cocks to the still, and the supernatant liquor — consisting chiefly of water, pyroligneous acid, and naphtha, with a certain admixture of tarry impurities—runs over, or is drawn off into a smaller receptacle, from whence it is pumped into the neutralizer. This neutralizer should be set on a higher level, that no further pumping, to the end of the acetate of lime process, may be necessary.

Returning for a moment to the first receiving tank into which the whole of the liquors from the condensers pass, a convenient form is shown in Fig. 14. A tank about 20 ft. long, 5 ft. deep, and 5 ft. wide, built of perfectly sound deals, which should be not less than 3 in. thick, without cracks, and firmly bolted together with 1-in. iron rods, is divided into three compartments, the divisions having a slight depression to allow the liquor to flow from one compartment when filled into the next, and so on till it finally flows over into the pumping well. The tar is deposited in the several compartments, and is drawn off for distillation. The products of distillation may be returned into the spout leading from the condensers. Very often, however, it is not deemed advisable to purify the tar in any way, and the whole of it is burned for fuel—mixed with sawdust, &c.—or is used for various purposes in the works. The lighter tarry and carbonaceous matters which rise to the surface as a scum, while the liquors are passing through the various tanks, are skimmed off and utilized as fuel.

If it be desired to obtain the pyroligneous acid by itself, or if a grey or white acetate of lime is required, the liquors from the tar settlers are distilled at a gentle heat, the naphtha passing over first, and the less volatile crude acid, mixed with various tarry and oily impurities, remaining in the still to be obtained by subsequent distillation. If it is only necessary to produce a brown acetate, the liquors are pumped up and mixed with lime in the neutralizer, as aforesaid, and the naphtha separated by after-distillation. A well-ordered works will have the necessary plant for both brown and grey acetate, so that command of more than one market for the absorption of the finished article may be obtained. For further details of these processes see "Lime, Acetate of."

Such is the manufacture of crude pyroligneous acid as carried on at an ordinarily-well constructed English works, and the process itself leaves comparatively little to be desired in the way of improvement. Manufacturers should, however, turn their attention to the better separation and utilization of the tar products and constituents, the utilization of the waste gases and the refuse from the neutralizers, and the direct purification of the crude acid. It would probably pay well, too, to establish small turneries in the works to use up the odds and ends of timber now wasted, or only used for fuel.

Owing to the exceedingly variable character of the chief raw material, wood, it is difficult to give definite yields and costs. They may, however, be approximately calculated from the following data. One ton of wood, costing 14s. delivered to the ovens, will yield 2½ to 3 cwt. of bark, and, if fairly dry, 5 cwt. of best charcoal, 1¾ to 2 cwt. of best brown acetate, or 1½ of grey, 1¾ to 2 gals. of "miscible" naphtha at 60° over proof, or 2¼ gals. of "solvent" naphtha at 45°. The labour in a works using, say, 45 tons of wood per week, will involve two men to charge and draw the ovens, two firemen, one neutralizer, one man to attend to the naphtha stills and condensers, one to work off the acetate of lime, carry it into the drying house, and spread and turn it while drying, and one general labourer. In these data no mention is made of the constantly varying incidental expenses entailed by wear and tear; and it is assumed that the works are well planned and substantially built. The consumption of fuel in such a works should not exceed 12 tons per week, even where the waste gases are not utilized.

The following tables, drawn up by Stolze, are interesting, as showing the amount and strength of products obtained from various woods:—

One lb. of Wood.	Weight of Acid.	Weight of Carbonate of Potash neutralized by 1 ounce of Acid.	Weight of Empyreumatic Oil.	Weight of Charcoal.
	ounces.	grains.	ounces.	ounces.
White Birch	7⅛	55	1⅜	3⅞
Red Beech	7	54	1½	3⅞
Large-leaved Linden .. .	6⅞	52	1⅞	3⅝
Oak	6⅞	50	1½	4⅛
Common Ash	7½	44	1⅜	3¾
Horse Chestnut	7⅜	41	1⅝	3½
Lombardy Poplar	7⅜	40	1⅜	3¾
White Poplar	7⅜	39	1¼	3¾
Bird Cherry	7	37	1¼	3½
Basket Willow	7⅜	35	1½	3½
Buckthorn	7½	34	1⅜	3½
Logwood	7⅛	35	1½	2
Alder	7⅜	30	1½	3½
Juniper	7¼	29	1¾	3⅝
White Fir	6⅝	29	2⅛	3⅜
Common Pine	6¾	28	1⅞	3½
Red Fir	6⅜	25	2¼	3¾

84 lb. of Wood.	Charcoal.	Charcoal per Cwt. of Wood.	Acid Liquor.	Specific Gravity of Acid Liquor.	Specific Gravity of Acid Liquor saturated with Lime.	Measures of Soda to neutralize Acid Liquors.	Incondensable Products.	Real Acid.
Birch	23½	31·33	45	1·046	1·080	70	15	1·86
Elm	21½	28·66	45½	1·036	1·075	83	17½	2·26
Willow	18	24·00	49	1·029	1·045	29	17	0·77
Beech, low temp. ..	24	32·00	46	1·039	1·090	115	14	3·06
Ditto, high temp. ..	20	26·64	47	1·034	1·067	90	17	2·40
Laburnum	20	26·64	46	1·030	1·055	75	18	2·00
Ash	23	30·68	48	1·035	1·078	92	13	2·45
Alder	20	26·64	48	1·030	1·065	70	16	1·86
Hawthorn	20	26·64	27	1·040	1·100	140	37	3·73
Young Oak	28	37·33	39	1·085	1·085	115	14	3·06

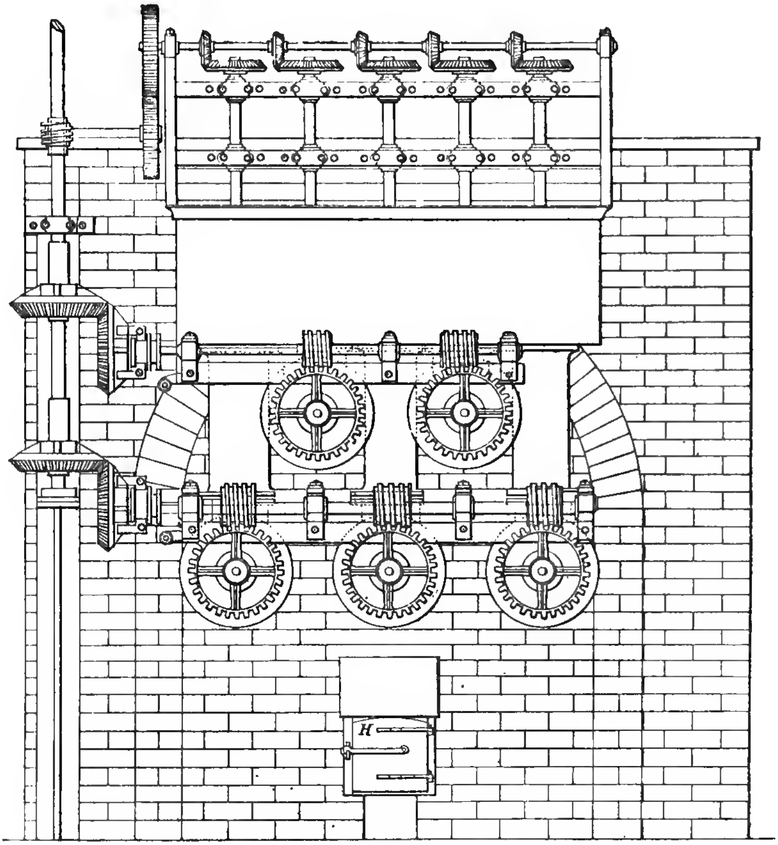
336 lb. of Wood.	Charcoal.	Charcoal per Cwt. of Wood.	Acid Liquor.	Specific Gravity of Acid Liquor.	Grains of Bicarbonate of Potash neutralized by one ounce.	Dry Acetate of Lime produced.
Beech	84	28·00	180	1·029	9½	25
Walnut	72	24·00	150	1·018	7	14½
Birch, cut three years	70	23·33	120	1·031	11	13
Oak	91	30·30	190	1·022	8	24
Ash	90	30·00	190	1·024	8	22
Apple	70	23·33	200	1·017	6	18
Wych Elm	70	23·33	180	1·018	8	16
Maple	77	25·66	145	1·018	6	20

The amount of charcoal obtained depends to a remarkable extent upon the length of time allowed for carbonization. Karsten gives the following interesting results of a series of experiments upon air-dried timber:—

Species of Wood employed.	Charcoal.	
	By quick charring.	By slow charring.
Young Oak	16·54	25·60
Old Oak	15·91	25·71
Young Beech	13·12	25·22
Old Beech	13·65	26·45
Young Alder	14·45	25·65
Old Alder	15·30	25·65
Young Birch	13·05	25·05
Old Birch	12·20	24·70
Young Deal	14·25	25·25
Old Deal	14·05	25·00
Young Fir	16·22	27·72
Old Fir	15·35	24·75
Young Pine	15·52	26·07
Old Pine	13·75	25·95
Lime	13·30	24·60

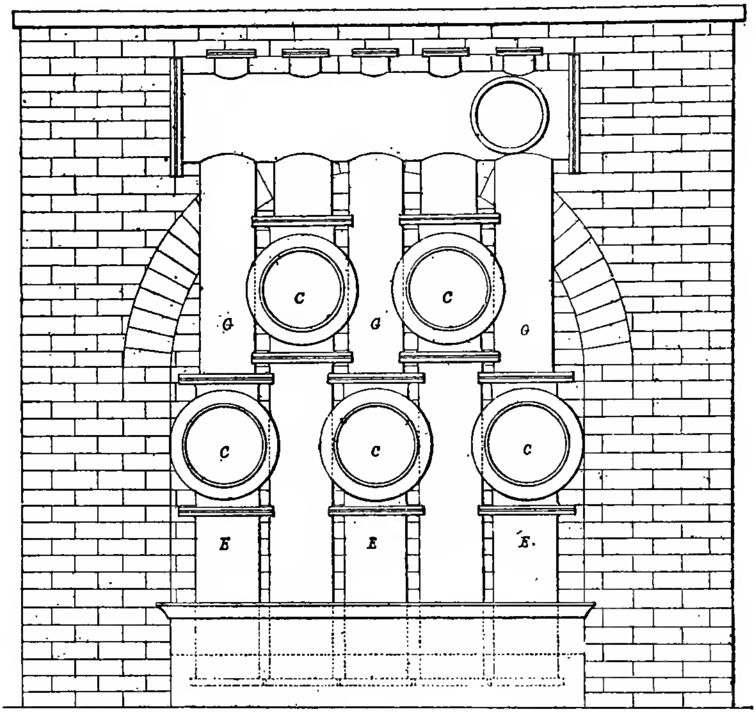
Many improvements and modifications of the process of wood distillation have been proposed, the most notable having reference to the treatment of wood in a finely divided state—sawdust, and the exhausted residue of various manufactures, such as tanning and dyeing. These bye-products, in their spent condition only a nuisance to the manufacturer, still contain all the elements required for the production of acetic acid. Their finely divided state has, however, presented a serious obstacle to their destructive distillation, as they form a dead mass in the retort, and allow of only partial

15.



surface carbonization. The processes of Messrs. Halliday and Bowers, both of which have met with considerable attention at the hands of manufacturers, overcome this difficulty by keeping the woody material in the retort in a constant state of forward motion. Mr. Halliday's process is shown in front and back elevation and longitudinal section in Figs. 15, 16, and 17. The materials are put into a hopper A, Fig. 17, from which an endless screw B carries them forward into the cylindrical retorts C, Figs. 16 and 17. Here they are taken up by a second screw D, and moved forward to the other end of the retort. The process of distillation is precisely the same as in the case of the ordinary timber, the charcoal issuing through a pipe E, into a vessel F, filled with water, and the gases passing off up G to the condenser. The fireplace is shown at H, Figs. 15 and 17.

16.

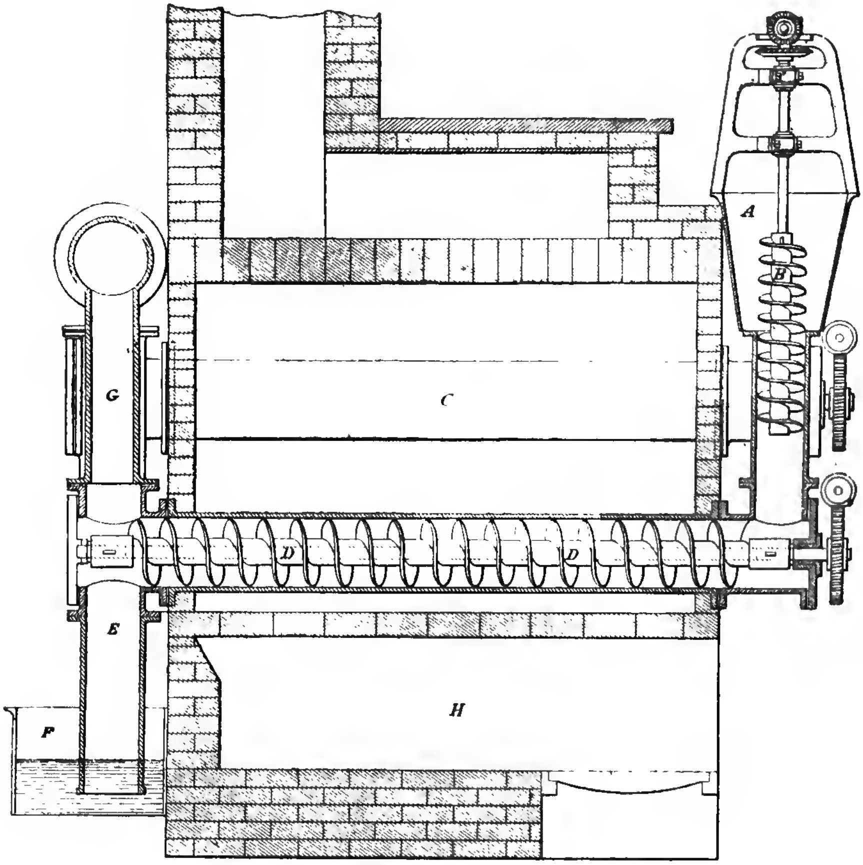


Mr. Bower's apparatus, adopted by four or five manufacturers in Lancashire and Yorkshire, is shown in Figs. 18, 19, and 20. Fig. 18 gives a longitudinal section of the drying flat, heated by the waste heat of the furnace; Fig. 19 a longitudinal section of the furnace itself, and Fig. 20 a plan of drying flat and furnace arranged conveniently side by side.

Referring to Fig. 18, the sawdust, if wet, or waste dye-wood, is tipped into a hopper A placed at one end of the drying bed, and slightly above it. The material escapes from the hopper, falls upon the drying bed, and is taken hold of by a series of scrapers fixed upon endless chains B B B which travel upon revolving drums C C. By these it is moved slowly over the heated plates to the far end of the flat, and falls over the edge into any convenient receptacle. It is then taken up by elevators and fed into the furnace or retort through a hopper D, Fig. 19. The grooved rollers shown at the bottom of the hopper, by which the supply of material to the furnace is regulated, are geared to revolve in contrary directions, and are set so that the points of the teeth approach each other very closely. They also revolve as nearly as possible in contact with the sides of the hopper, or with plates that can be "set up" towards the rollers so as to prevent escape of the products of distillation through the hopper. The woody material (admitted as may be required, and in the manner shown, into the furnace) is taken hold of and moved slowly along the bed towards the fire end by an apparatus exactly similar to that already described as part of the drying arrangement, and is discharged, perfectly carbonized, into a receptacle E filled with water, so constructed as to form a luting and prevent the escape of gases from the furnace. The charcoal in a finely divided state soon fills this vessel, and is cleared off by the revolving scraper shown at F. The products of distillation pass off to the condensers through the pipes G G, and are collected in the usual manner.

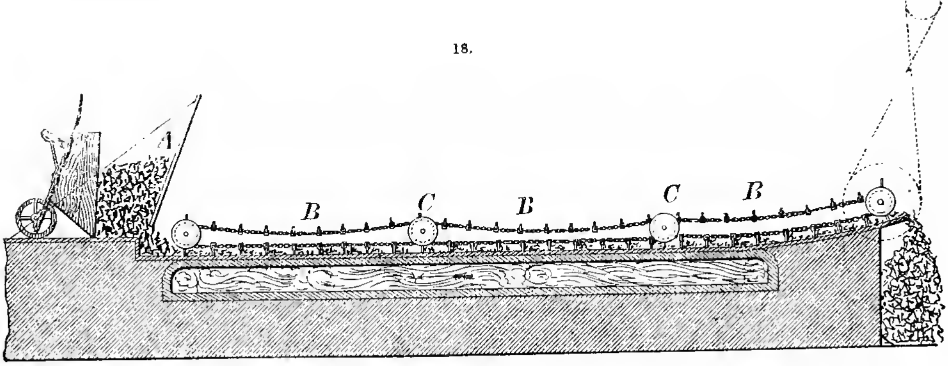
The many excellent points of this apparatus, which is very much to be preferred to the Halliday retort, will be readily appreciated, and when the drying bed and furnace are arranged side by side, as shown in Fig. 20, the machinery and steam-power required are reduced to a minimum. It will be noted that the material is never handled from the time of entering the drying bed to its exit from the furnace as charcoal, and as all the motions are slow the wear and tear of machinery are not great. One defect might be easily remedied. The scrapers now in use, and shown in cross section Figs. 18 and 19, move forward the woody material in small but unbroken heaps, the tops of which never get thoroughly dried. It would be better to serrate these scrapers alternately, as shown in Fig. 21. They would then act rather as claws, breaking up the lines of material into detached and small portions.

17.

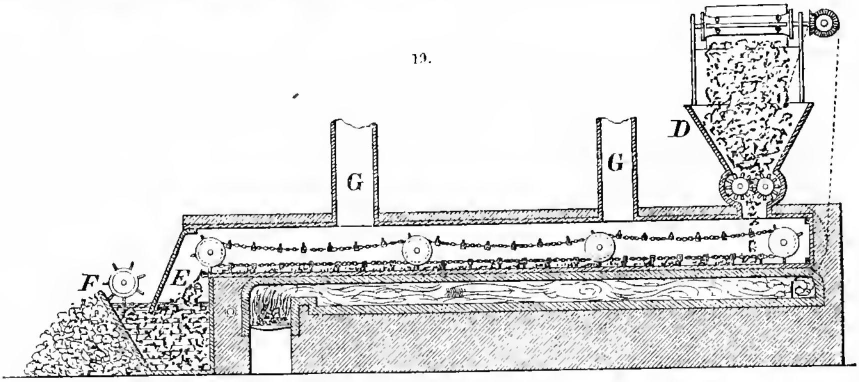


The returns from carbonizers of this description are somewhat unreliable. It is claimed that they not only get through very much more work, but also give more satisfactory results in the way of yields and costs than the ordinary process of timber distillation. In estimates of this kind it must be remembered that against a very large amount of work there is the increased cost of carrying the work on, and, probably from the more or less complete disintegration of the wood, the acid produced is contaminated with resinous and oily substances more intensely difficult to get rid of than is usually the case. Moreover, the charcoal produced is comparatively useless, and most of the woods used in dyeing, e. g. logwood, are not well adapted for distillation. Still, where an ample and low-priced supply of sawdust or spent dye-woods is obtainable—the latter are often to be had for the carting away—the cost of the products of the distillation of such materials must be low, and a further saving is effected in carriage, inasmuch as the process can be advantageously adopted in large towns where the pyroligneous acid, naphthas, and tar compounds can be readily and immediately utilized. It is unfortunate that the charcoal has to be obtained in a wet state, as it does not pay to dry it, and even when dried and ground it makes but an inferior "blacking." Probably something might be done by delivering it into tar and working it up into a patent fuel. Several attempts have been made to cool it in closed chambers without the aid of water, but its fine state of division renders it peculiarly liable to combustion when it is exposed to the air.

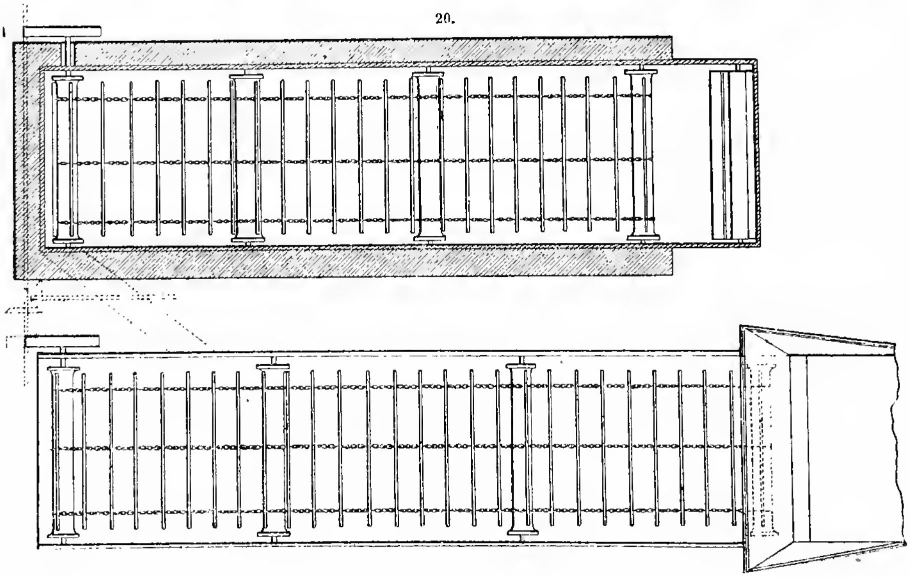
18.



19.

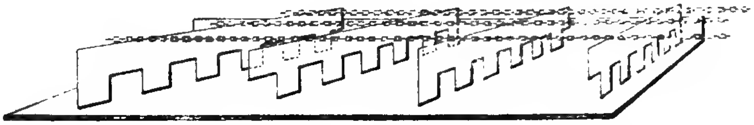


20.



An interesting development of the treatment of sawdust and similar woody material would be the absorption by them of waste liquors and the recovery of the absorbed substances from the charcoal after distillation.

21.



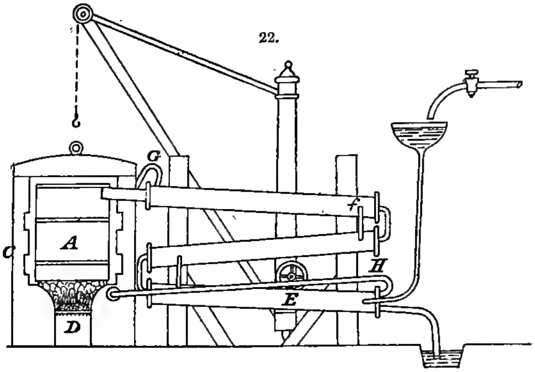
Superheated steam has been occasionally tried as a carbonizing agent in substitution for the ordinary coal fire, and has been the subject of several patents, but the difficulty encountered by obtaining the distillates in only a diluted form has never been overcome. Moreover, direct methods, such as those of Halliday and Bowers, have been devised and satisfactorily worked out, and the employment of waste wood products as a source of pyroligneous acid has of late been very much restricted by their extended utilization in other directions—for bedding and building purposes, &c. The chief value of superheated steam, as will be readily apparent, lies in its adaptability to wood in a finely divided state, in dealing with which the ordinary oven or cylinder breaks down.

Various processes have been set on foot for the extraction of acetic acid from the woody fibres used in paper making—in the preparation of "wood pulp"—the agent employed being steam at a high pressure, to avoid carbonization of the wood. The patent of Mr. George Fry, 1869, may be cited as an example. Insuperable difficulties have, however, been met with in the separation of the acetic acid from the methylic alcohol, formic acid, resins, &c., with which it is intimately mixed, and the processes have never been worked on any large manufacturing scale. The same must be said of the proposals to separate the acid from the accompanying volatile products by presenting to it, during carbonization of the wood, a substance with which it, and it alone, can combine. Desirable as some such process may be, and at first sight seemingly easy of accomplishment, only an imperfect product, of uncertain constitution, has been obtained.

As a step, however, in the right direction, Mr. Steedman's process (patented 1873) for the purification of the crude product of distillation should be noticed. He proposes to pass the impure acid in a state of vapour through a hydrocarbon, oil, or fat, kept sufficiently heated to remain throughout in a liquid state, and preferably at a slightly higher temperature than the acetic acid vapour, to prevent loss by condensation. The process is conducted in "a copper vessel, of a rectangular form, about 5 ft. long, 1 ft. wide, and 2 ft. 9 in. deep. This vessel has fixed inside of it three partitions of copper or wood, horizontal in cross section, but slightly inclined longitudinally. The partitions are open at alternate ends, and the vessel being filled with paraffin or other purifying substance, the acetic acid, which is introduced from the usual distillatory apparatus by a pipe leading in beneath the closed end of the lowest partition, travels along through the paraffin from end to end beneath the partitions, and is finally led from the top of the vessel to an ordinary condensing apparatus. The paraffin or other purifying substance in the vessel is kept heated by a coiled steam-pipe or steam-jacket, and is withdrawn from the vessel whenever it is fully charged with impurities from the acetic acid." Difficulties in regulating this process, its imperfect operation, except after repeated absorptions and waste of the purifying agents, have militated against its success. The words of the patent are quoted in the hope of drawing the attention of manufacturers to the desirability of improving upon the present roundabout way of obtaining a pure acetic acid.

Pyroligneous acid is chiefly prepared for the production of some of the acetates—lime, lead, iron, and copper; also, but to a comparatively small extent, for use as an antiputrescent. About fifty makers are in the trade in England, the chief localities where the manufacture is carried on being Lancashire, Yorkshire, and adjacent counties, and South Wales. There are also a few works in Gloucestershire, Somersetshire, and in the neighbourhood of London. The cost of a plant to work, say, 45 tons of wood per week, with acetate of lime process complete, is about 5000*l.* Distillation is also largely carried on in certain parts of France, Belgium, Germany, Russia, and Sweden, the continental processes being somewhat different from the English, and having a more definite reference to the article which it is chiefly desired to produce.

In France a good yield of acid is usually the main point, and the apparatus shown in Fig. 22 is extensively employed. The charge of wood is arranged in a cylindrical wrought-iron retort A, of a capacity of about 6 cubic yards. Near the top of this cylinder, and at the side is a short exit pipe B for the gases, tapering for adaptation to a connecting pipe. The mouth of the retort is closed by a strong iron cover, which is well luted, and the whole retort then hoisted into the brick furnace C, in the side of which is an opening to fit the exit pipe from the retort. Over the whole is embedded a cover of brickwork or other suitable material. At D is the fireplace. Heat being applied, the charge is first thoroughly dried, the connecting pipe is then fixed and carefully luted, and the products of distillation carried into the condenser. This is usually after the manner shown in Fig. 10, except that instead of a flow of water falling over the sets of pipes, these are themselves "jacketed" with pipes about 4 in. larger in diameter than themselves, and carefully closed at the ends. Water is conducted from a cistern set upon a higher level, enters the lowest jacket E, rises through the small connecting pipes, and finally passes off at G. The uncondensed gases are carried through a pipe H to the fireplace and utilized as fuel, being evenly distributed under the retort by a rose end and regulated by means of a stop-cock. When the flow of liquor ceases, and the connecting pipe between the condenser and the retort cools down, carbonization is complete. The retort is then hauled out of its seat in the furnace and another charged retort substituted for it. Sometimes condensation is effected by simply carrying the gases through a long arrangement of naked pipes, the heat passing off by radiation; or by conducting them into a series of connected wooden chambers; but where economization of water is not an important object the arrangement first described is most esteemed.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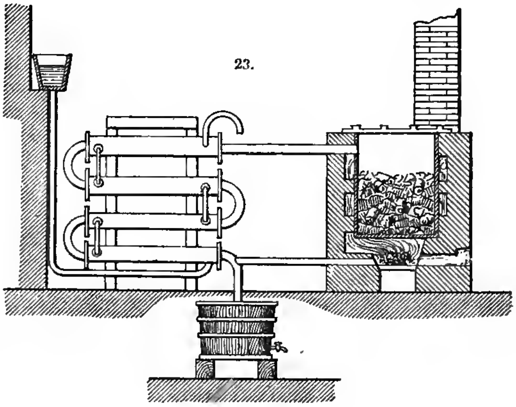

23.

Another apparatus of very convenient form and extensively used is that of M. Kestner's. The drawing, shown in Fig. 23, will be readily understood after a study of our own wrought-iron boxes or ovens of Gloucestershire and South Wales. The retort may be made of either wrought-iron or cast-iron plates bolted together.

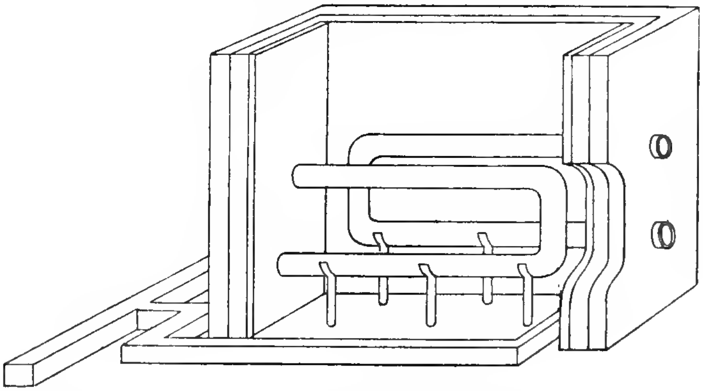
In Germany and Belgium, in districts where a good yield and quality of charcoal are chiefly desired, the furnaces of Schwartz and Reichenbach are esteemed and largely used. These are built of fire-brick, and are often of great capacity, up to 5000 or 6000 cubic feet. Schwartz's furnace resembles an ordinary English coke oven, and the process followed is very similar to that of coke or lime burning, the fire traversing the whole of the interior of the furnace, but with the admission of only sufficient air to carbonize the wood. A free draught is secured by making "flues" with the larger pieces of timber and filling in the smaller pieces loosely; in this way, too, an even distribution of the fire and heat is established. The products of distillation pass off through openings near the bed of the furnace into convenient receptacles and condensers. It is known when the carbonization is complete by the smoke issuing from the chimney turning from black to a bluish white. After being left to cool for about twenty-four hours, a little water is sprinkled over the charcoal from holes in the top of the furnaces, hitherto kept closed, and the whole mass raked out.

In Reichenbach's furnace, which is square, carbonization is effected by heating to redness a series of pipes or flues about 12 in. in diameter, which are carried through the sides of the furnace, and doubled back again. The products of distillation pass off, as in the case of the furnace of Schwartz, through openings at the sole of the furnace, whence they issue into canals and pipes in which the tar is deposited and the acetic acid and other volatile products condensed. Reichenbach's oven is shown in Fig. 24 in section. The method of working will be apparent. The best charcoal, i. e. the most evenly carbonized, is obtained from Schwartz's apparatus.

In Russia and Sweden it is usual to carbonize in conical-shaped pits with a vessel placed alongside, but at a slightly lower level, in which all the tarry and acid products collect. The process is carried on chiefly for the sake of the tar,—coniferous woods, yielding 12 or 13 per cent. as against 8 or 9 per cent. from foliaceous woods, being selected, and only an inferior charcoal produced.

In some parts of France and Germany where there is a rank growth of heather or brushwood, the following process is occasionally adopted:—the material, the cost of which is the expense of cutting, is packed into retorts of wrought iron, shaped like an inverted cone, and is set on fire, only just sufficient air being admitted through convenient openings to effect carbonization. The smoke and products of distillation pass off through a bent tube at the apex of the cone, and are conducted into suitable condensers and settlers.

24.



Schwartz's somewhat peculiar process for obtaining acetic acid from wood may also be noticed. He cuts up the timber into small pieces and arranges it upon bogies in such a way as to allow a current of air to pass freely in all directions through the mass. The bogies are then run into cone-shaped ovens, all outlets are closed, and heat applied externally. The hot air within the oven is driven through the wood by means of fans, and without any actual carbonization a large yield of a peculiar sort of firewood is obtained, and a certain amount of acetic acid and tarry matters. It is claimed for this process that the results are highly profitable, but it is difficult to see how the manifest loss of the products of distillation, which only complete carbonization effects, can be made up.

The third method of preparing acetic acid is by the distillation of certain metallic acetates—soda, lime, lead, or potash—with sulphuric or hydrochloric acid; or, as in the case of binacetate of copper, by heat alone. The process usually employed on a large scale is the distillation of acetate of soda with sulphuric acid; in this way the bulk of the pure acetic acid of commerce is prepared.

Six cwt. of soda acetate is put into a jacketed copper still, heated either by direct fire underneath or by steam, and 312 lb. of sulphuric acid, of a specific gravity of 1·84, added, and intimately mixed with it. The still is then closed in, luted, and connected with a condensing worm of earthenware (preferably of porcelain or even silver), set in a convenient vessel. All the joints of the apparatus should be made of silver. A gentle heat being applied, distillation is allowed to proceed until a faint empyreumatic odour comes from the distillate which runs from the condenser into a suitable receiver. The final products of distillation should thereafter be collected in a separate receiver and re-distilled. If the operation be carefully conducted with fairly pure materials, and at not too great heat, the acid comes over colourless, at about 1·05 sp. gr., containing about 35 per cent. of anhydrous acetic acid. Glacial acetic acid is obtained by distilling the product of the first operation with fused calcium chloride, and cooling the distillation. Below 15°, crystals are deposited, which are re-dissolved in their own mother liquor and re-distilled with calcium chloride until the whole of the acid crystallizes. Above 16°, these crystals deliquesce, yielding a very pure acetic acid of 1·063 sp. gr. Usually only the first part of the process described is followed, an acid at 1·05 being all that is desired by the bulk of consumers. For culinary purposes, pickling, &c., the strong acid is reduced by the addition of five times its weight of water.

The sulphate of soda left in the retort is sold for the purpose of being worked up in the ordinary sulphate process—the manufacture of the salt from chloride of sodium and sulphuric acid—and is worth about 25*s.* per ton. The charge, as above, of 6 cwt. of acetate of soda and 312 lb. of acid, should yield 6½ cwt. of strong acetic acid. The cost of 1 ton of 1·05 sp. gr. acid is about as follows:—

	£	*s.*	*d.*
17 cwt. acetate of soda	18	0	0
7 cwt. sulphuric acid	1	0	0
Fuel	1	5	0
Wages		10	0
Packages		12	0
Wear and tear, &c., and proportion of management expenses ..		2	0
	21	9	0
Less sulphate of soda	1	5	0
	£20	4	0

The selling price of the acid is 2¾*d.* per lb. The cost is usually enhanced by the small amount made.

If the acetic acid from this process does not come over perfectly colourless or free from empyreuma, it may be purified by infusion with animal charcoal, or by allowing it to stand for ten days or so in tubs containing beechwood cuttings.

The plant for the manufacture of, say, 2 tons of acetic acid per week, costs about 1000*l.* About eight makers are engaged in the trade in the neighbourhood of London.

When it is not required to obtain an acid of great purity it may be prepared by distilling brown acetate of lime with sulphuric or hydrochloric acid. When the former is employed, the salt is first broken up and intimately mixed with the acid in any suitable arrangement, usually a cast-iron cylinder, about 5 ft. long by 2 ft. in diameter, set horizontally in brickwork, and having a revolving axis fitted with arms, whereby the acetate is brought into a finely divided state, and at the same time the mixture is thoroughly agitated. A convenient charge consists of 5 cwt. of the salt to 3 cwt. of acid at 1·84 sp. gr. The contents of the cylinder in a half liquid state are drawn off through an opening in the lower part of the front end of the cylinder and placed for distillation in cast-iron trays. These trays vary in size from 4 ft. long, 3 ft. wide, and 2½ in. deep, to 18 in. square and 2½ in. deep. They are transferred to the bed of any suitable furnace, and kept separate by means of rods of iron laid lengthways and transversely. Sometimes a special furnace is built, with a bed 8 ft. 6 in. long by 6 ft. 6 in. wide, and 3 ft. from sole to arch, but usually some unused iron retort is pressed into service, and answers all purposes. In either case heat is applied from a fireplace underneath, and a pipe from the further end of the furnace or retort carries off the products of distillation to any suitable condenser. The acetic acid is largely contaminated with sulphuric acid, sulphur, tarry, oily and various organic matters, from which it is purified by re-distillation with bicarbonate of soda or bichromate of potash. The charge of acetate and sulphuric acid, as above, should yield 7½ cwt. of crude acetic acid of a specific gravity of 1·05. For the re-distillation, cast-iron, copper, iron lined with lead, or earthenware retorts may be used, copper being upon the whole the best.

Distillation with sulphuric acid has been of late years to a great extent abandoned in favour of the newer process with hydrochloric acid, and is now carried on to a very small extent except by manufacturers of sugar of lead, &c. For some of these subsequent processes the impurities referred to are of slight moment; indeed the crystals of sugar of lead obtained by treating litharge with acetic acid produced by the sulphuric acid process are better, finer, and of a purer colour than when hydrochloric acid has been used. A perfectly satisfactory reason for this has not been ascertained; probably the sulphuric acid carbonizes the organic bodies contained to so large an extent in even the finest acetate of lime, and so renders them more easily got rid of. It must be remembered that, even when by repeated re-distillation the acetic acid is rendered to all appearance colourless these organic matters may still be present.

Distillation with hydrochloric acid upon a large scale is often carried out in the simplest possible manner, very little labour or plant being required. Good brown acetate, containing 70 per cent. of real acetate of lime, is dissolved in, and distilled with, an acid of 1·16 sp. gr., the proportions varying with the quality of the lime salt and its constituents. Usually every 100 parts of good acetate will require 95 parts of acid. An ordinary jacketed still and copper condenser-pipes may be used. The acetic acid comes over at 1·05 to 1·06 sp. gr., has a slight brown coloration, and a strong empyreumatic taste and smell. It is, however, sufficiently good to make a very fair sugar of lead, and is largely sold for the purpose,—also for further purification. Occasionally this rough acid is re-distilled at a gentle heat before being sent into the market. It is worth about a penny per pound.

A very much better article, however, is obtained by the following process. A pure brown acetate of lime is first prepared by thoroughly settling, or even filtering, the saturated liquors, after the naphtha has been expelled, skimming off all the impurities which rise to the surface, and transferring only the clear liquor to an evaporating pan. Here it is evaporated to one-half its bulk and hydrochloric acid is added until litmus is just reddened. The resinous bodies still contained in the lime liquors are thereby further separated out and the creasote and other volatile compounds decomposed and driven off by further evaporation. The quantity of hydrochloric acid which it is necessary to add varies of course with the strength and quality of the crude acetic acid, but may be averaged at 5 lb. to every 33 gallons of the liquor left after the naphtha has been expelled. The solution of lime salt is now boiled down to dryness, being stirred frequently during desiccation to allow of the free emission of all vapours. By this means all volatile empyreumatic substances are driven off, and an almost inodorous acetate of lime, of a brownish colour but remarkably pure quality, is obtained.

Iron plates heated by a fire underneath are sometimes employed for the final drying and charring;—a more certain clearing of the salt is thereby ensured, especially when the quantity operated upon is large. A brown acetate is preferred to a grey, because by saturation of the acid liquors *before* distillation a certain amount of the impurities are carried down by the lime.

The lime salt, carefully prepared in this way, is next distilled with hydrochloric acid of about 1·16 sp. gr., and a very good acetic acid of 1·06 sp. gr. with 40 per cent. of anhydrous acid obtained. If the separation of the resinous compounds which rise to the surface, by skimming or filtration, is carefully attended to, the acid comes over perfectly colourless, with a slight ethereal odour which may be got rid of altogether by digestion with animal charcoal, or distillation with 3 per cent. of bichrome. Inasmuch as an acid of 1·06 sp. gr. is rarely required by consumers, the mixture of lime salt and hydrochloric acid may be advantageously diluted with water—preferably before distillation, as the acetic acid comes over more freely from a weak than a concentrated solution. The following proportions may be recommended:—

100 parts of lime acetate;
95 parts of hydrochloric acid;
25 parts of water;

which should yield 95 to 100 parts of acetic acid of 1·05 sp. gr.

A slight excess of hydrochloric acid in this process is not of much consequence. It can be readily got rid of, and indeed when the acetic acid is subjected to further purification, is no evil. The excess, however, must be no more than to render the distillate slightly turbid when tested with nitrate of silver. This point should be carefully attended to.

With the reservation already set forth, the process of distillation with hydrochloric acid is very much to be preferred to that with sulphuric. In deciding, however, which method to adopt, the manufacturer must take into account his position and the relative costs of the raw materials, as there is not sufficient advantage on either side to counterbalance these incidental circumstances. The wear and tear of plant with hydrochloric acid is slightly less than with sulphuric, and the resinous compounds are kept in a harmless state. The sulphate of lime too, formed in the distillation of the lime salt with sulphuric acid, is apt to form a crust on the bottom of the retort, and cause the metal to crack, besides wasting a certain amount of heat. When the process just described is carried out in its entirety, and carefully, an acid is obtained little inferior to that produced in the ordinary way from acetate of soda and sulphuric acid.

A similar process has been adopted to some extent on the Continent for the production of acetic acid from brandy vinegar, but in this case of course there is not the same amount of tenacious impurity to be got rid of. Strong brandy vinegar, containing up to 12 per cent. of anhydrous acid, is saturated with lime, and the turbid solution filtered and evaporated to dryness in an iron pan. The dry salt obtained is perfectly white, as the colouring matters contained in the solution are oxidized by the action of the air. The decomposition of the acetate of lime is effected by hydrochloric acid in the manner described, but as there is less admixture of foreign substances than in the acetate obtained from pyroligneous acid, a larger proportion of hydrochloric acid is required for the decomposition, viz. about 130 parts of acid to 100 parts of lime salt.

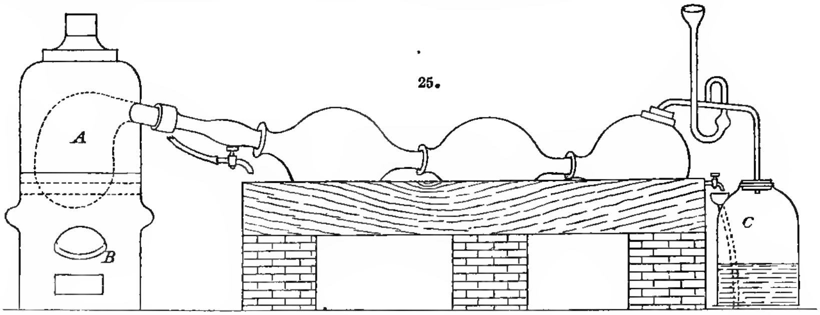
The final purification of the acetic acid obtained may be effected by any convenient method. No extraordinary plant is required for these processes. The usual naphtha stills and evaporating pans of the brown acetate process may be used, and for the distillation with hydrochloric acid a copper still with leaden or copper condensing pipes laid in water. Earthenware has been tried, but copper and lead are preferable as lasting longer, and in no way do they contaminate the acetic acid if the operation be conducted with care.

The production of acetic acid from acetate of lime has assumed large proportions of late years, as much as 5000 to 6000 tons of brown acetate being annually consumed by the trade. The chief seats of the industry are Lancashire, South Wales, and London. The product is known by the name of *second* acid, or simply "seconds."

The manufacture of acetic acid from the acetate, or, more correctly, the binacetate, of copper is of very old standing. From the time of the alchemists until a comparatively recent date the bulk of the acetic acid used was obtained by this method, now pursued almost entirely for the subsequent manufacture of the well-known aromatic vinegar. The copper salt is prepared by dissolving verdigris in hot acetic acid and allowing the solution to cool. The acetate crystallizes out in dark-green crystals, which yield, upon the application of heat, strong acetic acid, slightly admixed with acetone. The process of distillation is shown in Fig. 25.

The crystals of acetate, which should be anhydrous and kept as dry as possible, so as to make a strong distillate, are introduced into a suitable glass or earthenware retort A, and a gentle heat applied from a fire at B. The acid distils over, and collects in a series of glass coolers, placed in cold water. The last of these is furnished with a Welter's tube, one arm of which dips into water or distilled vinegar in a vessel C, where all previously uncondensed vapours are collected. As soon as the acid comes over freely the temperature is raised, and gradually increased until distillation is complete, shown by the receivers becoming cool and the bubbles in the final condenser C ceasing altogether. The fire is then extinguished, the apparatus disconnected, and the receivers are emptied. The first acid that comes over is weak, diluted with whatever moisture may be in the copper salt.

If desirable, this may be collected separately. Various precautions should be observed during distillation, as the vapours come over exceedingly hot. The temperature may be easily regulated by observing the rate at which the air bubbles through the liquid in the final receiver D. If there is any vigorous displacement, the fire should be immediately checked. The water in the basins round the receivers should be renewed from time to time, but carefully, to prevent breakage, as the receivers get very hot. A trough or spout of running water may be advantageously substituted for the ordinary separate basins. The retort should be well filled with the copper salt, so as to have as small an admixture of air as possible, and both retort and receivers covered, the former with some non-conducting material, and the latter with cloths kept constantly damp. Finally, all joiutings should be perfectly dry before heat is applied.



25.

During the distillation, fine portions of the copper salt are usually carried over, and give the distillate a pale-green colour. It is rectified by careful re-distillation, for which purpose the same, or a similar, apparatus may be used. If it be desired to obtain the whole of the acid from the copper salt, the last portions that come over should be collected in a separate receiver, as they are slightly empyreumatic. Twenty lb. of acetate should yield 10 lb. of crude, and 9½ lb. of the re-distilled acid, of a specific gravity of about 1·08 when the contents of all three receivers are mixed together. In the retort is left, after the first operation, a mixture of metallic copper with a little charcoal, amounting in all to about one-third of the weight of acetate used.

This process is still carried on in France to a considerable extent for the production of aromatic vinegars, for which purpose the acetic acid thus obtained is manipulated with various essential oils, camphor, and aromatic herbs, such as rosemary, thyme, &c. These preparations are known by several other names—acetum prophylacticum, Marseilles vinegar, *vinaigre des quatre voleurs*—the latter from the four thieves who, during a plague at Marseilles, plundered the sick and dead, escaping unhurt themselves through a plentiful use of the medicated vinegar. For further details of the manufacture see "Aromatic Vinegar."

The last process for obtaining acetic acid by the distillation of its salts which it will be necessary to notice is that patented by Mr. H. B. Condy in 1868, and now in successful operation in Newcastle-upon-Tyne.

Proceeding from the already established fact that a solution of acetate of lime and chloride of calcium in equivalent proportions yields, when slowly evaporated, crystals of calcium aceto-chloride ($CaCl, CaC_2H_3O_2 + 5H_2O$), Mr. Condy demonstrated that the salt may be obtained readily and pure in quality even when a black or brown acetate of lime is employed. The patent may then be divided into two parts, (1) the preparing of the peculiar lime salt, (2) the production of acetic acid therefrom.

In the manufacture of the aceto-chloride of calcium, 12 cwt. of brown acetate of lime are dissolved in 500 gals. of boiling water, and the solution is allowed to settle thoroughly, an operation usually requiring twenty hours, or thereabouts. The clear liquor is then transferred to another vessel and about 7 cwt. of dry chloride of calcium dissolved in it, the mixture being well stirred and heated during and after the addition of the chloride. This quantity required, 7 cwt., varies with the amount of impurity present; or, if the chloride be used in the state of solution, the amount of water must be taken into account. In addition, however, to the quantity required to form the aceto-chloride, there should be an excess of about 20 per cent. The mixed solution of acetate of lime and chloride of calcium should stand at a specific gravity of 31° Beaumé; if weaker or stronger it should be concentrated or diluted until it registers the desired strength; it is then drawn off to crystallize. The mother liquor from the first crystallization is evaporated till a strength of 31° Beaumé is attained, transferred to the crystallizing pans, and a second crop of crystals of aceto-chloride taken off. This process of crystallizing down the mothers is repeated until five crops are obtained, the liquor from the second crop being brought to 33° Beaumé, from the third 35°, and from the fourth 36°. The last mother liquor retains nearly all the empyreumatic compounds of the original salt, and the five crops of crystals, which are of remarkably uniform character, contain all the lime salt worth extracting. The final "mothers" may be distilled with sulphuric or hydrochloric acid in the manner already described for the production of a second quality of acetic acid.

The five crops of aceto-chloride are next mixed together, carefully washed with water, and allowed to drain. They are then dissolved in about twice their weight of water, and to the filtered solution a further quantity of about 10 per cent. of chloride of calcium is added. The reinforced solution is evaporated to 30° Beaumé, and finally crystallized in precisely the same manner as before to produce four crops. The last mothers from this second operation may be added to the previously obtained impure acetate solution for treatment with sulphuric or hydrochloric acid.

This process may be modified in one or two ways, by the use of distilled acetate, or by the use of pyroligneous acid. In the latter case the acid must be neutralized with lime and tested for brown acetate, a solution containing 1 part of the salt in 10 parts, requiring the proportions stated above. As brown acetate of lime is a very uncertain article, of constantly varying constitution, it is advisable to test the hot mixture during evaporation, by setting a sample aside to cool from time to time, after 30° has been attained, to see if a good crop of crystals forms. The standards given above are only indications of the strengths required by an average sample of good acetate. If distilled acetate of lime be used instead of brown, the proportions will be 8 parts of the lime salt to 6 parts of chloride of calcium.

It is very advisable in all cases to get rid of a certain amount of the impurities, always present, by roasting the acetate before dissolving. For this purpose any unused wood cylinder, say 7 ft. long by 4 ft. in diameter, may be used, a grating being placed near the bottom, which should touch the sides of the retort at as few points as possible. The acetate is placed in shallow sheet-iron trays, similar to those used in the distillation with sulphuric acid, about 2 in. deep, and arranged one above another on the grating until the retort is filled. The trays are separated by rods of iron laid the lengthways of the retort. A gentle heat is then applied from a fire underneath until the exit pipe from the retort begins to get cool, shewing that all the water and volatile impurities have been driven off. The fire is then drawn and the whole allowed to cool down. This operation takes about forty-eight hours for completion.

Instead of roasting the acetate, the aceto-chloride may be treated in a similar manner, or the mixture of acetate of lime and chloride may be filtered through animal charcoal, or any similar substance capable of separating out the empyreumatic bodies. The process described, however, is that usually employed.

To obtain the acetic acid from the crystals of aceto-chloride, they are distilled in the usual manner with hydrochloric or sulphuric acid in any suitable still and condensing arrangement. The best proportions are 112 parts of aceto-chloride to 24 parts of sulphuric acid of a specific gravity of 1·84—preferably diluted with twice its volume of water—or 100 parts of the lime salt to 50 parts of hydrochloric acid. Whichever acid is used, the distillation is more readily effected when the solution in the retort is well diluted with water. This has already been pointed out in describing the ordinary process of obtaining "second" acid by distillation.

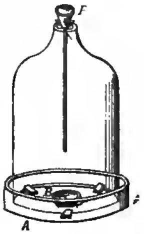
The acetic acid produced in this way is purified by re-distillation with an alkali in the proportions of 1 lb. of alkali to 10 gallons of acid.

As yet only a very small quantity of the acid that comes into the market is obtained by Mr. Condy's process, there being a prejudice against it on the part of consumers, which seems to be entirely unfounded.

The production of acetic acid from the other acetates, of lead, silver, potash, &c., is not of sufficient importance to require notice.

Besides the three chief methods described—acetous fermentation, wood distillation, and the distillation of the acetates—acetic acid is occasionally obtained by the distillation of vinegar, and, for laboratory purposes, by the direct oxidation of alcohol through the medium of spongy platinum. This substance possesses the property of absorbing within its pores several hundred times its own weight of oxygen, and the alcohol, presented in a state of vapour, undergoes combustion and is converted into acetic acid. The operation may be conducted on a small scale by means of the apparatus shown in Fig. 26. Air is admitted between the rim of the bell-jar and the dish A in which it is supported; the platinum black is placed in a small porcelain saucer B and alcohol is dropped upon it through the funnel E, which terminates in a fine point. The acetic acid condenses and collects in the dish.

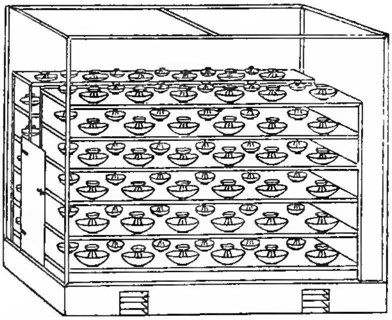
26.



On a larger scale, a series of shallow earthenware or porcelain vessels are arranged on shelves fixed about 12 inches apart in a glass case, or a wooden box with a glass cover, to admit the heat of the sun. In each dish is placed a small tripod about $1\frac{1}{2}$ to 2 in. high, bearing a watch glass, the bottom of which is well covered with spongy platinum.

The lower porcelain dishes are conveniently filled with alcohol, and the temperature of the case raised by any suitable means to about 32° (90° F.). The spirit is converted into a state of vapour, which, coming in contact with the air held in the pores of the platinum, is oxidized into acetic acid, and falls back into the dishes or collects in a receiver arranged at the bottom of the case. To convert the whole of the alcohol into acetic acid, or to keep up a continuous production, it is of course necessary to renew the exhausted air of the case from time to time. The apparatus is shown in Fig. 27.

27.



Formerly, and especially on the Continent, where the duty on alcoholic liquids is low, this process of direct oxidation was largely carried on. It has, however, been found that a considerable loss of alcohol takes place through volatilization.

A considerable number of waste and bye-products exist which contain considerable quantities of acetic acid, and in the treatment of which a good deal might, and will, be done. The obstacles usually encountered are the large quantity of material to be treated, the difficulty of separating the impurities, and the comparatively small value of the acid obtained. The waste liquors from the manufacture of various indiarubber goods may be cited as an example. These liquors contain considerable quantities of acetate of lime, but mixed intimately with hyposulphite of lime (and lead), and contaminate the product if simple distillation with sulphuric or hydrochloric acid be attempted. It has been proposed to employ chlorine to convert all the sulphur acids and salts present into sulphate of lead, which can be filtered off or allowed to subside.

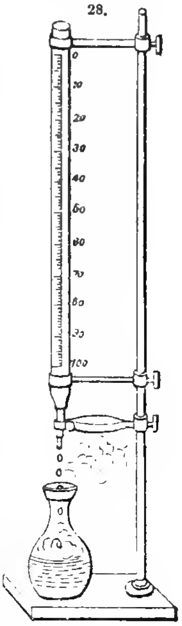
Special details relating to the determination of the strength of acetic acid are interesting rather to the chemist than the manufacturer. As, however, it is often necessary for the latter to be in possession of some ready means of ascertaining the value of his product, or purchase, it may be stated that three methods of testing may be employed:—(1) neutralization with pure carbonate of soda or potash, and determination of the quantity required to saturate the acid; (2) the specific gravity after neutralization with hydrate of lime; (3) the simple specific gravity by acetometer. It has already been shown (see Mohr's table) that the last-named method is very unreliable, and can only be used as a rough test or within certain limits. It must be borne in mind that the test by acetometer is interfered with by the varying amounts of foreign and organic bodies, always present except in the case of a purified sample, which increase the density of the liquid; and, furthermore, that the results vary for different temperatures. The following table, drawn up by Oudemanns, shows this difference between 15° and 40°, in liquids containing from 1 to 100 per cent. of acetic acid.

Acetic Acid $C_2H_4O_2$ per cent.	Density.			Acetic Acid $C_2H_4O_2$ per cent.	Density.		
	0° C.	15° C.	40° C.		0° C.	15° C.	40° C.
1	1·0016	1·0007	0·9936	21	1·0359	1·0298	1·0166
2	1·0033	1·0022	0·9948	22	1·0374	1·0311	1·0176
3	1·0051	1·0037	0·9960	23	1·0390	1·0324	1·0187
4	1·0069	1·0052	0·9972	24	1·0405	1·0337	1·0197
5	1·0088	1·0067	0·9984	25	1·0420	1·0350	1·0207
6	1·0106	1·0083	0·9996	26	1·0435	1·0363	1·0217
7	1·0124	1·0098	1·0008	27	1·0450	1·0375	1·0227
8	1·0142	1·0113	1·0020	28	1·0465	1·0388	1·0236
9	1·0159	1·0127	1·0032	29	1·0479	1·0400	1·0246
10	1·0176	1·0142	1·0044	30	1·0493	1·0412	1·0255
11	1·0194	1·0157	1·0056	31	1·0507	1·0424	1·0264
12	1·0211	1·0171	1·0067	32	1·0520	1·0436	1·0274
13	1·0288	1·0185	1·0079	33	1·0534	1·0447	1·0283
14	1·0245	1·0200	1·0090	34	1·0547	1·0459	1·0291
15	1·0262	1·0214	1·0101	35	1·0560	1·0470	1·0300
16	1·0279	1·0228	1·0112	36	1·0573	1·0481	1·0308
17	1·0295	1·0242	1·0123	37	1·0585	1·0492	1·0316
18	1·0311	1·0256	1·0134	38	1·0598	1·0502	1·0324
19	1·0327	1·0270	1·0144	39	1·0610	1·0513	1·0332
20	1·0343	1·0284	1·0155	40	1·0622	1·0523	1·0340

Acetic Acid $C_2H_4O_2$ per cent	Density. 0° C.	15° C.	40° C.	Acetic Acid $C_2H_4O_2$ per cent.	Density. 0° C	15° C	40° C.
41	1·0634	1·0533	1·0348	71	1·0875	1·0737	1·0497
42	1·0646	1·0543	1·0355	72	1·0879	1·0740	1·0498
43	1·0657	1·0552	1·0363	73	1·0883	1·0742	1·0499
44	1·0668	1·0562	1·0370	74	1·0886	1·0744	1·0500
45	1·0679	1·0571	1·0377	75	1·0888	1·0746	1·0501
46	1·0690	1·0580	1·0384	76	1·0891	1·0747	1·0501
47	1·0700	1·0589	1·0391	77	1·0893	1·0748	1·0501
48	1·0710	1·0598	1·0397	78	1·0894	1·0748	1·0500
49	1·0720	1·0607	1·0404	79	1·0896	1·0748	1·0499
50	1·0730	1·0615	1·0410	80	1·0897	1·0748	1·0497
51	1·0740	1·0623	1·0416	81	1·0897	1·0747	1·0495
52	1·0749	1·0631	1·0423	82	1·0896	1·0746	1·0492
53	1·0758	1·0638	1·0429	83	1·0896	1·0744	1·0489
54	1·0767	1·0646	1·0434	84	1·0894	1·0742	1·0485
55	1·0775	1·0653	1·0440	85	1·0892	1·0739	1·0481
56	1·0783	1·0660	1·0445	86	1·0889	1·0736	1·0475
57	1·0791	1·0666	1·0450	87	1·0885	1·0731	1·0469
58	1·0798	1·0673	1·0445	88	1·0881	1·0726	1·0462
59	1·0806	1·0679	1·0460	89	1·0876	1·0720	1·0455
60	1·0813	1·0685	1·0464	90	1·0871	1·0713	1·0447
61	1·0820	1·0691	1·0468	91	..	1·0705	1·0438
62	1·0826	1·0697	1·0472	92	..	1·0696	1·0428
63	1·0832	1·0702	1·0475	93	..	1·0686	1·0416
64	1·0838	1·0707	1·0479	94	..	1·0674	1·0403
65	1·0845	1·0712	1·0482	95	..	1·0660	1·0388
66	1·0851	1·0717	1·0485	96	..	1·0644	1·0370
67	1·0856	1·0721	1·0488	97	..	1·0625	1·0350
68	1·0861	1·0725	1·0491	98	..	1·0604	1·0327
69	1·0866	1·0729	1·0493	99	..	1·0580	1·0301
70	1·0871	1·0733	1·0495	100	..	1·0553	1·0275

The first method—neutralization with the carbonate of an alkali—is usually adopted for all careful testings. A "standard," or "test," solution is prepared by dissolving, say, 530 grains of pure carbonate of soda in 10,000 grains of distilled water. This standard solution may, of course, consist of any quantity, provided that the right proportions are carefully registered; it should be kept well stoppered. A known weight of the sample of acetic acid is weighed off into a flask and a little litmus solution dropped in. The standard solution is then added until the solution just turns blue. It is then well boiled to drive off the carbonic acid which would redden the solution, and if the blue colour has disappeared a little more of the standard solution is added to the boiling mixture until a permanently purple hue is induced, showing complete neutralization of the acid. A simple rule-of-three calculation then gives the amount of acetic acid present in the sample, since every 106 parts of the pure dry carbonate of soda put into the standard solution are equivalent to, or indicate, 120 parts of pure acetic acid. The standard solution must be very delicately used as the point of neutralization is approached, that there may not be an excess of alkali added. The apparatus best adapted for the process is shown in Fig. 28, Mohr's burette.

28.



Acetic acid, especially the "second" acid, obtained from the acetate of lime, is liable to contamination with considerable quantities of sulphuric or hydrochloric acid if the process has not been carefully conducted. Positive adulteration with these acids, too, is frequently resorted to by vendors with the idea that the acetic acids keep better (a mistaken notion), or to increase unduly the amount of acidity. A rough test of any sample may be readily made by boiling it with a little potato-starch for about ten minutes, allowing it to cool and adding a few drops of iodide of potassium. If the acetic acid be pure, the blue colour of iodide of starch will immediately make its appearance, but if either sulphuric or hydrochloric acid be present the starch is converted upon boiling into dextrin, and no blue colour becomes visible.

A separate qualitative test for the presence of sulphuric acid is the addition of a soluble salt of barium, when the insoluble barium sulphate precipitates in the well-known form of a white heavy powder. This is an exceedingly delicate test, the precipitate making its appearance when so small a proportion as $\frac{1}{1000}$th of the adulterant is present. If the quantity be so very small, however, the mixture requires a little time and vigorous shaking before the precipitate settles out. The presence of hydrochloric acid may be ascertained by the formation of a white precipitate of chloride of silver upon the addition of a few drops of nitrate of silver.

In testing vinegars for sulphuric acid, the presence of certain natural and soluble sulphates should be remembered, and made allowance for, as the sulphuric acid in combination will show upon the addition of the barium salt, in the form of a very slight precipitate.

All these processes of testing are of course only rough, i. e. *qualitative*, methods of ascertaining if the acid as manufactured or consumed is of good or inferior quality. The presence of free sulphuric acid is particularly hurtful if the acetic acid or vinegar be intended for pickling or any culinary use, as it injures the coats of the stomach. Only distilled water should be used for testing, as spring and river waters often contain certain soluble sulphates.

The Acetates.—It has been said that acetic acid forms with various bases a series of valuable salts. These are for the most part readily soluble in water, the least soluble being the silver and mercury salts. All are decomposable by heat, most of them yielding carbonic anhydride, acetone, and an empyreumatic oil. Those, however, which are most easily decomposed, and contain bases forming stable carbonates, are resolved into acetone and a carbonate of the base. Heated with a large excess of a fixed caustic alkali, they are resolved at a temperature below redness into marsh gas and alkaline carbonate. Distilled with sulphuric acid they yield acetic acid, with sulphuric acid and alcohol acetate of ethyl. Heated with arsenious acid, they give off the odour of cacodyl. The most important of the acetates will be described in alphabetical order.

ALUMINA, ACETATES OF.—Acetic acid forms with alumina a series of salts, the exact constitution of which is still somewhat doubtful, but which are all exceedingly valuable in the arts. The sesquiacetate, or "red liquor" of the calico-printers, is perhaps the most extensively used. It is obtained by mixing solutions of lead acetate and alum, allowing the preparation to cool and settle, and filtering off, or decanting, the clear liquor from the insoluble lead sulphate. Equal weights of alum and acetate may be used, but some makers prefer a smaller quantity of the lead salt. Usually a little chalk, soda ash, or soda crystals is added, in the proportion of 5 to 10 per cent. of the weight of alum, to neutralize the free acid present. Red liquor is also prepared, in a similar way, from mixed solutions of alum and lime acetate, lime sulphate settling out, but the product in this case usually retains a certain amount of the sulphate, which impairs the colour, and makes the cloth finish rough. Sulphate of alumina may be advantageously substituted for alum. Not only does the sulphacetate of alumina give as strong a red liquor as that prepared from ammoniacal alum, but the cost is less. Choice of the materials is, however, governed by the prejudices of the consumer or the purposes for which the liquors are made.

The method of manufacturing a good red liquor is as follows:—50 gallons of acetate of lime liquor marking 24° Tw. are heated up to 60° (140° F.) in a copper pan, and 200 lb. of ammonia alum in a crushed or roughly powdered state are well stirred into it, the temperature being kept up until the alum is thoroughly dissolved. This operation usually takes a couple of hours. About 12 lbs. of ground chalk are then stirred into the mixture, which is allowed to cool and settle. The clear supernatant red liquor is then siphoned off, and should register about 20° Tw. The residue, consisting chiefly of sulphate of lime, retains a considerable amount of the mordant, and should be washed with hot water. The washings form a weaker red liquor, or are used to dissolve a fresh batch. The red colour is imparted by mixing with the clear liquor a small quantity of a preparation of lichens. Other good recipes are:—

90 gals. of acetate of lime liquor at 24° Tw.;
372 lb. of sulphate of alumina;
34 lb. of chalk;

the red liquor from which marks about 16° Tw.

Or—

1132 lb. of boiling water;
453 lb. of sulphate of alumina;
379 lb. of acetate of lead;

the liquor from which should stand at 18° Tw.

Or—

150 gals. of boiling water;
460 lb. of alum (potash alum);
460 lb. of acetate of lead;

giving a red liquor of 12° Tw.

The following gives a good Resist Red Liquor:—

1 gal. water.
5 lb. alum.
2½ lb. acetate of lead.
¼ lb. soda crystals.

Acetate of lead gives more certain results than acetate of lime, as it is usually more to be depended upon in quality, the composition of the lime salt being so exceedingly variable. Ammonia alum is also an article of uncertain constitution, and should only be used when its real value can be ascertained by analysis. The sulphate of lime residue is more difficult to deal with than sulphate of lead, as it is much more bulky, and retains a greater proportion of the mordant, requiring therefore more careful washing. All the materials used should be of the best quality, the presence of iron in the alum being especially hurtful. As far as possible all red liquors should be made for immediate consumption, as they deteriorate when kept.

A very excellent mordant for alizarine colours is made on the Continent by dissolving precipitated alumina in glacial acetic acid. This method has been adopted occasionally in this country, but is exceedingly troublesome. Upon the whole, the crude pyroligneous is the best form of acetic acid for red liquor manufacture, as its very impurities help to give a certain stability to the compound by retarding oxidation.

A good English red liquor will contain from 3 to 5 per cent. of alumina, and the amount of dry acetic acid should be equal to twice the weight of alumina. The constitution of the liquors, however, varies very much with the particular localities and circumstances. Alumina mordants are excessively sensitive, and care must be taken not to heat the cloth too strongly when drying, or else only variable shades of colour are produced. This is especially the case when the mordants are used in a dilute state.

Acetate of alumina, always obtained in a liquid form, and standing from 12° to 20° Tw., is extensively used by calico-printers and, but in a less degree, by dyers, in fixing the colour upon the cloth. For some purposes—as in the printing of pale pinks—the solution is very much diluted, down even to 2° Tw. The mordants owe this property of fixing to their ready decomposition by heat, the acetic acid which they contain being liberated, and the base, with the colouring matter —for which as well as for the fibrous material it has a strong affinity—being deposited upon the cloth. As may be inferred from the name (mordre, Fr., *to bite*), the action of the mordant was formerly supposed to be simply mechanical, corroding and opening the fibre of the cloth, and allowing the permeation of the colouring principle. It will be readily appreciated that a mordant must be retained by only one portion of the cloth, the rest being left white or occupied by some other mordant or colour. At the same time, it must be used in the fluid state, so that the fibre may be thoroughly impregnated; and it is therefore necessary to guard against a natural inclination of the liquid to spread beyond its proper limits, aided by the capillary attraction of the cloth. For this purpose what are called "thickenings" are used—gum, starch, flour, &c.—which overcome the natural inclination of the mordant and the attraction of the fibre, and also allow of the application of a larger amount of mordant than could be made if the latter were a thin liquid. These thickenings, which are mixed with all mordants in printing and dyeing, are only temporary in their use, and have to be removed before the colours are finished.

The acetates of alumina do not act as well as cream of tartar and some other mordants in the treatment of *woollen* goods, owing to the very strong affinity existing between the base and the fibre of the material. The acetic acid is given off too rapidly, and the mordanting merely superficial.

Alumina salts as mordants seem to have been known about 140 years, the first patent being taken out by Chappell, in 1742, for a mixture of alum, arsenic, chalk, white argol, and lead acetate. The manufacture is carried on extensively in the Lancashire and Yorkshire cotton and woollen districts; also at Glasgow and at a few places in France. Altogether there are about fifty chemical manufacturers engaged in the trade in this country, but occasionally the calico-printer or dyer manufactures for his own consumption. The turn-out depends very much upon the varying strengths and qualities of the liquors required from time to time. In round numbers about 20 per cent. of the total alum manufactured in England is absorbed by the red liquor trade. The plant required is of the simplest and most inexpensive description.

Analysis of the acetates of alumina is but an unreliable test of their real value as mordants, the best guide being actual trial of any given sample upon cloth against mordants of already ascertained quality.

Ammonia, Acetate of, sometimes called *Spirit of Minderus*, is a colourless salt, obtained either by saturating strong acetic acid with dry ammonia, or by distilling a mixture of equal parts of lime acetate and sal-ammoniac—chloride of calcium remaining in the retort. It is used to some considerable extent in medicine as a sudorific in febrile and inflammatory diseases, singly or combined with opium, camphor, &c. Berthollet has proposed to obtain a pure salt by evaporating the solution of the commercial article with excess of ammonia. After cooling in ammonia vapour, the salt is broken up and kept in a jar filled with ammonia.

Copper, Acetates of—technically known as Verdigris. (Fr., *Vert-de-gris*; Ger., *Grünspan.*)—There are two principal acetates of copper, common verdigris—a sub-acetate—"blue" or "green," obtained by exposing to the air plates of copper in contact with the "marc" or refuse of grapes (i. e. the grapes after the juice has been expressed), and distilled verdigris, a neutral acetate, obtained by dissolving the common verdigris in hot acetic acid, and leaving the salt to crystallize out from the cooled solution. On account of the variable quality of the common verdigris, the distilled is often also manufactured from a mixture of sulphate of copper and acetate of lead; sulphate of lead remains an insoluble precipitate, and the clear acetate of copper is filtered off, concentrated by evaporation, and allowed to crystallize.

The process for obtaining common verdigris is as follows:—The refuse from the wine-presses is thrown into casks, which are loosely covered over with matting to keep out dust and dirt. It will be readily understood that the less severe the previous pressing of the grapes the better for the subsequent process. When placed in the casks the material should be disintegrated as much as possible, occupying at least double the space it did when compressed. Partial fermentation, with the generation of acetic acid, speedily commences, and is allowed to go on for about four days, until a test sheet of copper, immersed in the mass for four-and-twenty hours, is covered with a green layer of acetate. In the meantime the sheets of copper to be operated upon have been subjected to a careful hand hammering to ensure perfect consolidation, cut into pieces about 8 in. long, 4 in. broad and $\frac{1}{24}$th of an inch thick, then immersed in a strong solution of verdigris and stacked up to dry, or, to save time, dried quickly over a charcoal fire. When it has been ascertained by the test sheet that acetous fermentation in the casks has gone far enough, the small sheets of copper are heated to about 93° (200° F.) and sandwiched with the grape refuse, taking care to have a layer of the fermenting material both at the top and at the bottom of the cask. After a varying period of from twelve to twenty days the coverings are removed, and if the uppermost layer of material has become white it is judged that the operation is complete. The casks are then emptied, the grape refuse thrown away, and the sheets of copper, which should now be evenly covered with fine green crystals, set up to dry. After the lapse of about three days they are dipped in water (or, preferably, damaged wine, whence the trade terms of "one wine," "two wine," &c.), again set up to dry, and the verdigris formed scraped off with a knife. This process of dipping, drying, and removing the verdigris occupies about eight days, and is repeated until the whole of the copper is converted into verdigris. The damp salt when scraped off is kneaded with a little water, packed into leather bags (about 18 in. long by 10 in. in diameter, containing about 25 lb. weight), and exposed to the sun. When thoroughly dry it becomes a hard, tough mass, and is ready for the market.

This process was formerly almost entirely carried on in France and Belgium, especially in the first-named country, upon the vine-farms, where it forms part of the regular domestic routine. Now, however, considerable quantities of verdigris are made in England, Germany, and Sweden, where cloths steeped in pyroligneous acid, and the cider refuse, are the materials chiefly employed in the corrosion of the sheets of copper. The cloths require to be damped afresh every three or four days until the plates are covered with their even layer of crystals.

The distilled verdigris, obtained, as has been said, by crystallization from a hot solution of the common verdigris, or from a mixture of sulphate of copper and acetate of lead, forms dark-green crystals soluble in 14 parts of cold or 5 parts of hot water, and also in alcohol. It is extensively used in the manufacture of aromatic vinegar, as the source from which the acetic acid is obtained. This process of distillation has been already described. It is also used as a mordant, but is feeble in its action.

All the acetates of copper form valuable pigments; they are used in dyeing and calico-printing as "resists," (i. e. to prevent the indigo imparting a permanently blue colour to the cloth), and in various medicinal preparations. It should be noted that they are exceedingly poisonous. Commercial verdigris should not contain more than 4 per cent. of impurity—chiefly insoluble matter. It is, however, often adulterated with chalk or sulphate of copper. The amount of insoluble matter can be roughly estimated by the gritty feeling when the salt is moistened and rubbed in the hand. Brightness of colour is a rough test of quality. The presence of chalk may be readily detected by pouring a little hydrochloric acid over a sample of the salt. If chalk be present, effervescence will take place;—if pure, the verdigris will dissolve quietly in the acid. The solution may be filtered off from the insoluble impurities, and chloride of barium added. If sulphate of copper be present, the white, heavy precipitate of barium sulphate will immediately form. The impurities from the solution in hydrochloric acid, washed, dried, and weighed, should not exceed, at the outside, 5 per cent. of the weight of the original sample.

A good sample of verdigris will test as follows :—

Oxide of copper	43·50
Anhydrous acetic acid	29·30
Water	25·20
Impurities	2·60
	100·00

An *ad valorem* duty of 10 per cent. was until 1853 imposed upon the importation of verdigris. Since that time the trade has been free.

Copper, Aceto-Arsenite of.—By mixing 5 parts of verdigris with a hot solution of 5 parts of arsenious acid in 50 parts of boiling water, a fine green precipitate of aceto-arsenite of copper is obtained, insoluble in water. The addition of a little acetic acid is often necessary to prevent the formation of arsenite of copper, known by its yellowish-green colour. Aceto-arsenite is used to a considerable extent as a pigment, under the names of "Imperial" and "Mitis" green. When it is mixed with a little gypsum, or heavy spar, the pigment known as "Mountain" green is obtained.

Iron, Acetates of.—Under the name of "black" and "iron liquor," two of these salts are largely manufactured, the acetate of the protoxide and the acetate of the sesquioxide or peroxide. Upon concentration, the former crystallizes in small greenish white needles, very soluble in water. Both solution and crystals rapidly absorb oxygen when exposed to the air. The sesquiacetate is a dark red uncrystallizable liquid, of powerful astringent taste.

Two methods are employed for the production of the ferrous acetate, or "black liquor." That usually adopted on a large scale is as follows. Iron turnings, or indeed any refuse scrap iron, are digested with crude pyroligneous acid of a specific gravity of about 1·035, preferably at a temperature of 66°, but occasionally in the cold. The mixture is frequently stirred to separate as far as possible the tarry matter, which floats on the surface and is skimmed off. The metal rapidly dissolves in the acid forming the acetate of the protoxide. When a sample of the solution upon cooling registers a specific gravity of about 1·09 (18° Tw.), the whole is allowed to stand, the impurities are carefully skimmed off, and the liquor is ready for use. A certain quantity of hydrogen which is set free, and the tarry products, prevent, or at least retard, oxidation into the persalt. Owing to this tendency to absorb oxygen, the process should be carried out as rapidly as possible—therefore with the aid of heat—and if the solution has to be kept for any considerable length of time some metallic iron must be allowed to remain in contact with it.

A second method of preparation is by a double decomposition between acetate of lime and sulphate of iron. The copperas is dissolved in hot water, and added to acetate of lime liquor in the proportion of about five to one. Perfect decomposition is unnecessary, as a small proportion of undecomposed copperas does not injure the liquor. This method of manufacture is more expensive than that already described, and is usually only resorted to in times of pressure. A very pure liquor is made in some of the continental works by decomposing carbonate of iron by acetate of lead, acetate of iron remaining in solution.

The persalt is obtained by decomposing a solution of sulphate of iron—the ferric sulphate—by a solution of acetate of lime. The mixture is well agitated, sulphate of lime precipitates, and the ferric acetate remains in solution. It has a peculiar deep red colour, and usually stands, about 25° Tw.

The acetates of iron are largely used by calico-printers and dyers as mordants; the protosalt chiefly by the latter, the persalt by the former. A very common mordant, "pyrolignite," (*liqueur de ferraile, bouillon noir*), for black dyes, consists of a mixture of the salts, the ferrous acetate being first prepared and partial oxidation allowed. The ferrous salt produces blacks and all shades of purples and lilacs, also chocolate with acetate of alumina (red liquor). It is one of the most powerful of mordants, readily yielding up its acetic acid, and possessing great affinity for both fibre and colouring matter. The persalts are not such powerful mordants, but give a more uniform colour to a large surface from the impossibility of further oxidation during manipulation. Hence their use in preparing grounds where a large body of uniform colour is essential. Pyrolignite of iron is largely employed in the preservation of timber.

The manufacture of iron liquors is an important industry in Lancashire. Elsewhere they are only made for local consumption. The continental liquors are obtained in a more concentrated form, about three times as strong as the home manufacture. They are, however, of very fine quality. The only practical method of testing iron liquors is to try them on cloth against samples of an already known quality.

Iron mordants are probably of ancient use. The first English patent was taken out in 1780 by Flight, who proposed to steep iron in "water drawn from tar or tar oil," and to mix the liquor with starch or gum. In 1782, Boothman patented the steeping of iron filings, &c., in water mixed with some such fermentable vegetable matter as barley, wheat, or bran. This was practically the Indian method of yet earlier times.

An ordinary iron liquor will test as follows:—

Oxide of iron, calculated as protoxide	6·30
Acetic acid	7·20
Sulphuric acid	0·80
Tarry matter	2·30
Water	83·40
	100·00

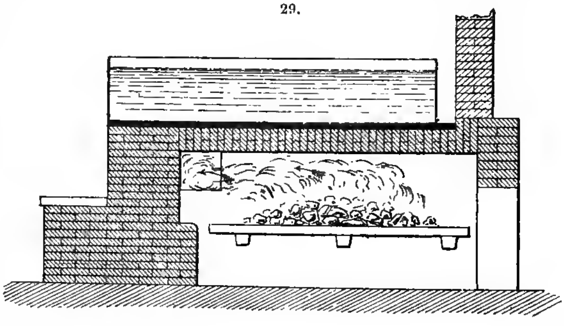
Liquors made from acetate of lime and sulphate of iron usually contain an appreciable quantity of sulphate of lime.

Lead, Acetates of.—The most important of this series of salts is the neutral acetate, technically termed "sugar of lead" from its sweet, but at the same time astringent, taste. It is also called salt of Saturn (Fr. *Sucre*, or *Sel, de Saturne;* Ger. *Bleizucker*). When carefully prepared, sugar of lead forms colourless, transparent, prismatic needles belonging to the monoclinic system, extremely light, though with lead as the base. The commercial article, however, is usually a confused mass of irregular crystals somewhat resembling loaf sugar, but of a yellowish colour if the acetic acid used has not been pure. The crystals are soluble in rather more than their own weight of cold, and ·75 parts of hot water; also in 8 parts of alcohol. At ordinary temperatures a very slight efflorescence takes place. Melted at a gentle heat, the water of crystallization is driven off, and an anhydrous acetate obtained. Beyond 100° (212° F.) the anhydrous salt is decomposed, losing acetic acid and being converted into a sub-salt. Distilled at a high temperature, acetic acid, carbonic acid, and acetone are given off, and finely divided metallic lead left in the retort. Great care should be taken in dealing with all preparations of this salt, as it is extremely poisonous. A good acetate should be completely soluble in water, and when the lead is exactly precipitated by dilute sulphuric acid, the clear supernatant liquid should be wholly volatilizable by heat. The aqueous solution is partly decomposed by the carbonic acid of the air, carbonate of lead being formed and a portion of acetic acid being given off.

There are three qualities of sugar of lead known in commerce, white, grey, and brown. The white, or purest, salt is the most esteemed, inasmuch as the chief use of the compound is to prepare other acetates, and it is therefore especially valuable for the acetic acid which it contains; when used as a mordant, however—for the sake of the *base*—the brown salt is the most economical, as it contains a larger amount of lead than an equal weight of white.

The process for the manufacture of the white salt upon a large scale is as follows:—A charge of best litharge is added to acetic acid—usually good "second" acid—in a copper pan about 6 ft. long, 4 ft. wide, and 1 ft. deep, with, preferably, a strip of lead soldered upon the bottom to prevent the acid acting upon the copper. The best proportions are 325 parts of litharge to 575 parts of acid, and the mixture should not be more than 5 inches deep. The pan is heated by a small coal fire placed underneath in the ordinary way, and—a precaution to be observed in all the processes—the mouth of the fireplace, and the fire-hole, should be situated outside the building, the pan being set against the wall. The plan is shown in Fig. 29.

29.



By this means a more perfect cleanliness is secured. The litharge is added gradually to the acid in the pan, and the mixture vigorously stirred up from the bottom during the addition and until the whole is thoroughly dissolved; an operation usually occupying about half an hour. The mixture must be tested from time to time to see that it is still acid, as the formation of any basic salt interferes with the after crystallization. As soon as a thorough solution is effected, the pan is filled up with water to within a couple of inches of the top—that is to say, the quantity of water added is equal in bulk to the solution itself. By this dilution the impurities are separated out, rise to the surface, and are skimmed off. The liquor is then thoroughly boiled and a judicious amount of the crystals from the mother liquor of previous crystallizations is dissolved in it. After cooling and settling, the clear liquor is siphoned off to a similar pan placed alongside, and set in the same fashion. The first "mixing" pan is carefully cleaned out, and a fresh batch of litharge dissolved. The liquor in the second pan is evaporated to about 1·50 density, samples being taken from time to time and set aside to cool in small shallow dishes, that it may be judged from the way in which they set if a proper degree of concentration has been reached. As soon as one of these samples upon cooling forms a compact mass of crystals, the liquor is siphoned off into shallow copper crystallizing pans about 3 ft. long, 2 ft. wide, and 4 inches deep, with bevelled sides. In these compact masses of crystals are formed. They are then taken into the drying room and emptied, the blocks of crystals being set up on end along a sloping bench (conveniently formed of two balks of timber set longitudinally) with a spout below to carry off the drainings, or "mothers," to a cistern sunk in the floor at the end of the bench. Only a gentle heat, about 32° (90° F.) from a fireplace outside the house, should be maintained in the drying room, as sugar of lead is somewhat dangerous; dry wood, linen, matting, and other fibrous materials impregnated with the salt being liable to take fire very readily. When drained and dry the crystals are removed into the packing room, which should be maintained at about the same temperature as the drying room. Here they are carefully scraped, broken up into fragments, and casked ready for the market. When of good quality the fragments consist of masses of beautifully white, small crystals, exceedingly light. If large crystals are required they have to be specially "grown." The scrapings from these first crystals in the packing room are added to the litharge solution in the mixing pan and worked over again.

The drainings from the blocks of crystals in the drying house are transferred to a pan similar in description to the mixing pan. Here a little acetic acid is added, the liquors are diluted with water to twice their bulk, the impurities that rise to the surface being skimmed off, and are boiled down to crystallizing point. After cooling and thoroughly settling, the clear liquid is siphoned off to shallow pans of copper, and "set" and dried in precisely similar manner to the first liquors. The blocks are broken up when removed from the draining bench, and worked over again by careful introduction into the litharge solution. These second crystals are sometimes called "numbers," and the pan in which they are diluted and evaporated, the "number pan."

All the residues—the settlings—from both the first and mother liquor processes are transferred to some suitable vessel and thoroughly washed with boiling water, the washings being added to the liquors in the mixing pan. The final residue may be dried in a retort and smelted for the lead it contains.

When the mother liquors get too impure to be crystallized in the manner described—when the blocks produced begin to come dirty—a pan of *grey* acetate is made. The liquors are transferred to one of the "number" pans, and worked up in somewhat similar fashion to the "numbers" themselves. The crystals, however, which are so impure as to possess hardly any crystalline appearance, are not added to the "white" process at any stage, but are kept strictly by themselves, and when broken up are sold as impure sugar—or "grey"—from the dull grey appearance of the fragments.

In the manufacture of white sugar of lead upon a large scale, it is found in practice that 1 ton of ordinarily pure litharge yields 31 cwt. of best acetate. Instead of being worked up in the manner described, the spent liquors may be treated with carbonate of soda or lime, carbonate of lead and supernatant acetate of soda being obtained. Stoneware or glass crystallizing vessels may be used instead of copper, but the loss from breakage is considerable.

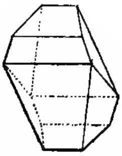
In some places in Germany a remarkably good white sugar is manufactured from spirits of wine, crystals of a very large size and beautiful transparency being obtained. The process is, of course, too costly to be carried on to any great extent, and only where there are exceptional facilities for producing the spirits of wine.

The process for making brown sugar of lead differs but little from that employed to produce white, except in the matters of plant and choice of materials. Distilled pyroligneous acid is saturated with litharge in a large tub, and the thick solution, after being thoroughly stirred up, is allowed to settle, and is then siphoned or run off into an iron pan 6 ft. long, 4 ft. wide, and 12 or 14 in. deep. Here it is boiled and diluted with a large amount of water, the impurities being skimmed off as they rise. The water must be added until the liquors have only a very slight coloration. They are then evaporated to crystallizing point, and run off into wrought-iron pans about 4 ft. long, 3 ft. wide, and 6 in. deep. When "set," the pans are turned over, the masses of crystals drained, dried, and broken up for market. A better article is made if the liquors are brought to the boiling point, and settled, before transference to the diluting and evaporating pan;—which may conveniently be hemispherical, and of sufficient capacity to hold 500 gallons.

Besides the processes described, acetate of lead, of exceedingly fine quality, may be obtained by exposing sheet lead to the action of air and acetic acid vapour in a closed chamber. A mixture of carbonate and acetate is formed upon the sheets, which is scraped off and dissolved in an excess of acetic acid. The solution is evaporated until a density of 2·30 is attained, and allowed to cool, when acetate of lead crystallizes out in truncated and flattened prisms of the description shown in

Fig. 30. If means be taken to secure rapid cooling, the crystals take the form of fine needles, separating out in clusters. Several patents have been taken out with a view to extend the principle of presenting the lead to the acetic acid in a state of vapour, but the process is expensive, and though producing a very fine article, cannot compete with the white sugar made in the usual way.

30.



Sugar of lead is used by dyers and calico-printers; also in certain medicinal preparations, for its sedative and astringent qualities, and in the manufacture of the sulphide of lead used by makers of indiarubber goods. Its solution forms, with caustic potash or soda, a white precipitate, which is soluble in an excess of alkali. About 2000 tons per annum are produced in this country, the process being chiefly carried on in South Wales and London.

Besides the neutral acetate, lead forms certain sub-salts or basic acetates, which deserve attention. These are obtained for the most part by dissolving powdered litharge in hot solutions of sugar of lead, as much as six times the normal quantity of base being taken up. They are used to some considerable extent as mordants in dyeing and printing, and as a "resist" for china blues. Considerable difficulty, however, is experienced in thickening them. The diacetate, crystallizing in long needles from a solution of 6 parts of sugar of lead and 7 of litharge in 30 parts of boiling water, is used in the manufacture of white-lead. The Goulard water of pharmacy, "Acetum Saturni," is an aqueous solution of various basic acetates, chiefly the tribasic salt—a white powder obtained by dissolving 3 parts of the diacetate and 1 of litharge in 9 parts of hot water. The manufacture of these basic acetates is carried on only to a limited extent.

Ordinarily good commercial acetates of lead should give the following results upon analysis:—

	White.	Brown.
Acetic acid	27·6	21·8
Oxide of lead	58·4	59·9
Water	14·0	15·5
Carbonate of lead and insoluble matter	—	2·8
	100·0	100·0

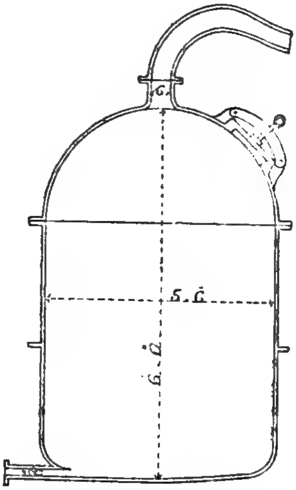
They may be tested by precipitating the lead as sulphide by a current of sulphuretted hydrogen, exactly neutralizing the acetic acid, which is liberated, by a standard alkaline solution, and calculating the result after the method described in treating of acetic acid.

Lime, Acetate of.—This salt, in its pure solid state, forms silky needle-shaped crystals with a bitter taste, which effloresce in the air, and are soluble in water and alcohol. Decomposed by the action of heat, acetone and carbonate of lime are formed. It is obtained by dissolving chalk in acetic acid until there is a slight excess of lime. The commercial article is of two descriptions, grey or white, sometimes called "distilled," and brown. Acetate of lime *liquor* is largely used in the manufacture of red liquors, having some such constitution as the following:—

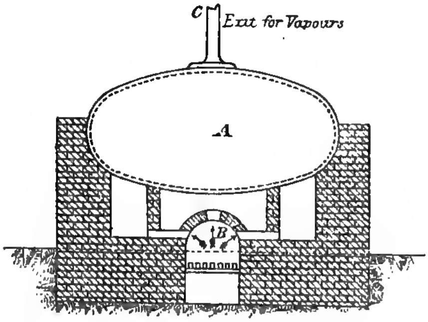
Acetic acid	9·50
Lime	5·20
Cloride of calcium	0·50
Chloride of sodium	3·22
Tarry matter	3·83
Water	77·75
	100·00

Upon a large scale the manufacture of lime acetates is carried on as a continuous process with that of the production of crude or pyroligneous acid, and the reader must therefore refer to that point in the description of wood-distillation, where the acid liquors, consisting of water, pyroligneous acid, naphtha, and various resinous and tarry matters, are run off from the tar-settlers and pumped either into the "neutralizer" or into stills. By the former process, when the lime is added to the whole body of acid liquors, brown acetate is produced; by the latter, grey. Taking the brown acetate process first, roughly powdered chalk, sometimes milk of lime, is added to the liquors in the neutralizer until by the litmus test there is a *very slight* excess. The mixture is well stirred from time to time, and the light tarry substances which rise as a scum to the surface skimmed off. After being allowed to settle for a short time the liquors are run or siphoned off into a still or boiler. Heat is applied from a fire placed directly underneath, or from a coil of steam piping within the still, and the naphtha compounds and bulk of the water are driven off. Convenient forms of this apparatus are shown in Figs. 31 and 32. In Fig. 31 A is a copper still in the form of a boiler, B the fireplace, C the exit pipe for the naphtha. When the latter ceases to come over, the acetate of lime liquor left in the still is run into an evaporating pan, and heat again applied from a fire below the pan or by a coil of steam-pipes in the liquor. Here it is kept gently simmering, and once more are the tarry impurities skimmed off as they rise. After a while the acetate crystallizes out from the concentrated liquor and forms a thin coating, which is taken off and put into baskets or any convenient form of drainer set on runners over the liquor. When drained it is carried up into the drying house, usually built on the top of the ovens. Two forms of evaporating pan are shown in Figs. 33 and 34. The first is the best, as the salt raked up upon the shelving end of the pan shown in Fig. 34 is apt to burn, and the drainings are returned to the pan cold. In some works the acetate liquor, instead of being allowed to crystallize out in the manner described, is boiled down to dryness in a pot of the form shown in Fig. 35. In this way, only an inferior article is obtained, but by evaporating to dryness in a shallow sheet-iron pan, similar to that shown in Fig. 33, and by carefully supervising the operation, a very fine acetate may be obtained; indeed, given the necessary experience and care, this is the best method of finishing.

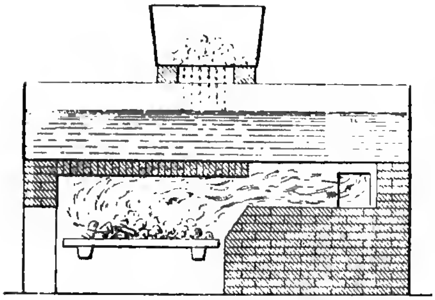
32.



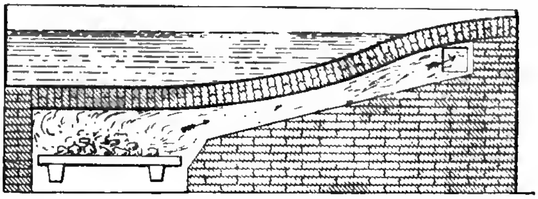
31.



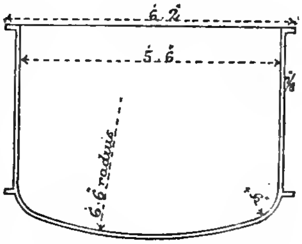
33.



34.



35.

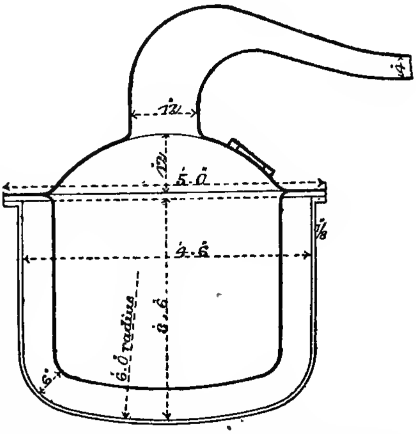


The acetate is spread upon the floor of the drying house in a layer from 2 to 3 in. thick, and must be carefully turned from time to time. The chief end of drying being to burn off gently and uniformly the carbonaceous and oleaginous substances contained in the salt, its manipulation in the drying house requires considerable care, skill, and attention. If spread in too thick a layer, or if not completely and carefully turned, these impurities are retained and the salt itself is decomposed. A good brown acetate is composed of light honeycombed fragments streaked here and there with charcoal, and with a pleasant, fresh smell. It should contain 70 per cent. of real acetate.

The naphtha—usually called "miscible"—coming over from the lime liquors, is at first very dilute. It is run from the first receiver into a cast-iron still heated by a fire underneath, condensed in a copper worm, and by three subsequent distillations in copper stills, jacketed, or with a steam-coil inside, is "worked up," as it is technically termed, to 60° over proof. The direct application of heat from a fire under the stills is dangerous, though this plan is often adopted. Distillation by steam is to be preferred. If a jacketed still be used, the jacket should be well up to the shoulder.

A good still of this description, made by Messrs. Robert Daglish and Co. of St. Helen's, is shown in Fig. 36. Occasionally "plate" or whisky stills are used. Further details concerning the naphtha processes will be given under "Pyroxylic Spirit."

36.



To obtain grey or white acetate of lime, the acid liquors after leaving the tar-settlers are pumped into a series of copper stills, heated preferably by a steam-coil inside. Here at a gentle heat the naphtha is first expelled. The acetic acid next distils over, is condensed, and run into a tank to settle. The tarry and oleaginous deposit in the stills is drawn off through a stopcock at the bottom. From the receiving tank the clear, or fairly cleared, acetic acid is run off or pumped up into the neutralizer and mixed with a slight excess of lime. The subsequent processes are precisely similar to those employed in the production of brown acetate, except that great care is taken to ensure purity, and a specially heated drying house is often provided, the floor of the house being heated by circular flues from an independent fireplace. By this means the temperature is more accurately regulated than when only the waste heat from the ovens is utilized. The naphtha from the grey acetate process is concentrated and purified by re-distillation in copper stills in a manner similar to that already described, but is only worked up to about 45°, or such a strength as will readily dissolve resins and gums. It is called "solvent," in contradistinction to the "miscible" wood naphtha, obtained as a bye-product in the brown acetate process. A very pure "white" acetate may be made by dissolving the salt from the drying floors in hot water, filtering the solution through animal charcoal, and evaporating the solution to dryness. Good grey acetate should contain 85 per cent. of real acetate.

The manufacture and sale of grey acetate has of late years considerably diminished, owing to the price, which averages about 30 per cent. more than brown. Inasmuch as the article at its best only contains 15 per cent. more real acetate, it is difficult to understand the very high price put upon it. There seems to be no reason why a good grey acetate should not be manufactured and sold at 12*l.* 10*s.* to 13*l.* per ton, in bags, free on rails, to yield a very fair profit.

The acetates of lime are used as mordants by printers and dyers; for the production of other compounds, such as acetates of soda, iron, alumina, and manganese; as a source of acetic acid by distillation with an acid, and in the manufacture of vinegar. They may be tested by dissolving in water and precipitating the lime by a slight excess of sulphate of soda, adding alcohol to prevent solution of the sulphate of lime formed. After filtration, the precipitate must be washed with a little dilute alcohol, and the lime determined from the sulphate. To estimate the acetic acid, the filtrate is evaporated to dryness, and calcined at a red heat to convert the acetate into carbonate of soda, the amount of which is ascertained by the alkalimeter, and the quantity of acetic acid calculated from it by reference to the combining proportions.

The advisability of securing more outlets than one or two for the products of wood distillation has already been noticed, the extra plant required for the production of a certain amount of grey as well as brown acetate, and for distillation with sulphuric or hydrochloric acid, being of comparatively slight cost. It is worthy of mention that a very good grey acetate and solvent naphtha may be obtained by distilling the tar liquors—the bottoms of the tar-settlers.

A considerable number of makers are engaged in the trade in South Wales, Gloucestershire, Lancashire, and Somersetshire. It is also becoming an important industry in the United States, where there are peculiar advantages for wood-distillation, but as yet the home article in the New York market fetches a lower price than the best English brands. The present value of good 70 per cent. brown acetate is about 11*l.* per ton in bags at the works; of grey, 15*l.* per ton. A considerable quantity is exported from this country.

Manganese, Acetate of, may be obtained in a pure state by crystallization from a strong solution of carbonate of manganese (diagolite) in acetic acid. The crystals are stable in the air at ordinary temperatures, soluble in three times their weight of cold water, and in alcohol. Upon a large scale the salt is prepared by mixing solutions of sulphate of manganese and acetate of lime or lead; sulphate of lime or lead precipitates, and, after settling, the clear acetate of manganese in solution is drawn off. The reaction is by no means a strong one, and the mixture must, therefore, be well agitated to ensure decomposition of the manganese salt. The use of acetate of lead is to be preferred, although the process is more costly than when a lime salt is employed. The best proportions are 4 parts of sulphate of manganese, 3½ of water, and 7 of good brown acetate of lead. The crystals should be in the form of pale rose-coloured splinters or small prisms.

Acetate of manganese is used as a substitute for bronze liquor (muriate of manganese) by dyers and calico-printers. The latter is the cheaper article, but the acetate is to be preferred, as it does not contain the same excess of free acid, whereby the cloth is injured. From these salts the colour known as "manganese brown" is obtained by impregnating the cloth with them and passing in lime or soda ash. Oxide of manganese (the protoxide) is precipitated upon the cloth and subjected to the oxidizing agency of the air, or, usually, the cloth is passed through a bath of chloride of lime. The manufacture is only carried on to a limited extent in Lancashire and other calico-printing and dyeing districts. Acetate of manganese is also used in medicine.

Mercury, Acetate of.—This salt can be produced in a pure state by dissolving the red oxide of mercury in pure acetic acid. It crystallizes out from the solution in delicate pearly scales. Usually, however, it is made by mixing acetate of soda and a solution of the bi-chloride of mercury.

Acetate of Mercury is a product of but slight importance. It is used by calico-printers and dyers, and in various pharmaceutical preparations.

Potassium, Acetates of.—Only slight reference need be made to this series of salts. The neutral acetate exists in the juices of many plants, and forms the carbonate of potassium found in the ash of calcined wood, the acetic acid being replaced by carbonic acid. It may be prepared by dissolving carbonate of potassium in acetic acid, or brown vinegar. If the latter is used the carbonate must be added slowly, and every portion of the mixture kept carefully acid to avoid the formation of coloured products by the action of the alkali upon the organic bodies contained in the vinegar. The salt forms white foliated crystals, which are very deliquescent and soluble in small quantities of water. They are also soluble in alcohol, but less readily. At a red heat they are decomposed into acetone and various hydrocarbons and empyreumatic products. The neutral salt is employed in medicine as a diuretic, and to some slight degree in printing.

Potassium diacetate may be conveniently formed by dissolving the neutral salt in an excess of acetic acid, and evaporating the solution to dryness. Fine needle-shaped crystals of diacetate separate out as the evaporation proceeds.

Sodium, Acetate of (Fr. *Terre foliée minérale;* Ger. *Essigsäure natron.*)—This salt, one of the most important of the acetates, forms small oblique rhombic prisms, soluble in 3½ parts of cold, and 1½ parts of hot water; also in alcohol, in various proportions depending upon the strength of the solvent. In its crystalline form it contains 3 atoms of water, which it loses when exposed in dry air. A liquid supersaturated solution may be formed by melting the crystals, and allowing the salt to deliquesce. In this way they take up seven atoms of water, the solution immediately crystallizing upon agitation with a small piece of the dry acetate. Gerardin has made some curious experiments touching the solubility of this salt in alcohol; with a solvent of 0·9904, and at the ordinary temperature of the air, 38 parts of the acetate are dissolved, but the alcohol loses its potency very rapidly upon concentration.

Acetate of soda may be obtained in a pure state by crystallization from an evaporated and cooled solution of carbonate of soda in pure acetic acid; or, of slightly worse quality, from a saturated solution of the alkali in "second" acid—that obtained from the distillation of acetate of lime with sulphuric or hydrochloric acid. On a large scale a good commercial acetate is produced in the following manner:—Grey acetate of lime is dissolved in water until the solution stands at 1·15 to 1·2 specific gravity. It is then filtered and run into a shallow sheet-iron vessel about 6 ft. long, 4 ft. wide, and 2 ft. deep. Here ground or roughly powdered sulphate of soda is slowly added, the mixture being kept well stirred up, until the whole of the lime separates in the form of sulphate. The proportions usually employed are 4 parts of sulphate of soda to 1 part of acetate of lime. The mixture should be carefully tested from time to time to ascertain if the whole of the lime has been precipitated. The addition of a little sulphate solution to a sample of the liquor will readily show when this point has been reached. When the precipitation is complete the sulphate of lime is allowed to settle down, and the clear supernatant acetate of soda liquor is siphoned off to the evaporating pans, which are of similar description to the mixing pan, heated by a fire beneath. The residue, which consists of sulphate of lime and various insoluble matters, is thoroughly washed with hot water that no acetate of soda may be wasted, the first washings being added to the liquor in the evaporating pan, and the weaker run off to aid in the dissolution of a fresh batch of grey acetate. Sometimes the liquors are evaporated in cast iron pots, 6 ft. in diameter and 3½ ft. deep, instead of sheet-iron pans. Here they are boiled down till a density of 1·30 is attained. During concentration whatever excess of sulphate of soda has been used crystallizes out and is scraped off and thrown into drainers, usually wicker baskets, placed on rods laid across the pan or pot, so that all the acetate of soda liquor may readily find its way back to the main body of solution. All impurities that rise to the surface during concentration are also carefully skimmed off. After being allowed to settle thoroughly, an operation usually requiring about nine hours, the clear liquor is run or siphoned off to small copper crystallizing pans, when it is allowed three or four days to set. The crystals are then emptied out, drained, and the mother liquor run into the evaporating pan again, where it is boiled down to 1·30 and again allowed to crystallize.

The mothers are treated in this way till they yield no further crystals, or only show a slight tendency to crystallize. They are then evaporated and calcined, and whatever acetate of soda is left is dissolved out by hot water and transferred to the evaporating pans. The successive crops of crystals obtained are sometimes re-dissolved in water, re-evaporated to a density of 1·50, purified by skimming, and re-crystallized before torrefaction. More usually, however, they are at once transferred to a cast-iron pot heated by a fire underneath and fused at a temperature of about 200°. All the water of crystallization is driven off, and the liquid froths up in a thick oily mass and gradually subsides. It is then ladled out upon iron plates to cool and harden. The firing of the fusing pot must be very carefully regulated—the temperature kept between 200° and 232° (395° and 450° F.). If white fumes come off, it is a sign that the acetate is undergoing decomposition, and the fire must be immediately slackened. When set into a hard, compact mass, the fused acetate is broken up into small fragments, dissolved in not too much hot water (one and a half to two times its own weight), and evaporated to a density of 1·50. After being allowed to settle for a short time, the solution is drawn off to shallow crystallizing pans of copper or wood lined with lead. After a lapse of three or four days the crystals are removed, washed, allowed to drain, and set on shelves to dry. They are then fit for packing. The mother liquor and the washings are run off to the evaporating pan to be worked over again. If the final crystals are in any way coloured, they are usually re-dissolved and treated as the first crystals from the crude liquor. It should be noted that precautions should be used in fusing the acetate to prevent it coming in contact with the fire, as it is capable of burning like tinder.

By this process, with various modifications, the bulk of the acetate of soda of commerce is produced. Distilled pyroligneous acid is sometimes employed instead of a solution of grey acetate of lime, and the methods of dissolving and filtering are various. Very fine crystals may be obtained by evaporating the solution of rough acetate in cylindrical vessels, made of wood lined with lead, by the agency of steam circulating in a coil of lead piping. By a slow crystallization, surrounding the pans with some non-conducting material, &c., larger crystals are obtained than by allowing the natural and more rapid setting. Filtration through animal charcoal, moistened with hydrochloric acid, is occasionally resorted to as a means of purifying the liquors in substitution for the process described.

One ton of grey acetate 82 per cent. should yield 21 cwt. of good acetate of soda. The most common impurities that are contracted in the grey acetate process are sulphate of soda, chloride of sodium, and acetate of lime. To prevent the appearance of the last-named salt, it must be most carefully noted that perfect precipitation of the whole of the lime is effected by admixture with the sulphate of soda. As is the case throughout all the processes for the production of acetic acid and the acetates—more perhaps than in other branches of chemical industry, because the materials operated upon are unusually variable in constitution—careful and unceasing supervision by an experienced eye and hand can alone ensure a good result.

The presence of sulphate of soda may be readily detected by dissolving the acetate in water, acidifying with hydrochloric acid and adding a few drops of chloride of barium; the heavy precipitate of barium sulphate separating out if the impurity is present. Chloride of sodium, proceeding from the use in excess of an imperfectly worked sulphate of soda, can be detected by acidifying a solution of the acetate in water with a little nitric acid, warming the solution and adding a drop or two of nitrate of silver. The presence of the chloride is shown by a white precipitate.

Acetate of soda is used chiefly in the production of the best qualities of acetic acid, by distillation with sulphuric acid in the manner already described; to some slight extent in the preparation of mordants, and in the preservation of animal and vegetable substances. One of its chief virtues as a preservative is that substances treated with it can be readily restored before use to their original appearance or consistency. The plan usually adopted is as follows:—The flesh to be preserved is sandwiched with powdered acetate of soda in a cask, in the proportions of about one part of the salt to four of flesh. Without being changed in constitution, the acetate abstracts the moisture from the flesh, and when the latter is withdrawn, may be used over again. To ensure the success of the process the temperature should not be below about 15° (60° F.), so that in winter the casks "in pickle" must be kept in a warmed room. The operation usually takes a couple of days, at the end of which time the flesh is dried in the air and packed. A little powdered sal-ammoniac is sprinkled over the meat, or fish, before cooking, and it is then thoroughly steeped in tepid water. The sal-ammoniac decomposes the acetate of soda, forming common salt (chloride of sodium) and acetate of ammonia, and the flesh resumes its normal appearance. Vegetables may be preserved in acetate of soda "pickle"—a liquor formed by dissolving the salt in three parts of water—in somewhat similar fashion.

The demand for acetate of soda has diminished of late years owing to the increased use of lime acetate as a source of acetic acid. There are now only about eight manufacturers in this country who are keeping their plant at work, the chief seat of the trade being South Wales.

STANNOUS ACETATE.—Acetate of the protoxide of tin is an unstable salt, crystallizing out in colourless needles from a strong solution of metallic tin in acetic acid. Upon a larger scale it is prepared by mixing solutions of tin crystals (chloride of tin) and acetate of soda, lime, or lead, a usual recipe being 103 parts of tin salt to 190 of good brown acetate of lead; the mixture is well agitated, allowed to settle, and the clear supernatant acetate of tin drawn off. Owing to a tendency to undergo oxidation upon exposure to the air the solution should only be prepared for immediate use. The salt is employed in dyeing and calico-printing to a limited extent to obtain an orange colour. It is, however, an uncertain agent from its unstable character, and gives, moreover, a "loose" colour, a defect that it shares with all other tin mordants on vegetable fibre.

ZINC, ACETATE OF.—This salt is only of slight importance; it is used medicinally, in a diluted state, as an astringent lotion, and, occasionally, in printing: it gives a fine orange-yellow on silk and cotton, but owing to its weak affinity for the fibre the colour is very unstable. It is obtained by calico-printers for their own use by dissolving 4 parts of sulphate of zinc and 7 of acetate of lead in hot water, allowing the sulphate of lead to settle out, and siphoning off the clear acetate. It may also be obtained in a pure state by dissolving metallic zinc in acetic acid, evaporating the solution, and crystallizing.

Acetic Ether; ACETATE OF ETHYL (GER. *Essigäther*; FR. *Ether acétique*), discovered by Lauragnais in 1759, is a fragrant, colourless liquid, possessing the agreeable odour of ether. It burns with a yellowish flame, and is soluble in water, alcohol, and ether. Heated with strong sulphuric acid it is converted into oxide of ethyl (common ether) and acetic acid: distilled with a mixture of limewater and chloride of lime it yields chloroform. The density of the liquid is 3·089, and of the vapour 3·067. Boiling point 73° (165° F.). Acetic ether may be conveniently prepared by distilling together 3 parts of acetate of potash, 3 parts of absolute alcohol, and 2 parts of sulphuric acid. The distillate is mixed with a little water to separate the alcohol, and digested with chalk or carbonate of soda until neutral. It is then agitated with chloride of calcium, or, preferably, with carbonate of potash, and finally re-distilled. During distillation care must be taken not to raise the temperature too rapidly. Upon a large scale acetate of lead is usually employed in place of acetate of potash in the following proportions:—16 parts of white lead acetate, 6 parts of sulphuric acid, sp. gr. 1·84, 7 parts of absolute alcohol, and 5 parts of water.

Acetic ether is used in various medicinal preparations; also for dissolving resins, sulphur, phosphorus, and essential oils in the preparation of varnishes. It is present in most wines.

Acetone; PYROACETIC SPIRIT (FR. *Esprit pyro acétique*; GER. *Essiggeist*), first observed by Courtenvaux in 1754, is a substance given off in the destructive distillation of all the acetates. In its pure state it is a colourless liquid, similar in appearance and odour to acetic ether. It is highly inflammable, burning with a pale yellow, smokeless flame, and is miscible in all proportions with water, alcohol, and ether. The density of the liquid is 0·792, of the vapour 2·022. The boiling point is 55·5° (132° F.).

Acetone is usually prepared by distilling acetate of lime or barium, carbonate of lime or barium remaining in the retort; also by distilling dried acetate of lead in an earthenware, glass, or iron retort with quicklime, in the proportion of 2 parts of the former to 1 of the latter. The crude product from the distillation of lead acetate is more or less contaminated with tar, and must be purified by saturation with carbonate of potash, and rectification with chloride of calcium. Acetone is also produced in the destructive distillation of citric and tartaric acids, of sugar, starch, and various gums, with powdered quicklime.

Of the sources named the acetate of barium is the best, the distillate coming over perfectly colourless—almost pure acetone. The lime salt, like the lead, gives a more or less contaminated distillate, since it is only decomposed at a high temperature, when the tarry and empyreumatic compounds come over.

Acetone is used to a considerable extent in dissolving resins, gums, and camphors. It is also a solvent of the lower nitro-cellulose compounds.

J. L.

ARSENIOUS ACID. (FR., *Acide arsénieux*; GER., *Arseniksäure*.) Formula As_2O_3.

Arsenious acid, commonly called arsenic, or white arsenic, is usually met with in the form of a white powder resembling flour, or of thick, white, brittle masses which are transparent when first made, but on exposure to the air for a short time become opaque; this change extends from the surface of the lump to the centre, giving it an appearance and fracture closely resembling that of porcelain. It may also be obtained in octohedral crystals by cooling in hot, saturated, aqueous solution. Arsenious acid is sparingly soluble in cold, but dissolves readily and completely in boiling water; in hot, dilute acids it also dissolves, though not as a rule forming salts. It is easily sublimed, volatilizing at 218° (424 F.); the vapour of arsenic is colourless and inodorous, provided that carbon and other reducing agents are absent; if heated in the presence of charcoal the vapour emits the characteristic odour of garlic, by means of which very small quantities of arsenic may readily be detected. Arsenious acid is one of the deadly poisons; two or three grains are sufficient to cause death. In case of poisoning by arsenic, an effective antidote may be prepared by precipating the hydrated sesqui-oxide of iron from ferric chloride or sulphate by means of a solution of magnesia or ammonia in excess; the arsenic on being brought into contact with this oxide of iron in the stomach is converted into an insoluble arsenite of iron, and thus prevented from entering the system.

Arsenious acid occurs native in the mineral *arsenite* or *arsenolite*; this mineral, however, does not occur in sufficient abundance to be valuable as a source of arsenic. By far the largest quantity of English-made commercial arsenic is obtained from *mispickel* or *arsenical pyrites*. This mineral contains from 43 to 46 per cent. of arsenic; it is found in large quantities in Devon, Cornwall, and South Wales, in association with tinstone, iron and copper pyrites, galena, and various other minerals. These latter are separated from the arsenical pyrites by mechanical means, arsenic being obtained from them, if present in sufficient quantity, during the subsequent smelting processes, as a bye-product. Arsenical pyrites, being practically worthless as an ore of iron, is treated solely for the arsenic which it contains. In Saxony, Silesia, and the Harz, arsenic is also obtained from ores of cobalt and nickel, some of which contain upwards of 70 per cent.

The manufacture of arsenious acid on a commercial scale has within the last twenty years risen to a position of considerable importance among the industries of Great Britain, and there is reason to believe that it has yet to see its best days, both in this country and on the Continent; owing to the discovery of new applications, and the further development of old ones, the demand for it is steadily increasing.

The details of the manufacture of arsenious acid will be given under the heading of "Arsenic."

CARBAZOTIC or PICRIC ACID. (Fr., *Acide picrique;* Ger., *Pikrinsäure.*) Formula $C_6H_3N_3O_7$.

This interesting and important substance is formed by the action of nitric acid upon carbolic acid, indigo, aloes, and a large number of other organic substances. It has become a very useful industrial product since the discovery and utilization of its remarkable colouring powers, and is now manufactured in considerable quantities from certain products of the distillation of coal, which contain carbolic acid.

Much care is required in the selection of the coal-tar oils employed, as those which are distilled from the coal at a low temperature contain substances which, on treatment with nitric acid, give rise to products not only useless for dyeing purposes, but detrimental to the crystallization of the picric acid. On this account, only those which distil over at about 180° or 200° (356 to 392 F.), and whose density is comparatively high, should be chosen, the best being those whose boiling point is between 190° and 200° (374 and 392 F.). The manufacture is at present carried on as follows:— The oils containing carbolic acid are mixed with a strong solution of caustic potash or soda; the alkali immediately unites with the carbolic acid, forming a dense liquid, which separates itself from the remaining portion of the oil, and forms a layer at the bottom of the vessel. If the oils are rich in carbolic acid, one-third of their weight of alkali is sufficient, but if they are poor the amount of alkali must be decreased in proportion. The alkaline phenate is withdrawn from the bottom of the vessel, and decomposed by means of hydrochloric or sulphuric acid, when the carbolic acid floats upon the surface of the solution of alkaline chloride or sulphate formed, and is drawn off for treatment with nitric acid. As the reaction between the carbolic and nitric acids is very violent, care is required when large quantities are employed, not only on account of the inflammable nature of the oils used, but the disengagement of gas is so copious and rapid that there is danger of the liquor being thrown over the sides of the vessel in which the reaction is carried on. Another important point is the amount of nitric acid employed; it depends entirely upon the richness of the oils, rectified as above, in carbolic acid, from six to eight times their weight being the average quantity required. The operation is usually carried on in an earthenware vessel, capable of holding from 12 to 15 gallons; this vessel is fitted with two tubulures, and is placed in a metal dish filled with fine sand, and heated by a fire from below. In one of the tubulures is placed a glass funnel, the outlet of which is very narrow, in order to prevent the too rapid entrance of the acid; the other is fitted with a curved glass tube, to carry away the nitrous fumes given off, and is attached to a suitable condensing apparatus. About 40 lb. of nitric acid, of sp. gr. 1·31, are run into the vessel, which is very gradually and gently heated to about 50° (122 F.), at which point the heat is removed; about 12 or 13 lb. of the rectified oil are now introduced in successive portions by means of the funnel, and on contact with the nitric acid a brisk effervescence ensues, large quantities of gas being given off and the temperature rising considerably. The picric acid dissolves as quickly as it is formed in the excess of nitric acid, small quantities of the latter being added from time to time in order to cool the mixture; the reaction is allowed to continue for twelve hours, and, after having become perfectly cool, the mixture is again heated to 50°, and about 28 lb. of nitric acid are added. Another twelve hours is sufficient to complete the reaction, which is hastened, towards the end, by gentle heating from below. When all effervescence has ceased, the excess of nitric acid is distilled off, and condensed for future use, and the solution of picric acid is evaporated in large earthenware vessels, heated on a sand-bath to the consistence of honey, when it is left to cool. The thick yellow paste thus obtained, after being washed free from nitric acid, is dissolved in boiling water, a little weak sulphuric acid being added in order to dissolve the resinous matter present. The solution is filtered, and set out in pans to crystallize; the resulting crystals are generally very impure, and are dissolved and re-crystallized until they are of a delicate lemon-yellow colour. These are dried and packed in casks for the use of the dyer.

Picric acid is bitter to the taste, and very poisonous; it is soluble in water, alcohol, and ether, forming yellow solutions. Its colouring properties were first discovered by M. Guinon, of Lyons; it is used for dyeing silk and woollen goods a bright yellow, alum being employed as a mordant. Cotton and flaxen goods are not dyed by picric acid. Some alkaline picrates have been employed instead of the acid by some dyers, though their highly explosive nature renders them quite unfit for these purposes. A mixture of picrate of potash, chlorate (or nitrate) of potash, and charcoal is used in France as an explosive for torpedoes, under the name of Designolle's powder; in this country, picrate of ammonia, nitrate of potash, and charcoal have been used as a bursting powder for shells, under the name of Abel's "picric powder" (see "Explosive Agents"). It has been said that picric acid was formerly largely used to adulterate beer, for the purpose of heightening the bitterness of its flavour.

CARBOLIC ACID. (Fr., *Acide carbolique;* Ger., *Carbolsäure.*) Synonyms: Phenic Acid; Phenol; Phenylic Hydrate; Phenylic Alcohol; Coal Tar Creosote. Formula: $C_6H_6O = C_6H_5,OH$.

Pure carbolic acid is a colourless crystalline solid, which melts at 42·2° (108° F.) to a colourless, limpid liquid slightly heavier than water. Carbolic acid boils when pure at 182° and distils without decomposition. The crystals readily absorb moisture from the air, whereby their fusing point is lowered, owing to the formation of a hydrate of the composition, C_6H_6O,H_2O, containing 16·07 per cent. of water, and melting at 17·2° (63° F.). In very moist air this hydrate absorbs still more water, and the product remains fluid at a still lower temperature. When water is gradually added to absolute carbolic acid as long as it continues to be dissolved, the resultant liquid contains about 27 per cent. of water (by weight), and thus approximates closely to the composition $C_6H_6O,2H_2O$, which requires 27·7 per cent. of water. If the liquid so obtained be really a compound, it is one of the weakest nature, for by agitating it with four volumes of benzene the carbolic acid is dissolved, and the water wholly separated. The liquid hydrous carbolic acid obtained as above is readily frozen by the cold resulting from the mixture of strong hydrochloric acid and crystallized sulphate of sodium.

Liquid hydrous carbolic acid dissolves in about 11·1 times its measure of cold water. This corresponds to a solubility of 1 part by weight in 10·7 for the absolute acid, the saturated solution containing 8·56 per cent. of real phenol. Although aqueous solutions of carbolic acid do not redden litmus paper, in weak alkaline solutions carbolic acid is much more soluble than in pure water. With equivalent amounts of the strong bases it forms definite compounds. The potassium and sodium salts are readily soluble in water, and are not decomposed on dilution.

Carbolic acid is miscible in all proportions with alcohol, glacial acetic acid, and glycerin.

Absolute carbolic acid is miscible in all proportions with ether, benzene, carbon disulphide, and chloroform. When aqueous carbolic acid is shaken with an excess of either of these solvents, the phenol dissolves, and the contained water separates.

In cold petroleum spirit carbolic acid is but slightly soluble. It may be obtained in fine crystalline needles by suddenly cooling the liquid by a freezing mixture.

The taste of carbolic acid is biting, and at the same time sweet. The odour is usually strong and characteristic, but both smell and taste are much less marked in very pure specimens than in the crude article.

Commercial carbolic acid often turns red in the light; the cause is uncertain.

Strong carbolic acid dissolves dry gelatin completely, but gelatin coagulates when carbolic acid is added to its aqueous solution.

Phenol coagulates albumin, is a powerful antiseptic, acts as a caustic on the skin, and is powerfully poisonous. When taken internally in a concentrated condition, it destroys life very quickly. Numerous instances of poisoning are on record in which carbolic acid has been taken or administered in mistake for medicine.

When applied externally, carbolic acid appears to act on the system by paralyzing the nerve-centres. It is a curious fact that even momentary contact of the strong acid with any considerable surface of the lower part of the body is usually fatal. Thus, a child who used a privy on the seat of which carbolic acid had been spilt, so that the liquid came in contact with his buttocks, died as a consequence. The foreman of a carbolic acid works stepped into a vessel of carbolic acid which wetted him up to the knees. He immediately jumped into water and took other precautions, but died the next day. On the other hand, carbolic acid has often been applied to the arms and upper part of the body with comparative impunity. In one instance, a man employed at a carbolic acid works, who often had his entire arms covered with the acid, died from the effects of some of the same acid spilt on his leg.

Associated with the real carbolic acid in the lower grades of the commercial article, there is always more or less of another body known as *cresol* or *cresylic acid*, which has the composition C_7H_8O, and is consequently the second member of the homologous series of which carbolic acid is the first.

Cresylic acid has a density of about 1·044. It closely resembles carbolic acid, but is liquid at ordinary temperatures, far less soluble in water than is carbolic acid, and boils at a higher temperature (198 to 203°). Several isomeric varieties of cresylic acid are known, having slightly different boiling points. One variety is solid at ordinary temperatures.

The presence of cresylic acid in samples of commercial carbolic acid greatly reduces their solubility in water and alkaline solutions, and lowers the melting point. Hence, none except the very best commercial samples of carbolic acid correspond exactly in properties with the pure substance. The lower grades of "carbolic acid," from which much of the pure substance has been separated, contain a far larger percentage of cresylic acid than of real carbolic acid. In taste and smell they are far more offensive than the pure article, but their antiseptic value is in no way diminished. In fact, cresylic acid is said to have an antiseptic power considerably above that of carbolic.

Carbolic acid is a constituent of the pharmaceutical preparation called *castoreum*, and is formed in many chemical reactions. It has also been observed in the tar obtained by the distillation of pine-wood. In practice, however, the whole of the carbolic acid of commerce is obtained from the tar produced by the distillation of coal for the manufacture of illuminating gas.

Coal—or gas—tar is of a very complex composition, and yields a variety of useful products. The carbolic and cresylic acids constitute a not inconsiderable proportion of the whole tar. It is obtained by a process of fractional distillation, supplemented by purification by solution in alkali, reprecipitation by acid, &c.

The quantity of tar operated on at one time, and the exact method of procedure, are conditions which vary considerably, but the following description gives a fair idea of the operation of fractional distillation as usually carried out at large works.

The first thing in the morning the still is charged with 1200 gallons of the tar, and the fire is lighted; in about an hour the tar begins to rise in the still, and the fire requires careful watching, until the actual distillation commences, which is usually about an hour later.

The first distillate consists of gases, ammonia water, and "first light oils," or naphtha; when 60 or 70 gallons have condensed, consisting of about ¼ naphtha and ¾ water, the distillation almost stops for a time, generally about an hour, or an hour and a half, during which time little but water passes over. The stoppage of the distillation is known as the "break," and during the subsequent period the still is said to be "on the rattles," owing to the peculiar noise with which the generation of steam is accompanied. When the temperature has risen somewhat higher, the still "comes off the rattles" and yields about 20 gallons of oil lighter than water ("second light oils"). The point at which the distillate begins to be heavier than water is found by observing whether in a small sample the oily or aqueous portion floats on the surface. As soon as the oil becomes heavier than water, the shoots are changed and the still is said to be "on the oil." In the course of the next three hours about 300 gallons are distilled. The first portion of this consists chiefly of naphthalene, which is very apt to block up the worm. After about 150 gallons have passed over, the nature of the product changes, the naphthalene being readily soluble in the oils then running. The still is now said to be "on the soft oils," of which about 100 gallons are obtained. After this, the oil begins to thicken on cooling, the approach to this point being ascertained by catching a few drops of the oil on a piece of cold iron. The product now running is known as "anthracene oils," and measures some 50 gallons. When the oil sets to the consistence of butter on cooling, the process is arrested, and the remaining 4 tons of pitch run out into a tank.

As thus carried out the distillation yields:—

	Gallons.		Per cent. by weight.
Ammoniacal liquor, about	50	=	4
First light oils	20	=	1½
Second light oils	20	=	1½
Creasote oils	250	=	22
Anthracene oils	50	=	4
Pitch	4 tons	=	67
			100

The proportions of the various products obtained vary considerably with the character of the tar and the manner in which the details of the operation are conducted.

The still and condenser employed in the above operation will be more appropriately described in detail in the section treating of coal-tar distillation, but it may be said generally that the apparatus used consists of a vertical cylinder of cast or wrought iron, having a movable top and bottom, both of which are convex upwards. A pipe near the top of the still admits the tar from the tank, and a large cock at the bottom suffices to run off the pitch at the end of the operation. The size and shape of stills used varies somewhat widely, but a desirable size is one which will work off a charge of 1200 gallons of tar in the course of ten or twelve hours, thus avoiding night work. Such a still will be about 7 ft. in diameter, and nearly the same in height. The condenser is usually a 4-inch socket pipe arranged in a rectangular tank. About 140 or 150 ft. of condensing length is sufficient for a still of the above size.

In a well-known works, in which the manufacture of carbolic acid is of primary importance, 20 tons of gas-tar are worked on; the first 200 gallons, consisting of "light benzols," &c., are of no use for the extraction of carbolic acid. When that measure of distillate has passed over, the shoots are changed, and the next 600 gallons are collected separately. This portion of the distillate corresponds closely with the "creasote oils" of the process previously described, and it is from these products that carbolic acid is always obtained.

In some cases these oils are redistilled, and the portion passing over between 150° and 200° C. used for the manufacture of carbolic acid. More frequently they are treated directly in the following manner:—

Two hundred gallons of the oil having a density of 1·000 to 1·005 are treated with alkali. 30 gallons of caustic soda solution of 1·34 specific gravity (= 68° Tw.) are diluted to 150 gallons with water, the liquid thus obtained added to the oil, and the whole well agitated together for two hours. By this treatment the carbolic and cresylic acids become dissolved in the alkaline liquid, while the naphthalene and other hydrocarbons and oils of neutral character are left unacted on. The mixture is next allowed to settle for about four hours, when the alkaline solution is drawn off and neutralized with sulphuric acid. This causes a separation of the carbolic and cresylic acids from the aqueous liquid, on the top of which they form an oily layer. Time having been allowed for this to separate thoroughly, it is skimmed off and allowed to settle in tanks for several days, when it is ready for casking.

It is sometimes stated that hydrochloric acid may be substituted for the sulphuric, but this cannot be done with advantage.

The caustic soda employed must be free from nitrates (which are commonly present in some varieties), or on neutralization the nitric acid set free will act violently on the carbolic acid, producing awkward consequences.

The crude carbolic acid obtained as above contains a considerable but variable proportion of cresylic acid, and sometimes of still higher homologues. When to be used simply as a disinfectant, the crude product is sufficiently pure, but for certain medical and other purposes a superior preparation is required.

The proportion of cresylic acid contained in crude carbolic acid may be ascertained approximately by the following process, which is also very similar to the method of purification adopted on a large scale.

One thousand fluid grains of the sample are placed in a retort and distilled, the liquid which passes over being collected in graduated tubes. Water first condenses, followed by an oily liquid. When 100 fluid grains of the latter have been collected the receiver is changed. The volume of water is then read off. If the oily liquid floats on the surface, it contains light neutral oils. It should be heavier than water, in which case it may be regarded as hydrous acid containing about 50 per cent. of real carbolic acid.

The next portion of the distillate consists of absolute acid, and when it measures 625 grains the receiver is again changed. The residue in the retort consists wholly of cresylic acid and still higher homologues of carbolic acid. The 625 grains measure of absolute acid contains variable proportions of carbolic and cresylic acid. These may be approximately estimated by determining its solidifying point, which should be between 15° and 24° (59° and 75° F.). Having ascertained this temperature, a mixture of pure carbolic and cresylic acids is made in such proportions as to have the same solidifying point. This must be adjusted by trial; or a series of standard specimens may be prepared. The exact point of solidification can be more sharply read if a minute fragment of crystallized carbolic acid be added to induce the commencement of the change of state; or the sample may be solidified, and the liquefying point noted.

As excess of cresylic acid prevents solidification, in some cases a second fractional distillation should be resorted to, the process being arrested when the thermometer rises to 190° C.

The same principle as the above is adopted for the purification of carbolic acid on a large scale. Cresylic acid boiling at a considerably higher temperature than carbolic, a tolerably perfect separation of the two acids can be effected by repeated fractional distillation.

Cresylic acid being itself a liquid, the presence of it in carbolic acid tends to lower the melting point, so that the inferior grades of carbolic acid are liquid at ordinary temperatures. Another cause for their fluidity is the presence of water, which is taken up by the coal-tar acids to a greater extent than is commonly supposed. The best test for the freedom of carbolic from cresylic acid is to drive off any water by boiling the sample in a tube for a few minutes, and to ascertain the solidifying point of the remainder. When pure, carbolic acid solidifies at about 42° (108° F.).

In addition to cresylic acid, which is a normal constituent of crude carbolic acid, the commercial article is frequently largely adulterated with neutral coal-tar oils (naphthalene oils), which are of very little value as disinfectants. If purified by solution in alkali, carbolic acid cannot contain more than traces of these bodies; hence their presence in quantity is always due either to imperfect manufacture or to their subsequent addition as adulterants. Specimens of so-called "carbolic acid" are sometimes sold containing only a few percentages of real coal-tar acids. These products are probably the refuse neutral oils resulting from the treatment of the anthracene oils with soda.

The presence of neutral coal-oils in carbolic acid may be detected, and their quantity estimated with sufficient accuracy by the following simple process.

Into a graduated tube pour 100 fluid grains of the sample to be tested, and add gradually—noting the effect produced—twice its volume of a solution of caustic soda (free from alumina), containing 9 per cent. of real hydrate of soda. A solution of this strength will have a density of about 1·090, or 18° Tw. The tube is then closed and well agitated. The coal-tar acids will be completely dissolved by the alkaline liquid, whilst on standing any neutral oils used as adulterants will form a separate layer above or below the other according as the admixture consisted of the light or the heavy oil of tar. By the volume occupied by the oily stratum the extent of the adulteration is at once indicated. After noticing whether the tar-oil is "light" or "heavy," a volume of petroleum spirit (commercial "benzolene") equal to that of the sample taken, may be advantageously added. Its employment facilitates the separation of the oily stratum and renders the reading off of its volume more easy and accurate. Of course, the volume of petroleum spirit used must be deducted from that of the total oily layer.

Carbolic acid has met with numerous applications, and the number of its uses is continually extending.

When heated with oxalic acid it yields the colouring matter known as *aurin*, or *rosolic acid.*

By the action of nitric acid, carbolic acid yields *picric acid*, which has met with extensive application as a dye and an explosive agent.

When acted on by sulphuric acid, carbolic acid forms *sulpho-phenic acid*, the salts of which have been extensively employed in medicine.

By combining carbolic acid with soda, and acting on the heated product with carbonic acid gas, *salicylic acid* is generated, and is now manufactured extensively, by this reaction.

The purer varieties of carbolic acid are largely employed in medicine. It is used both internally and externally, and is employed in the form of ointment, spray, and in various other ways.

The valuable antiseptic properties possessed by carbolic and cresylic acids have caused them to be very widely used for disinfectant purposes. For this purpose they have been employed in the liquid state, in the form of soap, and as disinfecting powders. The preparation of the latter is now extensively carried on.

Carbolic Acid Disinfecting Powders differ considerably in their nature according to the material used as a basis and the proportion of carbolic acid introduced. In some cases, the basis of the powder is slaked lime, but the resultant "*carbolate of lime*" has been proved to be of little value for disinfecting purposes. "Macdougall's Disinfecting Powder" is made by adding a certain proportion of crude carbolic acid to an impure sulphite of calcium, prepared by passing sulphurous acid over ignited limestone. The product often contains far more sulphate than sulphite, and not unfrequently contains free lime, which reduces its disinfecting value. "Calvert's Carbolic Acid Powder" is made by adding carbolic acid to the silicious residue resulting from the manufacture of sulphate of aluminium from shale. Sand, clay, and other materials are sometimes used. Good carbolic acid powders should contain at least 12 or 15 per cent of crude carbolic acid. They are liable to lose 1 or 2 per cent. of the acid by volatilization. Some powders in the market contain only 4 or 5 per cent. of total oils, of which less than half are really carbolic and cresylic acids, the remainder being worthless tar-oil.

The proportion of crude carbolic acid contained in silicious carbolic acid powders may be readily ascertained by the following process. 1000 grains of the sample are placed in a retort and heated over a flame. Crude carbolic acid distils over and may be collected in a graduated tube. The process is continued till nothing more distils. The heat should be pushed to dull redness and the retort occasionally shaken. On standing, the aqueous portion of the distillate separates from the oily liquid, and the volume of the latter may be read off. The loss in the process is usually about ·8 per cent., which may be added to the result obtained. The crude carbolic acid obtained may be examined for neutral coal-oils by the process described above.

The manufacture of carbolic acid is of comparatively recent growth, having been originated by the late Dr. F. Crace Calvert, of Manchester. The manufacture is probably increasing, but is still chiefly confined to Manchester and the neighbourhood, and is in comparatively few hands. The manufactured article is disposed of chiefly to wholesale chemists, druggists, and drysalters; to the manufacturers of dyeing materials and disinfecting powders, and in other ways indicated by the uses to which the article is put. (See also article on "Coal-tar Products.") A. H. A

CARBONIC ACID. (Fr., *Acide carbonique;* Ger., *Kohlensäure.*) Formula CO_2.

Although carbon dioxide in its natural state possesses no acid properties, and therefore the designation "carbonic acid" as applied to it is somewhat misleading, it seems desirable, under the popular acceptation of the term, to describe the nature, properties, and chief sources of the four forms of the oxide with which we are acquainted, viz. the gaseous, solid, and liquefied anhydride, and the aqueous solution of the gas which alone is the true carbonic acid. It may be said at the outset that there are few bodies more important than carbon dioxide to which so inadequate attention has been given by chemists and physicists. Known and utilized from the daysof Paracelsus, its composition, even, was not demonstrated until Lavoisier turned his attention to the subject. It was then established that the true proportions were as nearly as possible 28 per cent. of carbon, and 72 per cent. of oxygen. Carbon dioxide has been known by a variety of names:—carbonic acid; fixed air (so called by Dr. Black, who, in 1757, separated it as a definite constituent of limestone, and from its absorption by solutions of caustic alkalies); mephitic air (from its noxious and destructive properties); and carbonic anhydride, or carbon hydride; kohlensaures gas; kohlensäure; gaz sylvestre; spiritus sylvestris.

Gaseous carbon dioxide is a colourless body, with a slight sweetish taste, and is one and a half times heavier than air. It is not inflammable, nor does it support combustion, though potassium and sodium decompose it—the former when heated to redness. Forming a food for growing vegetation it is yet exceedingly destructive of animal life when inhaled. When perfectly dry, it does not redden litmus, and, in fact, possesses no acid properties. It is soluble in about its own weight of water at ordinary temperatures, forming the aqueous carbonic acid. Carbonic anhydride is an exceedingly stable body, being decomposable at only a very great heat; the solution is as unstable.

Few bodies are so widely diffused as gaseous carbon dioxide. It is a constituent of the air to the extent of 0·4 per cent. by volume, it exists in expired air up to 3·5 per cent., and in the air of crowded rooms to 0·5 or 0·78 per cent., through the oxidation of the carbon contained in the body, and is necessary to the growth of vegetation. It is produced in the ordinary process of oxidation or combustion of all substances containing carbon, in the various processes of fermentation, and in the decay of animal and vegetable matter. From the craters of volcanoes, from fissures in the ground, in mines, wells, and quarries, the gas is continually evolved in enormous quantities. It is produced by the decomposition of the carbonates either by heat or by the action of stronger acids. Finally, it is a constituent of the natural effervescing waters of Vichy, Spa, Kissingen, Ems, Carlsbad, &c., &c. The amount of the gas present in the best known of these natural springs is as follows:—

Cubic Inches of Carbon Dioxide in 100 Cubic Inches of Water.

Carlsbad	58
Ems	51
Saratoga (Congress Spring) ..	114
Kissingen	96
Marienbad	105
Pyrmont	160
Spa	136
Püllna	7
Schlesischer (Obersalz-Brunnen)	98
Auschowitz (Ferdinands-Brunnen)	154
Eger (Franzens-Brunnen)	154
Selters	126
Fachingen	135

Carbonic anhydride may be readily formed by heating carbonate of lime to redness in an iron, brick, or earthenware retort or furnace. The usual method of preparation, however, is by decomposing marble or chalk by dilute hydrochloric or sulphuric acid. Hydrochloric acid is the better agent, as the insoluble sulphate of lime which is formed when sulphuric acid is used coats the chalk and hinders further decomposition. The residue sets very hard also, and is difficult to remove from the generating vessel. Chloride of calcium forms a useful bye-product, and is readily soluble.

Under ordinary conditions as a gas, carbon dioxide may be readily liquefied by varying the temperature and pressure. For this purpose, at 0° (32° F.) a pressure of thirty-six atmospheres is required; as the temperature is raised, greater pressure is required, until the gas refuses to be liquefied under any pressure. This point—the "critical point," as it has been designated—is rather over 32°. Under the ordinary pressure of the atmosphere a temperature of $-87°$ (which may be produced by evaporating liquefied ammonia over sulphuric acid in vacuo) is required to effect liquefaction. The body obtained by these methods is a thin, colourless liquid, lighter than water, and four times more expansible than air. It is miscible in all proportions with ether, alcohol, naphtha, and turpentine, but floats on the surface of water. Its specific gravity at $-10°$ is 0·9951, at 0°, 0·9470, and at $+20°$, 0·8266. These figures show the extraordinary expansion of the liquid upon increasing the temperature, its coefficient of expansion being greater than that of any other body. The boiling point of liquid carbon anhydride is − 78·2° under a pressure of 760 mme. Its tension at different temperatures is shown by the following table :—

Temperature.	Pressure in mme. of Mercury.	Temperature.	Pressure in mme. of Mercury.
− 25	13007·02	+ 15	39646·86
− 20	15142·44	+ 20	44716·58
− 15	17582·48	+ 25	50207·32
− 10	20340·20	+ 30	56119·05
− 5	23441·34	+ 35	62447·30
0	26906·60	+ 40	69184·45
+ 5	30753·80	+ 45	76314·60
+ 10	34998·65		

The spontaneous dehydration of liquefied carbon anhydride, and the readiness with which it is converted into the gaseous compound upon variation of pressure and temperature, has led to its adoption as a motive power. Little beyond experiment has yet been done in this direction, but if the difficulty of first cost could be got over, or if some ready way could be found of recovering the gas and re-liquefying it, so as to make a continuous operation, there seems to be little reason why it should not to some considerable extent supersede the use of steam. So far about 7 lb. of coal are required to produce a sufficient quantity of "carboleum," as this substance has been called, to do the work of one horse-power per hour. It has been prepared at Newport, Rhode Island—at the United States naval station—for the purpose of driving torpedoes, but the difficulties both of cost and extensive plant seem at present to be insuperable, a steam-engine to work the compressing pump and an arrangement of freezing mixture being required. Given a sufficient pressure, of course the freezing arrangement might be done away with, but the compressing of the air in the receiver up to 80 lb. per square inch would be necessary.

Divers apparatus for liquefying carbon anhydride have been devised, those of Thilorier and Natterer being the best. Thilorier employs two strong wrought-iron cylinders, into one of which is introduced about 5 lb. of bicarbonate of soda and 7 pints of water. A copper tube containing 2½ lb. of sulphuric acid is then lowered into the mixture and set on end, the top of the cylinder being firmly closed with a cap, into which the delivery tube, fitted with a carefully constructed stop-cock, is introduced. By inclining the retort or "generator," for which purpose it may be conveniently swung in an iron frame, the acid is allowed to run gradually out of the tube and mix with the bicarbonate. In the meantime the second cylinder or "receiver," kept cool by means of a freezing mixture or ice, has been connected with the delivery tube of the generator, and when the sulphuric acid has set free gaseous carbon anhydride from the bicarbonate of soda, the cocks are opened, and the gas allowed to rush over into the receiver, where it condenses by its own pressure.

At Vienna another plan, that of Professor Beims, has been tried, but too great a quantity of fuel is required to allow of its being commercially successful. By this method the gaseous anhydride is freed from bicarbonate of soda by heating the latter up to 371° (700° F.) in closed strong iron vessels, and condensed, as in the case of Thilorier's apparatus, by its own pressure.

A very excellent process is the following :—a mixture of chalk and water is introduced into the generator, which is fitted with an agitator. The acid is run in gradually from a vessel placed above, and thorough admixture secured by agitation. When liberated, the gas is conducted through a vessel called the "washer," containing water, into the receiver, where it is kept until a pressure of about 100 lb. to the square inch is attained. It is then taken through a set of refrigerating pipes into the compressing cylinders, and from thence into the "holders," which are carefully surrounded by a freezing mixture. The holders should be made of thin sheets of steel placed in successive layers with overlapping joints, and soldered together with pure tin, the outer case being carefully rivetted. Considerably less work is manifestly put upon the compressing engine by the gas being stored in the receiver until it can be introduced into the compressing cylinder at an already high pressure.

Faraday first liquefied carbonic anhydride by decomposing carbonate of ammonia by sulphuric acid in a sealed bent glass tube. Gore has proposed to condense, after a somewhat similar manner, in strong glass tubes closed with guttapercha stoppers. By Natterer's process, to which reference has been made, the gas generated by the action of sulphuric acid upon bicarbonate of soda is pumped by means of a force-pump into a strong wrought-iron vessel, in a similar manner to the pumping of air into the receiver of an air gun. As soon as the volume of gas pumped in amounts to about thirty-six times the volume of the receiver, every stroke produces condensation. This apparatus has also been used for liquefying nitrous oxide gas.

When liquid carbon anhydride is suddenly freed from pressure, it is instantaneously converted into the gaseous form, and by the operation such intense cold is produced, that a portion of the liquid is frozen. It then forms the solid anhydride, a white, snow-like mass. Though this substance has so low a temperature as − 78°, it can be handled without inconvenience, owing to a constant volatilization, which keeps it from actual contact with the hand. Wetted with ether, solid carbonic anhydride forms the most effectual freezing mixture known, a temperature of −110° being obtainable, and mercury instantly solidified into a lead-like mass. If when liquefying the gas at a temperature of −87° the pressure is increased to four atmospheres, a solid mass is obtained, which has the transparency of ice, and may be divided into crystals, which have the action of intense heat when pressed between the fingers.

It remains only to notice the aqueous solution of carbon dioxide, the only real acid form of the compound. The gaseous anhydride dissolves in its own volume of water, giving a solution of 1·0018 sp. gr. with a sharp acid taste, and possessing decided acid properties. By boiling this aqueous solution, however, the gas is evolved, and litmus no longer reddened. It is owing to this that hard water can be softened by boiling, the carbonate of lime yielding up its carbon dioxide, and being deposited in the kettle or boiler in the shape of "fur." If the gas be simply passed into water, only about two-thirds of the bulk of the solvents is taken up; but if the pressure is increased or the temperature diminished, the solubility is very much greater. Hence water impregnated with the gas at a high pressure immediately parts with it when the pressure is removed. For further details of this part of the subject see "Aerated Waters."

The following table gives the volumes of carbonic anhydride absorbed by 1 volume of water under a pressure of 760 mme., and at the temperatures indicated:—

Temp.	Vols. of Gas absorbed.	Temp.	Vols. of Gas absorbed.
0°	1·7697	12°	1·1018
2	1·6481	14	1·0321
4	1·5126	16	0·9753
6	1·3901	18	0·9318
8	1·2809	20	0·9013
10	1·1847		

The column marked *a* in the annexed table shows the volume of gas absorbed at the ordinary temperature of the air, and under the pressures indicated by the column marked P.

P	*a*	P	*a*
697·71	0·9441	2188·65	3·1764
809·03	1·1619	2369·02	3·4857
1289·41	1·8647	2554·00	3·7152
1469·95	2·1623	2738·33	4·0031
2002·06	2·9076	3109·51	4·5006

Carbonic acid, the aqueous solution of the gas, forms a series of exceedingly valuable salts called "carbonates." They are obtained by the direct action of the acid, or by the joint operation of the anhydride and water, upon metallic oxides or hydrates. In no case does the anhydride unite with a base without the intervention of water. Certain of the carbonates are also very readily produced by precipitating a soluble metallic salt with an alkaline carbonate. For the most part they are soluble in water and insoluble in alcohol; they are decomposed by the action of heat, and of water with the aid of heat.

The carbonates constitute an exceedingly important set of compounds, whether they be viewed from a geological, chemical, or purely industrial standpoint. The limestones form no inconsiderable portion of the earth's crust, and the value of these under their several forms of chalk, mountain limestone, and marble, is too well known to be insisted upon. The carbonates of potash, soda, ammonia, and lead, are prepared on a large scale for various purposes. Some of the most valuable metallic ores are carbonates. The most important of these salts are the carbonates of baryta, copper, iron, lead, lime, magnesia, potash, soda, and zinc.

All the carbonates, soluble and insoluble, are decomposed with effervescence by the strong acids. The gas which is given off is colourless, and of a somewhat pungent odour. If it be passed into milk of lime, or into a mixture of chloride of barium and caustic ammonia, a white precipitate is thrown down, though often not until the liquor has been heated. The same effects are produced by passing the gas into a solution of acetate of lead. These precipitates dissolve with effervescence in dilute nitric acid.

In analyzing a substance in order to determine the quantity of carbonic acid in combination, it is a common practice to ascertain the loss of weight which the substance undergoes when treated by other acids. It is necessary, however, when this method is adopted, to take care that vapour of water be not evolved along with the gas. The quantity of carbonic acid contained in lime and carbonate of lime is usually determined in this manner. J. L.

CHROMIC ACID. (Fr., *Acide chromique;* Ger., *Chromsäure.*) Formula CrO_3.

This acid does not occur in nature, but it may be prepared from its salts in several ways, in the form of beautiful, deep red, needle-shaped crystals. The following are the most important methods:—

1. By the decomposition of bichromate of potash by strong sulphuric acid. One volume of a saturated solution of the bichromate is poured gently into one and a half volume of oil of vitriol, the mixture being carefully stirred during the operation; on cooling, the chromic acid separates out in long needles of a beautiful red colour. These are dried and purified from sulphuric acid by re-crystallization.

2. By treating chromate of baryta with a large excess of strong nitric acid. This method is employed by Mr. Charles Watt. The nitrate of baryta formed by the reaction is insoluble in nitric acid, and may be easily separated from the chromic acid by decantation, or by filtration through asbestos. The filtrate is evaporated to dryness, the nitric acid being volatilized; the residue is pure chromic acid. If the quantity of nitric acid required be large, it may be condensed and employed a second time.

3. By the decomposition of chromate of lead by sulphuric acid. The mixture is allowed to stand for twenty-four hours and is then diluted. The sulphate of lead thus formed is filtered off and the filtrate evaporated at a gentle heat. If the chromic acid be required to be perfectly pure, the crystals are dissolved in pure water and re-crystallized.

Chromic acid dissolves in a small quantity of water, forming a dark-brown liquid having an acrid, astringent taste. It is a powerful oxidizing agent, readily giving up part of its oxygen and passing into the sesquioxide. It reacts upon alcohol with such energy that the latter becomes inflamed.

Free chromic acid is seldom used in the arts as an oxidizing agent. A mixture, however, of a solution of bichromate of potash with sulphuric acid and some neutral vegetable matter yields the free acid. Obtained in this manner, it acts as a powerful bleaching agent, and is often used as a substitute for chlorine in calico-printing, the corrosive properties of the latter rendering it unfit for many purposes.

Pure chromic acid is used in mounting microscopic objects, to harden preparations of soft tissues. When combined with oxide of tin, it forms one of the pink colours used in porcelain-painting.

CITRIC ACID. (Fr., *Acide citrique;* Ger., *Citronsäure.*) Formula $C_6H_8O_7$.

This acid was isolated and distinguished from tartaric acid, which it closely resembles, by Scheele in 1784. The citric acid of commerce consists of beautiful white crystals, prismatic in form, and, according to an analysis by Dr. Ure, of the following composition: carbon, 33·00 per cent.; hydrogen, 4·63 per cent.; oxygen, 62·37 per cent. Citric acid exists in the juice of many fruits, especially in lime juice and lemon juice, from which it is obtained on a large scale. The juice of gooseberries and currants has also been used as a source of this acid.

The outlines of the manufacture of citric acid from lemon and lime juice, as carried on at the present time, are as follows:—After clarification, the juice is heated to about 100° C., and powdered whiting (carbonate of lime) is added until the liquor is saturated, a point readily determined by its ceasing to effervesce; the whiting should be added in small quantities, suitable to the amount of liquor under treatment, and the mixture is kept constantly agitated by machinery until the whole of the citric acid present has been converted into insoluble citrate of lime. When this is the case, the mixture stands until the citrate of lime has settled, when the supernatant liquid is run off, and the residue well washed by adding and decanting cold water, the agitating apparatus being set in motion after each addition. The washed citrate is next decomposed by means of hot sulphuric acid, sulphate of lime, and free citric acid being formed. The former is got rid of by running the contents of the vessel into a settling tank close at hand, in which the heavy sulphate is retained, while the solution containing the citric acid flows into vessels in which it is concentrated by steam-heat. The concentrated citric liquor is pumped into a cistern, from which it is ladled into filters, made usually of canvas; the filtrate runs into crystallizing pans placed beneath, in which it stands until the crystals cease to form. The mother-liquors are run back into the concentrating pan.

If a very pure article be required, it is customary to place a small quantity of animal charcoal in each of the filters; this serves to decolorize the liquid, and to free it from insoluble foreign matter. The crystals may be dissolved and re-crystallized until they are obtained perfectly pure and of large size; but when ordinary commercial citric acid is required, one process of crystallization is usually enough.

The lime juice from which the acid is prepared is imported from Sicily, the south of Italy, and from the West Indies. After removing the seeds and peel, the fruit is strongly expressed, and the juice collected; it is evaporated in copper pans until it has a density of about 1·234, when it is a thin, dark-brown, syrupy liquid, containing about 32 per cent. of free citric acid. An instrument termed a *citrometer* is sometimes used to measure the amount of citric acid contained in the juice, but this method is not to be relied on, owing to the variableness of the quantity of insoluble and saccharine matter present in the sample, as well as to the fact that during the concentration of the juice, part of the acid is invariably decomposed and carbon thereby set at liberty; the dark colour of the juice is also due to the presence of free carbon. It is imported into this country in casks containing about 100 gallons.

The vessel in which the decomposition takes place is a wooden tub, conical in form, and of any convenient size; this tub is fitted with suitable agitating gear, worked by machinery above. The juice is run in from a cistern, by means of a metal pipe provided with a stop-cock, having been previously heated to about 100° C. Small portions of common whiting, finely ground, are added successively, the contents being well agitated the while, until the mixture ceases to effervesce. It should be observed that the reaction with litmus or turmeric affords no indication of the point at which all the citric acid is converted into citrate of lime, owing, it is said, to the formation of an acid citrate, and also to the presence of phosphoric acid, which is always to be found in the crude lime juice; these bodies are with difficulty neutralized by chalk, and render the mixture distinctly acid when considerably more chalk has been added than is sufficient to combine with the whole of the citric acid. The liquid may be, and sometimes is, neutralized by the addition of milk of lime, but the practice is objectionable, and has been discontinued by the best manufacturers, on account of the mucilage precipitated by the lime, which hinders the filtration and crystallization of the concentrated liquor. It was formerly the custom to get rid of these mucilaginous matters by subjecting the crude juice to a process of fermentation, but this has been generally given up as unnecessary.

When the addition of more chalk produces no effervescence, the agitating gear is stopped, and the contents of the tub are allowed to settle; the clear liquor, containing much soluble impurity, is run away by means of a tap. The citrate of lime is now washed rapidly, but thoroughly, with warm water, the contents are well stirred up, again allowed to settle, and the washings again run off; this process is continued till the citrate is thoroughly cleansed. It is then ready for decomposition, which is carried on in the same vessel. The proportion of sulphuric acid required to effect this is about 9½ parts of strong acid, diluted with six times its weight of water, to every 10 parts of chalk previously used. The acid is run in while still hot, and the mixture kept in a state of agitation for about twelve hours, or until the whole of the citric acid is decomposed. This operation complete, the whole contents are run off, while still well mixed together, into a shallow leaden vat, placed immediately beside the decomposing tub, and connected with the bottom of the latter by means of a leaden pipe. The heavy sulphate of lime, which may afterwards be sold as manure, sinks immediately to the bottom of this vat, leaving the citric acid liquor free to flow into the concentrating vessel placed at its side; this vessel is made of wood, lined on the inside with lead, and furnished with a leaden coil, which lies at the bottom of the pan, and through which steam is constantly passing. In order to render the concentration more speedy, the wooden sides of the pan enclose a row of metal pipes, through which also steam is made to pass. The steam is withdrawn as soon as a thin film appears on the surface of the evaporating liquid, and care must be taken that this point is not passed. On withdrawing the steam, the concentrated acid is run or pumped into a convenient cistern, and from this it is ladled into canvas bags suspended from a wooden frame, beneath which are placed rows of circular leaden basins; the liquor running through is retained in these basins, all mechanical impurities being left behind in the bags. As soon as the crystals cease to form, the mother-liquors are poured back into the concentrating pans, and the citric acid is carefully detached from the basins. The article thus obtained is sufficiently pure for ordinary purposes, and represents the citric acid of commerce.

During the process of evaporation in the leaden vats, the concentrated liquor invariably becomes contaminated with more or less lead. When the acid is used for the preparation of aerated waters, this becomes a serious difficulty, owing to the poisonous nature of lead compounds; it has been proposed to obviate this by employing vessels of wood or earthenware.

All solutions of organic acids are liable, during concentration by heat, to undergo a process of decomposition, by which carbon is liberated, and the article more or less damaged thereby. Hence much care is necessary in order to prevent the heat from becoming too great, if the liquor be evaporated in open steam pans, and the difficulty experienced in avoiding this contingency was for many years a constant source of annoyance to manufacturers of citric acid. An arrangement by which the liquid is concentrated in a vacuum, at a constant temperature, was invented and patented by Pontifex, in 1856. This apparatus is known as the Pontifex vacuum pan, and though a complicated and expensive piece of machinery, seems to be the only effectual means of overcoming this troublesome obstacle. It will be fully described and illustrated in the article on tartaric acid.

Owing to this liability of citric acid to decomposition, a cheap and easy method of converting the lemon and lime juice into some stable citrate, before exportation, would be an inestimable advantage, both to the exporters of the juice and the manufacturers of the acids. Attempts have been made to effect this, but hitherto without much success, and the subject is still worth the attention of those interested in this important branch of manufacture. Lime as a base for citric acid is out of the question, as, unfortunately, citrate of lime is as unstable as the acid itself. Perret has employed magnesia as the base with a considerable amount of success, though the time occupied in effecting the crystallization of the tri-basic citrate is a manifest disadvantage. Another matter to which the manufacturer would do well to give his attention, is the objectionable waste of time in the processes of evaporating, filtering, &c.; the attainment of more economy in this respect is much to be desired, and would amply repay careful consideration.

A patent was granted a few years ago for a method of producing citric acid, in conjunction with tartaric acid and alcohol, and in a state of extreme purity, from an African plant called the *tamarinha;* the plant is cut while green, and subjected to pressure, by which means the juice or sap is extracted; the three above-named substances are obtained separately from the sap by subsequent chemical processes. We do not know whether this method of preparing citric acid has been found successful on a commercial scale, but it is scarcely probable.

The following method of obtaining citric acid is due to Dr. Price;—The crude juice is saturated with an alkaline carbonate, or with the ammoniacal product distilled from gas-liquor: 150 parts of chalk or 90 parts of milk of lime are now added for every 192 parts of citric acid contained in the juice. Heat is applied, and the ammonia distilled off into another portion of the juice. The decomposition of the citrate of lime by sulphuric acid, and the subsequent processes, are carried on in the usual way.

Citric acid is constantly adulterated with tartaric acid; the fraud is readily detected, if tartar be present in any quantity, by dissolving a portion in water and adding a small quantity of a strong solution of acetate of potash, or other potash salt, when a crystalline precipitate of cream of tartar will show itself on the sides of the vessel.

The first crops of citric acid crystals, which are brownish in colour, are used largely by the calico-printer as a "resistant" for iron and alumina mordants; when the acid is required for other purposes, it is necessary to subject it to one, or even two or three more crystallizations, according to the degree of purity wished for. The above application of the acid is the most important, though citric acid is also widely used in the manufacture of aerated waters (see "Aerated Waters"), to which it imparts an agreeable and cooling acerbity. It is used medicinally as an antiseptic and scorbutic, in the place of lemon-juice.

The manufactures of citric and tartaric acids are usually carried on in the same works, and are, in the main, identical. To avoid repetition, further detailing of the particulars of the manufacture of the acid under consideration has been deferred for treatment under the latter acid.

GALLIC ACID. (Fr. *Acide gallique;* Ger. *Gallussäure.*) Formula $C_7H_6O_5$.

This acid exists in many plants and vegetables in small quantities, but it is usually obtained from a substance contained in nut-galls which is called "tannin." The most simple method is to submit powdered nut-galls to the action of the atmosphere for about three months, placing it in a cool spot and keeping it moistened with water; after a short time the mass swells up and becomes mouldy. At the end of this time it is submitted to pressure, the escaping liquid being rejected so long as it runs out coloured; the remainder is digested with boiling water, which, after being filtered and allowed to cool, deposits crystals of impure gallic acid. To purify these, they are re-dissolved in seven or eight times their weight of boiling water, a little animal black being added to decolorize the solution.

Another method of converting tannin into gallic acid is due to Liebig. It consists in extracting the tannin from the pulverized gall-nuts with water, and precipitating the solution with sulphuric acid diluted with seven or eight times its weight of water. The whole is boiled for a short time, during which the conversion takes place. The liquor is concentrated at a gentle heat, and on cooling deposits nearly colourless crystals of gallic acid.

The first of these methods is, however, the most convenient, and it is in use at the present time, the manufacture being carried on as follows;—The nut-galls are carefully chosen and sorted over, the most valued being the green ones, which furnish 40 per cent. of their weight of gallic acid; the white variety is not nearly so rich, and is usually rejected. The nuts are reduced to powder and placed in a large, shallow leaden basin; in this they are moistened continually for some days with warm water, which is added as long as it is absorbed by the nuts; when this is complete the whole is placed in a compact heap, so as to retain as much warmth as possible. At the end of a few days fermentation sets in, and the surface of the heap becomes covered with a thick, grey mould. At the expiration of about three months the fermentation is complete; during the whole of this time the mass should be moistened whenever it shows any signs of becoming dry. The nuts are next submitted to a heavy pressure, and for this purpose they are placed in a solid wooden press, tied up in bags made of cloth. The expressed liquid runs out in a thick, black stream, and contains much gummy and extractive matter which would seriously interfere with the subsequent crystallization. The nuts are next digested in boiling water in a wooden vessel lined out with lead and heated by a steam-pipe from below; the whole should be constantly stirred with a wooden paddle during the process of ebullition. A small quantity of dilute sulphuric acid is added to the hot liquor, for the purpose of converting any unfermented tannin into gallic acid, and of facilitating the subsequent processes of filtration. An hour or two after the addition of the acid, the steam is turned off, and the contents are left to stand for twelve hours; the clear liquor is then run off and filtered through cloths, while the residue is collected and boiled a second time in the same manner. The liquors are concentrated in leaden basins, into which steam is introduced by means of a leaden pipe; as soon as a thin film appears on the surface the steam is withdrawn and the concentrated liquor is allowed to cool. At the end of twenty-four hours the crystallization is complete, and the crystals of crude gallic acid are drained, and re-dissolved in a leaden vessel, and the hot solution is filtered through a strainer before being once more left to crystallize. The crystals thus obtained are still slightly coloured, and in order to purify them they are dissolved in water, and a small quantity of animal black is added to the solution. After filtering, a few drops of hydrochloric acid are added for the purpose of dissolving traces of gallate of iron, which would impart a yellowish tinge to the crystals. A third and final crystallization affords beautiful white, silky needles of gallic acid, in which form it is sent into the market.

Gallic acid is inodorous, and has a slightly acid taste. It dissolves in 100 parts of cold water, and in 3 parts of boiling water; also readily in both alcohol and ether. Gallic acid was at one time largely consumed in photography, indeed the demand for it seems to have grown with that art, but of late it has been abandoned in favour of *pyrogallic acid*, a substance obtained by the decomposition of gallic acid by heat.

PYROGALLIC ACID.—When gallic acid is subjected to a gentle heat, it decomposes into several substances, one of which is called pyrogallic acid. It is prepared in the following manner:—The liquor pressed out from the fermented nut-galls is reduced to powder, and placed on a metal dish over a sand-bath; when the temperature has reached 150° C., the heat is diminished, as the mass will itself rise to 200° without further heating. Three hours' heating is sufficient to convert the whole into pyrogallic acid.

A modification of this process has been employed by Liebig, by which he has obtained more beautiful and more abundant crystals. Crystallized gallic acid, perfectly dry, is mixed with twice its weight of pumice stone, and the mixture is placed in a tubulated retort heated by a sand-bath; the retort is covered with sand, and in its tubulure is fixed a tube through which carbonic acid gas is introduced into the interior; a glass receiver is fitted to the arm of the retort. The sand-bath is heated gently, and the crystals of pyrogallic acid formed are rapidly drawn out of the retort into the receiver by the current of carbonic acid gas. When the distillation is complete, the receiver will be found to contain a thick, concentrated solution, which, on cautious evaporation, yields a quantity of pyrogallic acid representing no less than 30 to 32 per cent. of the gallic acid employed.

SULPHURIC ACID. (FR., *Acide sulphurique;* GER., *Schwefelsäure.*) Formula of the anhydrous acid SO_3; of the hydrated acid, H_2SO_4.

This acid being an essential means employed in the manufacture of all the important acids which follow in their alphabetical order of treatment, it has been judged desirable to displace it from that order, for the purpose of rendering subsequent descriptions of processes more simple and easier to be understood.

The varieties of sulphuric acid met with in commerce are three in number, viz. anhydrous sulphuric acid, or sulphuric anhydride; Nordhausen, or fuming acid, a distillation from anhydrous acid, or subhydrate mixed with monohydrate; and ordinary sulphuric acid, known on the Continent as English acid, composed of monohydrate and a varying proportion of water or higher hydrates, and which when fully concentrated is usually called "oil of vitriol."

Sulphuric anhydride is a viscous, crystalline, fibrous, asbestos-like mass, which can be kneaded between the fingers. Its sp. gr. is 1·97 at 20° C. (68° F.). It is colourless and odourless, and burns on the tongue, destroying the moist skin. It melts at 25° C. (77° F.), and boils at 35° C. (95° F.), yielding a colourless vapour, which in the presence of moist atmosphere forms a white mist owing to the formation of sulphuric hydrate. On this account also it fumes at ordinary temperatures in damp air, and dissolves very rapidly in it. In bright red heat the vapour decomposes into sulphurous acid and oxygen.

Nordhausen acid is an oily, thick-flowing liquid, generally brownish-hued from the presence of organic matters, having a sp. gr. of 1·850 to 1·900, and containing at 1·854 sp. gr. 10·7 per cent. by weight of anhydrous acid, and 89·3 per cent. of monohydrate. It fumes and evaporates rapidly in a moist atmosphere. Cooled to 0° C. (32° F.), it gives crystals of subhydrate.

Ordinary English sulphuric acid is a combination of sulphur, oxygen, and hydrogen, and may be expressed by any of the following formulæ: H_2SO_4; SO^3H_2O, or $\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2$. Its density or specific gravity is 1·850, and 100 parts should contain 81·5 parts anhydrous acid and 18·5 parts water, or 92-93 per cent. by weight of monohydrate and 8-7 per cent. of water. It behaves very like the sesquihydrate; boils at 327° (620° F.), solidifies at a temperature 3 degrees below the freezing point of water, and remelts at 10° (50° F.).

Sulphuric acid is a powerful solvent, nearly all metals being dissolved by it, even in a dilute state. Also other reducing agents, such as carbon, phosphorus, sulphur, &c., exert a deoxidizing action upon concentrated acid, but with more difficulty and at a higher temperature. It combines very energetically with free bases to form sulphates, and is very difficult of elimination from such salts again. It is exceedingly hygroscopic, being capable of absorbing fifteen times its bulk of water. It combines with water most powerfully, and with great evolution of heat and generation of steam if mixed suddenly. With water it forms several compounds capable of assuming definite crystalline shapes.

Sulphuric acid exerts a severe carbonizing or dehydrating influence upon organic substances, and then assumes a more or less darkened colour. In a pure state it should be quite colourless and inodorous, and in that condition it presents an oily appearance, whence its familiar name oil of vitriol (often shortened to o.v.) is derived.

The two first-named varieties of commercially known sulphuric acid never occur in a natural state. The last named is seldom met with in a free state on account of its great solvent powers. Nevertheless, an Andean river, the Rio Vinagre, contains 0·1 per cent. of the acid, and is calculated to produce some 38 tons daily. Besides some smaller Andean streams which are acidulous, a volcanic spring in New Grenada contains upwards of 0·25 per cent. of this acid. It is, however, commonly found in intimate combination with bases forming sulphates. The principal sulphates are those of aluminium, barium, calcium, copper, iron, lead, potassium, and strontium; alunite, heavy spar, gypsum, blue vitriol, green vitriol, anglesite, kainite, and celestine being the names by which these natural salts are generally known.

Ordinary sulphuric acid results from the oxidation of sulphurous oxide, the hydration of sulphuric oxide (anhydride), as we have already seen, and from other chemical reactions; but the method commonly adopted, and among manufacturers universally, is the first named. The sulphurous oxide is derived from burning brimstone or pyrites, and is oxidized by the intervention of nitric acid, supplied either in the liquid form, or as a salt undergoing decomposition. The principal supply of oxygen is derived, however, not from the nitric acid, but from the atmospheric air, in whose presence (as in that of steam) the reaction is allowed to proceed.

Sulphuric acid may be justly described as the most important of the chemical products, since in consequence of its numerous applications, it has become the "mainstay of our present industrial chemistry."

The production of the acid is achieved in two separate ways: (*a*) by the burning of sulphur or sulphides to produce sulphurous acid, which is subsequently oxidized to form sulphuric acid; and (*b*) the decomposition of sulphates by heat. By the first-named process, which is by far the most general, only a hydrated acid of about 1·558 sp. gr. is commonly produced, and from which it is impossible to evaporate all the water, but only such proportion as to leave the monohydrate $HOSO_3$. By the last-named process, however, an anhydrous acid is liberated, which may either be used as such, or may be dissolved in monohydrated acid to produce Nordhausen. But the cost of production by this method is so much greater than by the other, that it is adopted for the manufacture of acid to be used for purposes which demand a stronger acid than can be made by the combustion process.

The production of acid by the combustion process is always assisted by nitric acid gas, derived either from the decomposition of nitrates by the action of sulphuric acid (conducted in a portion of the kilns), or from liquid nitric acid introduced into some part of the chamber system.

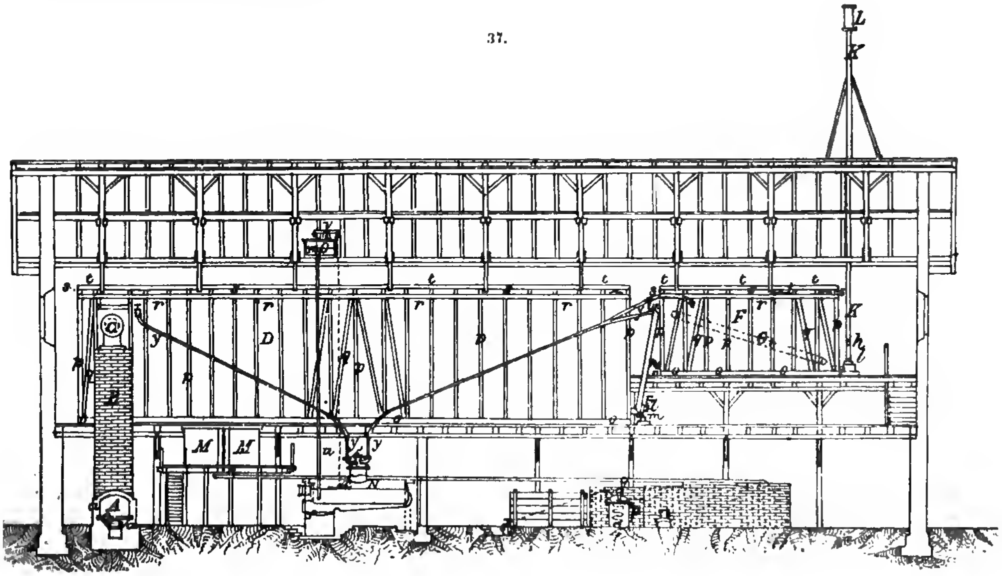
The apparatus and manipulation necessary in the production of acid by combustion of sulphur (brimstone), aided by nitric acid gas from the decomposition of nitrates (of potash, or soda, but almost exclusively the latter), will now be considered.

Figs. 37 (plan), 38 (longitudinal section), and 39 (vertical section taken through the chambers), show a small manufactory capable of producing daily about 30 to 35 cwt. of acid, at 1·850 sp. gr.

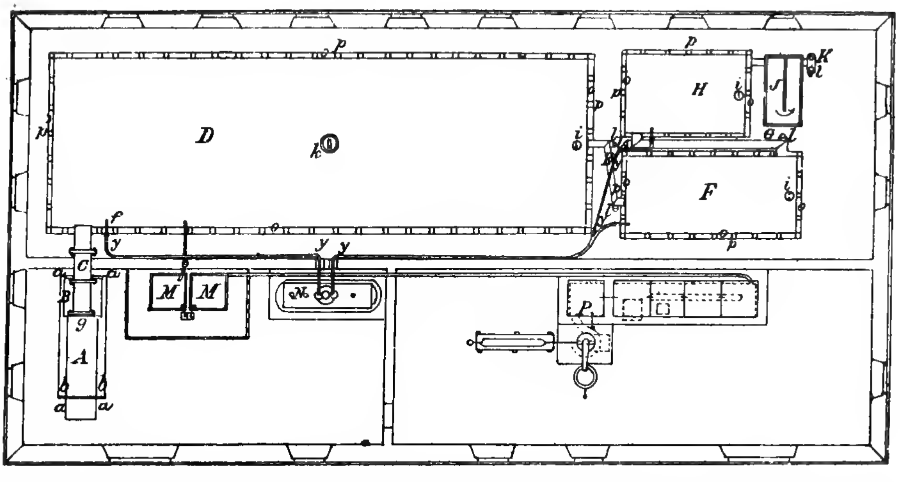
The same letters of reference are used in each of these three figures.

A is the brimstone kiln, made of well-burnt bricks, and bound together by iron bars *a*. In front of the retaining walls the strong iron plates *b* are fixed, and held by the four tie-bars *a*. The nuts visible at *a* are for screwing the plates tight up to the wall. The front plate is pierced by a door through which the charge is introduced, and in which is a hole for the admission of a constant current of air. These openings should not be made larger than requirements demand, and they must be fitted with iron closures.

37.



38.

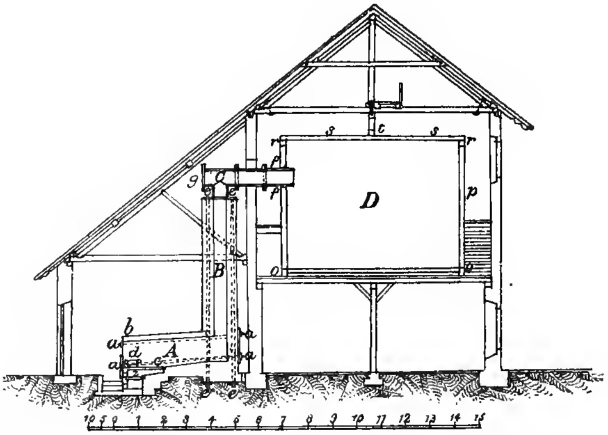


The charge of sulphur is introduced regularly every hour on the cast-iron plate *c*, under which is a fire-place, *z*, for the purpose of heating the plate at the commencement of the operation, or whenever it may become necessary to do so, but it is not by any means indispensable, and is wanting in many works. The joints are carefully plastered up after admission of the charge.

The decomposition of the nitre with sulphuric acid is conducted in the cast-iron pots, *d*. These are filled with the materials outside the kiln, and are introduced immediately after the brimstone.

The gases formed by the combustion of the brimstone and the decomposition of the nitre, mixed with atmospheric air, stream through the vertical channel B to the first leaden chamber. This channel is built of brick and strengthened by iron bolts, *e*. The connection between this channel and the first leaden chamber is made by the cast-iron tube C. At *f* the lead of the chamber wall is drawn over the tube and, after the joint has been well stopped with putty, an iron clamp is tightly bolted round. At *g* the tube is fitted with an iron man-hole plate, and the joints similarly made tight. This plate is removed from time to time, in order that the foreign matters, carried with the gases in the form of dust and here deposited, may be cleared out. All joints must be made with the greatest care and stability, for to obtain good working results it is essential that there be not the slightest communication between the atmosphere and the interior of the chamber, save through the kilns.

39.



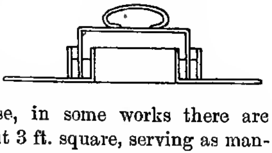
From the tube C the gases pass into the first leaden chamber D at *f*. In this chamber, measuring 71½ ft. long, 22 ft. 9 in. wide, and 17 ft. 10 in. high, the greater part of the acid is condensed. The gases which do not condense here escape by the opening at the end and near the floor of the chamber into the leaden connection pipe E, which conducts them into the upper part of the second chamber F. This chamber is only 22 ft. 9 in. long and 10 ft. 6 in. in width and height. The still remaining gases flow hence by the exit opening near the floor, through the leaden pipe G, into the third chamber H, made of the same width and height as the second chamber, but only 16 ft. 3 in. in length.

The small residual portion of the gas leaves this chamber by the exit flue near the bottom, and passing through the vessel J, in which a small proportion of sulphuric acid is still formed, escapes finally by the vertical chimney K. This conducts the vapours, consisting chiefly of nitrogen, from the air, the superfluous oxygen, some sulphurous acid, and, when the operation is well managed, a considerable portion of nitric or hyponitric acid, into the atmosphere. In order to watch the colour of the gases, windows are placed in all the flues or connection pipes, either in the form of glass panes let into the side and top, or in the shape of a glass cylinder the full size of the pipe.

The chimney K is provided with a slit, into which a leaden damper *h* can be introduced, and by opening and shutting this the draught can be regulated as desired. Sometimes, instead of a simple damper, the flue is enlarged and a perforated damper is introduced, the holes in which are, collectively, just equal to the diameter of the flue. By closing some of the holes the draught may be lessened. In order to prevent the wind from interfering with the draught, the top of the chimney is provided with a cylinder L, open above and below, and of larger dimensions than the chimney pipe. In many works the gases are conducted to the main chimney, instead of into this special substitute.

The roof of each chamber has an opening *i*, closed by a cover, which stands in a rim filled with water, or useless acid. Figure 40 shows the arrangement. This serves to show the character of the gas, which is necessary to be studied in regulating the process. They are often of glass for admitting light into the chamber, which latter is then furnished with corresponding side windows, at a convenient height for seeing into the chamber. On suspending the chambers their ventilation is much hastened by removing these covers. The roof of the first chamber, being necessarily of greater length, may have two such covers with advantage. Besides these, in some works there are openings in the side walls of the chambers, near the bottom and about 3 ft. square, serving as manholes. Workmen entering the chambers wear boots of thin sheet-lead, as a protection against the acid. During the working these openings are closed by wooden lead-covered doors, which are fastened tight up to the leaden wall of the chamber by supports from the chamber framework. The joints between the door and the chamber wall are made tight with putty, generally prepared from pipe-clay and the refuse of rapeseed oil refineries. These holes are seldom or never met with in this country.

40.



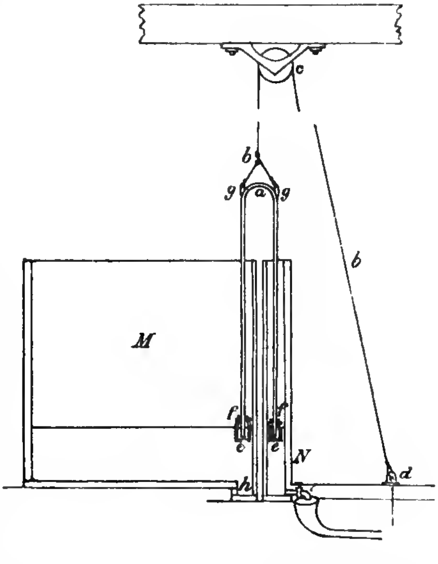
Further, it is necessary to provide a small hole in the side of the first chamber, just opposite the point where the gases enter, with a diameter of about an inch, which is stopped by a stoneware stopper and used as we shall indicate presently. The connection pipes also are provided with holes for watching the process as seen at *l*. When it is not possible to lute the covers with water they must be made secure with putty. Each connection pipe, as well as the chimney K, is provided at its lowest point with a small double bent tube, as seen at *m*, Fig. 37, which is so made that no gas can issue from it, but that the acid which condenses within may escape, drop by drop, and be collected in a vessel for testing; this serving as another guide in the conduct of the process.

Each chamber, as seen at *n*, Fig. 38, has an overflow pipe, so that the acid runs continually from the third to the second chamber, thence to the first, and from it into the reservoir M, so that, however fast it may condense in the chambers, it shall remain at a constant level in them.

The reservoir M, which is a wooden tank lined with sheet lead, serves to show the exact quantity of acid made. In order to do this, it is so arranged that the acid may be led into either of the two reservoirs. When one is full, it is run into the other. They are of exactly similar dimensions, and furnished with a scale and a float, so that it is easy to calculate the volume of acid made daily from the figures indicated. By noting the specific gravity, the exact quantity obtained can be reckoned.

With this arrangement, it is not advisable to draw the acid direct from the reservoir by taps, as through carelessness, or their not fitting tightly, the acid may continually escape in drops, and thus the correct make cannot be ascertained. It is better to draw it off by means of siphons. This is shown in Fig. 41.

41.



The siphon *a*, of bent leaden pipe, hangs from a light iron chain *b*, which runs over the pulley *c*. It can thus be raised or lowered at will, and may be temporarily suspended at any height by fastening the string at *d*. Both legs of the siphon, one inside the reservoir, the other outside, terminate in little leaden vessels *e*, hanging on knobs with which the siphon is furnished at *f*. These are for the purpose of preventing the siphon from running dry when the acid gets so low in the cistern as to be below the siphon mouth. To effect this, however, the ends must be kept at exactly the same level. This is easily managed, as the siphon depends from two points, as shown at *g*. In order that the cistern may be completely emptied, it is given a little well at *h*, into which the vessel *e* can completely enter. To avoid the splashing of the escaping acid, it is not run into the open air but into the lead-lined vessel N, of the same height as the cistern M. This box has a tap at the bottom which regulates the outflow of the acid. During the feeding of the cistern M, the siphon is drawn up above the highest level of the acid. The bottoms of the chambers and of the reservoirs M may be of 7 lb. sheet lead, while, for the sidewalls and the tops of the chambers and for the connection pipes and the smaller parts of the apparatus, 5 or 6 lb. lead will suffice.

The overlapping sheets forming the chamber linings were formerly beaten together and joined with a cement, or fastened by tin solder. Now, however, they are melted together by means of a hydrogen gas flame, without bending the lead edges together. In this way, not only a great saving of time and cost is secured, but it is especially valuable as giving a much more durable seam, for even with tin solder the acid soon found its way through.

The support of the sides and roofs of the chambers is aided by a strong timber framework, and they are erected in the following manner:—On the strong and level plank flooring of the chamber are spread the leaden sheets destined to cover the floor. They are carefully beaten flat with wooden mallets, in such wise that each sheet shall overlap the next about an inch. This is then "burnt" on to the underlying sheet with the hydrogen flame. In order to give the bottom of the chamber the form of a basin in which to hold the acid, each sheet is turned up vertically about nine inches high all round the chamber.

Before proceeding to erect the side lead, the floor is covered with straw overlaid with planks, so that it shall not receive any damage; often, also, the bottom lead is the last to be put in. The timber work is then proceeded with. Four beams, marked *o*, are laid round the upturned edge of each chamber, and serve to keep it in place. The uprights *p* are then morticed into the beams and strutted by the braces *q*. Then the four crowntrees *r* are morticed on to the uprights and struts. Now follows the erection of the sheet lead.

As the burning together of the leaden sheets is much more quickly and easily effected in a horizontal position than in a vertical one, the small sides of the large chamber and all the sides of the small ones are burnt first and afterwards raised in one piece. The long sides of the large chamber must be divided into two or three portions for raising. They are finally connected by vertical seams, and then form one complete sheet. For this purpose a strong wooden platform is made, on which the lead may lie. This is so placed that the edge which corresponds to the lower edge of the side sheet shall be close against the upturned edge of the basin, so that the sheet can be very easily raised into place by pulley blocks from the upper edge. On this platform the sheets may be joined, as on the floor of the chamber. In estimating the height of the sheet, about nine inches in excess is allowed, as it is necessary that a portion be turned over the crowntree *r*, and firmly nailed to it.

As soon as the sheets are joined ready for raising, chalk lines are drawn on them indicating the position of the uprights *p*. On these lines, and about 1 ft. 6 in. apart, are burnt leaden straps about four inches square. Then the top edge of the sheet is bent over the edge of the platform and there fastened, and the whole is then raised into position tight against the framework of the chamber. The straps correspond with the uprights, and are nailed to them. The platform is then removed for further use, as before. When all the side sheets are thus erected, the remaining joints must be "burnt" up. A good upright seam can be made by a workman of sufficient practice, in whose hands the lead will not drop down on application of the flame, but rather adhere to the already-formed portion of the seam.

When the sides are completed, the roof is commenced. For this purpose trestles are brought into the chamber, and on them a platform is constructed. On this platform the leaden sheets forming the top are spread out and lapped two or three inches over the crowntree. They are then burnt into one complete sheet, thus closing the chamber. On this ceiling are burnt a series of straps, running parallel to the short sides of the chambers. Between each double row a beam or joist *s* is laid, whose ends reach the crowntrees *r*, and to which the straps are securely nailed. Thus, these joists support the ceiling. To prevent the joists from sinking, a strong beam *t* is laid athwart their middle, and supported by iron clamps depending from the framework of the timber roof of the works, where such roof is required; but in this country they are seldom or never used, and the joists are sufficiently stout to need no support. The wooden platform, &c., is then removed from the finished chamber.

According to this plan the sides of the chamber remain distinct from the basin-shaped floor, but descend into the acid lying there, so as to shut in the interior atmosphere. It has been noticed that especially this portion of the lead has been rapidly corroded when the acid contained much nitric acid, an eventuality often occurring through careless management. To avoid this, in many works the sides are burnt to the bottom, so that all the acid is shut into the interior. When the process is properly conducted, however, this precaution is not necessary.

The steam required is generated in an ordinary boiler shown at N in Figs. 37 and 38. The lowest pressure should be from 1½ to 2 atmospheres. The boiler is provided with a water gauge, safety valve, and steam gauge, which latter may simply be a U-shaped open glass tube containing mercury. The water inlet is easily regulated through the copper tube *u*, Fig. 37, which, reaching to the roof beams, has more than sufficient height to overcome the pressure of the steam. This pipe, opening out into a funnel at the top, is fed with water from the cistern O. A plug *w*, hanging on the balance *v*, serves to regulate the outflow. When the float *x*, inside the boiler, sinks with the level of the water, the plug is lifted and the water can flow, but the plug is replaced so soon as the said float rises sufficiently.

The steam passes into the chambers by the copper pipe *y*, 2-in. bore. It enters near the gases, and in the same direction. The copper pipe terminates, in each case, just outside the chamber in a tap for regulating the amount of steam admitted, and provided with a gauge for that purpose. The other end of the tap is joined to a short piece of leaden pipe projecting about an inch into the chamber, and burnt to the chamber wall. In many works, the steam is introduced into the connection pipes just at their commencement, so as to assist in mixing the gases and air.

Sometimes also, to economize fuel, the boiler is heated by the flame of the burning sulphur. In this way the heat of the gases in the chamber will be correspondingly diminished however, which may injuriously affect the conduct of the operation, especially in a small works during the winter season. Serious suspension of operations, too, may result from an injury to the boiler, which can easily happen. Therefore, heating the boiler in this manner is only advisable where fuel is excessively dear, or where the climate is so hot that it is beneficial to reduce the temperature of the chamber gases.

It is scarcely necessary to state that the dimensions given above are by no means constant, but that they are variable at pleasure in accordance with the quantity of acid it is desired to make. The larger the works the lighter is the cost of construction in proportion to the make, and the easier the conduct of the operation. Chambers may be found in most parts of England of far greater dimensions than those given above. In working them it is advisable not to have a correspondingly enlarged sulphur kiln, but rather to use two smaller kilns, and to charge them alternately. In this way the quantity of gas in the chambers is maintained at a more constant volume, as the sulphurous gas is less weakened by the periodical influx of air.

The brimstone-burner described above necessitates that the door shall be kept open for some time at each charge; in this way an excess of air is admitted just when the sulphur has burnt off. This is productive of bad results. For this reason many plans have been devised for differently arranged burners in which the evil might be lessened, but they have either not succeeded in accomplishing the desired end, or from possessing some new fault or difficulty have not come into general use.

The essential part of Kuhlmann's burner consists of four cast-iron retorts of the form used in making coal gas. In front are doors for admitting the brimstone, furnished with air-holes, and behind are pipes for the escape of the gases. The gases pass from the retorts first into a large ante-chamber in which they form a uniform mass, and, when sublimation takes place, deposit a soot-like dust of sulphur.

Petrie invented a furnace which altogether does away with the introduction of the sulphur through a door that needs opening. The sulphur is made to enter by a hopper or funnel placed on the top of the furnace. The ascending heat of the sulphur burning below brings down a new supply, so that the feeding is constantly kept up so long as the hopper is duly replenished. In front, the furnace has a perforated door for ventilation, and which is only removed for cleaning out the furnace.

It is not possible, however, by this apparatus to keep the sulphur regularly supplied, and also the brimstone easily becomes sticky from overheating, and does not then flow well. These are decided defects. The only modified form of brimstone burner which has been received with favour by manufacturers is Harrison Blair's furnace. This furnace consists of two distinct compartments, in one of which the sulphur is partly burnt, partly sublimed, while in the other the combustion is completed by a further addition of atmospheric air. In spite of the great heat generated in the furnace the sublimation caused by it is infinitesimal, and this heat offers a decided advantage in that it enables the Glover tower to be used, which is impossible with any other form of brimstone kiln. We shall presently show the great gain effected by the use of the Glover tower.

In Harrison Blair's furnace, the furnace bed is slightly dished, and slopes to within 2 ft. of the door, where a raised platform is made, on which the residue, scraped off the floor once every twenty-four hours, may lie exposed to the heat until the next day's residue is drawn up in a similar manner. The door is a loose iron plate in an iron frame, slightly inclined to make a tight joint, and easily removable; in it are drilled a number of holes for the admission of air, which can be closed at will by a sheet-iron slide. The brimstone is introduced through a hopper, from which an iron pipe 7 in. in diameter descends to within 6 in. of the floor of the furnace, and is protected by another pipe of larger diameter. A fire-clay damper regulates the passage of the gases from the first part of the kiln to the second part, and by opening or closing this damper a larger or smaller quantity of brimstone may be burned in a given time—within certain limits, of course.

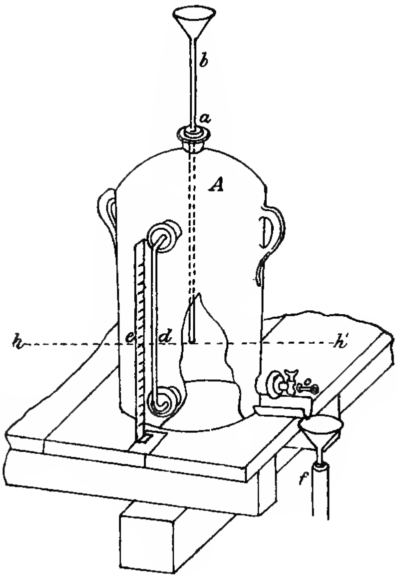
The sulphurous acid and sulphur vapours passing to the combustion oven, are met by a current of air, admitted through an aperture, which is provided with a damper 8 in. by 3 in. for regulating the admission of the exact quantity necessary for the perfect combustion. This is ascertained by taking out the small stopper; the admitted air should produce no flame. The roof of the combustion oven is of fire lumps supported on dwarf walls, and forming at the same time the floor of the nitre oven. The gases rise into the nitre oven and pass over the nitre pots. These nitre pots are renewed every two hours in alternate sets, each set remaining six hours in the oven. Iron doors corresponding with each compartment provide for their removal. The gases now mixed with those arising from the decomposition of the nitre, pass under a cast-iron dome, for the purpose of being deprived of a portion of their heat, and thence by a cast-iron chimney 24 ft. in height, to a small cooling chamber, 6 ft. wide, 18 in. high, and 18 ft. long, the roof and floor of which are covered with water, which communicates with the sulphuric acid chamber. These two last-named portions of the kiln, as well as the cooling chamber, may be dispensed with, without in any way interfering with the working of the kiln, and in fact when used in conjunction with a Glover tower, the gases are taken direct from the combustion oven into the tower.

In a furnace of the dimensions 2 ft. by 4½ ft., 26 tons of brimstone have, it is said, been satisfactorily burnt in a week, and the same furnace may be made to consume only 5 or 6 tons weekly by admitting less air to feed the combustion. It is also said to have been found that a much larger quantity of brimstone may be safely burnt in the same chamber-space than is the case with ordinary burners.

When the necessary nitric acid gas is not derived from the decomposition of nitre with sulphuric acid in the sulphur kilns in a gaseous form, but is instead introduced into the chambers as a liquid, much more plant is necessary.

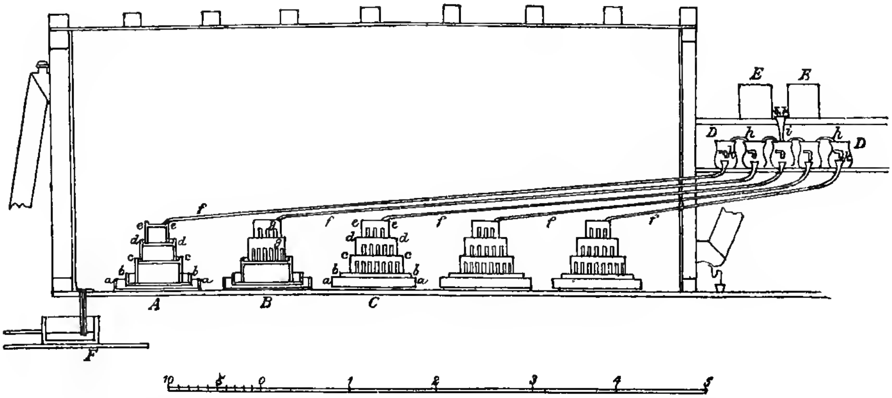
Ready-made nitric acid cannot well be admitted to the chambers otherwise than in a tiny stream, and it is imperative that the flow shall be kept absolutely constant and regular, so that the acid may be utilized as constantly as it is required. This object is most easily achieved by a Marriotte vessel, which gives a perfectly regular outflow, and is in use in most works. Fig. 42 shows such a vessel. The stoneware vessel A, which holds the nitric acid, is closed by a perforated indiarubber cork *a*, in which the glass tube *b* is fastened, so that no air can pass through the joint. This pipe forms the only way by which air can be brought into the vessel A to fill up the space left by the acid flowing out at the tap *c*. The pressure of the atmosphere above the line *h h'*, to which the glass tube reaches, regulates the outflow, and this pressure remains constant so long as the acid does not sink below that level. In order to observe the rate of flow, recourse is had to the glass register *d*, which is tightly screwed on to the vessel, and may be read off by the adjacent scale *e*. The filling of the vessel is effected through the open glass tube *b*, which is furnished with a funnel at the top for this purpose. It is necessary first to draw out the cork *a* somewhat, in order to admit of the escape of the displaced air; this may be avoided, however, if a second smaller tube be inserted into the cork, which may be closed by a pinch-cock, and only opened when the vessel is about to be filled. The escaping acid flows through glass or stoneware tubes, whose commencement is seen at *f*, into one of the leaden chambers.

42.



In many works the flow of nitric acid is regulated by two cisterns, such as are shown at E, Fig. 43. These are filled alternately once every twelve hours with the requisite supply, so that each is filled once per twenty-four hours. The flow of acid to the chambers is conducted from both the cisterns into the same vessel; when the one has delivered half its acid the other is become quite empty and is filled anew. In this way the changes of pressure are better compensated, and a more regular flow of acid is obtained than by one single open cistern, but it is unnecessary to say that the same regularity cannot be secured as by the Marriotte vessel.

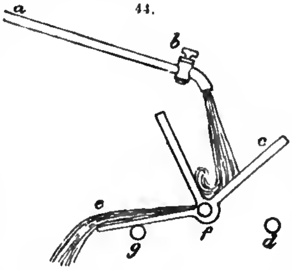
43.



The nitric acid introduced into the chamber must be spread over a great surface, so that the sulphurous acid gas may come as much as possible into contact with it. For this purpose a cascade apparatus is used, consisting of cylindrical vessels of pipe-clay, arranged as shown in the figure. At A is seen a vertical section of the whole system, B gives only the under part in section and a view of the upper part, C shows a view of the whole. Each system is composed of four pipe-clay vessels, one inside another. The lowest vessel *b* is about 2 ft. 6 in. in diameter, and stands in the leaden saucer *a*, in which is a little powdered sulphur to assist in securing the perfect level of the vessel. The upper vessels decrease in size about 8 in. each, thus producing cascades over which the acid tumbles. The lowest vessel *b* is a simple saucer, each of the other three, on the other hand, is furnished with a bottom about ⅛ to ⅜ in. from the edge, and divided into two parts. Round about the under part are holes *g*, which, as shown at B, begin under the bottom and reach under the edge of the next lower vessel. Thus the nitric acid as well as the chamber gases find free circulation inside the apparatus, so that the greatest possible reaction may take place on the whole surface of the acid. The nitric acid is conveyed to these apparatus by the pipes *f*, which are also made of stoneware, and are introduced through the chamber wall from the jar D. These last are fed by the funnel *i* over the centre jar, either from the cisterns E, or from the Marriotte vessel. The jars communicate with each other by the side siphons *h*, which maintain the acid at a constant level. Each jar supplies one cascade inside the chamber with acid by the taps *k*. These taps are placed at such a height as to prevent the level becoming so lowered as to unset the siphons.

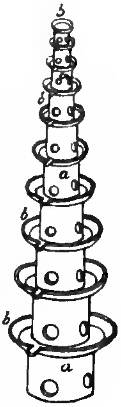
The regular delivery of acid in the cascades can also be achieved by a pipe-clay rocking trough, Fig. 44. The acid is run from the cistern by a pipe *a*, fitted with a tap *b*, into the half of the trough marked *c*. As soon as this is full, the trough falls over in consequence of the change of the centre of gravity (as it turns on its axis at *f*) until the stop *d* holds it. Thus it empties itself. At the same moment the half *e* is raised and brought just under the mouth of the pipe *a*, and is thus filled with acid in turn. Then the trough falls over until stopped by the knob *g*, and the acid flows out on the opposite side. The acid delivered thus intermittently from the trough is caught in vessels standing underneath the flow pipes, and carried through corresponding cascade apparatus. The pipes must also be of equal diameter, and of such small bore that the volume of nitric acid which flows at each fall of the trough is sufficient to completely fill them all, so that each may deliver the same proportion of the acid.

44.



This arrangement is superior to the last in that the jars are done away with, and only the cistern tap needs regulating. On the other hand, it has the disadvantage that it would not be possible to notice the accidental stoppage of any of the tubes, and that the flow is not made continuous but intermittent. Also the tumbling of the trough may become interfered with by an accumulation of dirt.

45.



The above-described cascades are now altered to a simpler form in many works, with the advantage that the jars are dispensed with and the acid admitted to one series only.

Fig. 45 shows this arrangement. It consists of a pile of cylindrical tubes *a*, and flat round plates or saucers *b*, all of stoneware. The diameter of these pieces constantly decreases as the column rises, so that the nitric acid flowing into the uppermost saucer overflows into the second, then into the third, and so on. The lowest saucer is about 2 ft. 6 in. diameter, and about 2½ in. deep, and the highest is about 5½ in. wide, and 1½ in. deep. The cylinders are provided with openings through which the nitric acid and the chamber gas can freely circulate.

This disposition possesses the following defects:—

1. If the glass or stoneware pipe, through which the acid is introduced to the chamber from without, should break during working operations, and thus render it necessary to insert another, it is very difficult to make sure that the new one shall exactly reach the uppermost saucer.

2. It may easily happen that in such a case the unstable pile may be disarranged or even altogether upset.

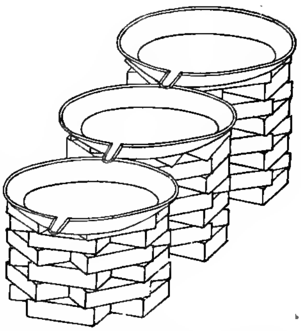
3. The topmost saucers are so small that in a very short time they become filled with mud, principally composed of solid matters introduced with the kiln gases, and this is especially the case when using pyrites.

On this account it has become more general to use stoneware or pipe-clay saucers all of one size, viz., about 2 ft. 6 in. diameter, and 2½ in. deep. Twelve of these are placed terrace-like, one behind another, in one of the chambers, in such manner that the lip of each higher one reaches over the one immediately below so as to deliver the acid into it. The saucers are arranged on loosely stacked piles of fire-bricks, as shown in Fig. 46.

Whilst the nitric acid is slowly passing along the apparatus, it is acted upon by the sulphurous acid gas present and reduced to hyponitric, or even nitrous acid, which enters into the volume of the gases; the sulphuric acid then gradually formed in the upper part of the chamber atmosphere finally reaches the floor of the chamber free from nitric acid.

Formerly it was common to devote two small chambers, called drums, to the nitric acid. These were 22 ft. 9 in. long, 9 ft. 9 in. wide, and 11 ft. 6 in. high, or were cylindrical and about $11\frac{1}{2}$ to 12 ft. diameter, and were placed between the sulphur-burner and the large chamber. In the second of these the before-mentioned apparatus was placed. They stood at a somewhat higher level than the first small chamber into which the sulphuric acid flowed as fast as it formed, and whose only purpose was to give the sulphurous acid full opportunity to act upon it and free it from nitrogen compounds. Into this chamber only so much steam was admitted as was necessary to prevent the formation of chamber crystals or to decompose such crystals when formed. The acid collected in this first small chamber flowed into the large chamber.

46.



With properly conducted working, the first "drum" is unnecessary, for it is quite easy to produce sulphuric acid free from nitrogen compounds in the same chamber where the nitric acid is decomposed, if only the sulphurous acid is allowed time enough, and the amount of steam so regulated that the acid produced contains more than 4 equivalents of water to 1 equivalent of acid. More recently, these small chambers for the decomposition of the nitric acid have been done away with in many works, and the process allowed to go on in the first large working chamber. It must be remarked, however, that in this arrangement it is impossible to get a perfect combination of the nitric acid with the sulphurous acid, which is a great defect.

We have already shown the part played theoretically by the nitric acid in the manufacture, and have now described the construction and general arrangement of the apparatus employed in its introduction to the working process. There now remain to be considered the conditions necessary to ensure the most perfect results.

Though the conduct of the process of the manufacture of sulphuric acid looks remarkably simple, it depends upon so many chemical and physical conditions that it is often difficult when things go wrong to find out the true cause of the mischief.

The principal points needing attention are:—

The temperature.

The draught and inlet of air.

The steam.

The way in which the gases are taken through the chambers.

Temperature.—The temperature exercises an important influence on the conduct of the process and acts differently in the various parts of the apparatus.

In the sulphur-burner too high a temperature will volatilize the sulphur, and form "flowers of sulphur," which collect in the first chamber. To avoid this evil, the burner is built in the form of a high vault, with thin walls, and of larger dimensions than necessary, and in many works the roof and the front and back walls are made of iron plates. The iron bed-plate should be at least four square feet for every one cwt. of brimstone burnt per twenty-four hours, and often twice or thrice that size is given to it. The greatest degree of heat is reached immediately before the insertion of a new charge, and thus it may easily occur that a part of the new charge be volatilized. This may be prevented by damping the new charge beforehand. While it is necessary to take care that the temperature of the bed-plate does not rise too high, it is equally important to watch that other parts of the apparatus do not become too cool.

The specific gravity of the gases passing up the vertical shaft on their way to the chambers will be lessened by the heat, and in consequence the draught will be increased by the influx of air.

The temperature in the chambers assists and hastens the formation of sulphuric acid, so long as it is not allowed to exceed about 60° C.; in a much higher temperature the nitrogen compounds may be reduced to nitrous oxide, or even to nitrogen itself. Further, the gases in the first chamber must be kept at such a temperature (according to experience, about 40–50° C.) that the water not yet forming hydrate ($4HOSO_3$) may be maintained as steam, as its condensation weakens the sulphuric acid formed, and the nitric acid gas condensed at the same time is no longer available in the process.

In confirmation of these remarks, it has been found that it takes longer to get chambers into working order when commencing operations in cold weather than when a start is made in warm weather, and that when the chambers have been subjected to cooling, either from atmospheric causes or from irregularities in the working, the acid produced at such a time is weaker than usual, and contains more nitric acid. In cold climates, too, the relative consumption of nitre is greater in winter than in summer. Hence it follows also that in very small works it becomes necessary to cover in the connection pipes between the kilns and the chambers, and often to place the chambers themselves in a closed building, so as to protect them from the ill effects of the weather. In warm climates only can the chambers safely be left exposed. In small works, too, it is imperative that the moisture admitted to the chambers be really steam, and not mere water as is sometimes the case.

Draught and Supply of Air.—The force of draught by which air is drawn into the sulphur-burner, and by which the kiln gases are drawn through the chamber system and out again (or what remains of them) into the atmosphere, has as much to do with the process as the temperature. This draught arises from several causes, but principally from the stream of hot gases in the channel connecting the kilns and the chambers. As the specific gravity of sulphurous acid is more than double that of air, it may be imagined that the kiln gases are not lighter than air. But it may be well to know what is their real specific weight. As a basis for the calculation we must take the following figures.

At a temperature of 0° C., and a barometrical pressure of 760 mme.

1 litre of dry air will weigh	1·2932 grm.
1 „ oxygen „	1·4298 „
1 „ nitrogen „	1·2562 „
1 „ sulphurous acid „	2·8731 „
1 „ steam „	·804313 „

Now one volume of oxygen forms, with the amount of sulphur burnt in it, one volume of sulphurous acid, which requires a further half-volume of oxygen to form sulphuric acid. Then for every 14 volumes of sulphurous acid containing 14 volumes of oxygen, there are required an additional 7 volumes of oxygen to form sulphuric acid. This oxygen, however, is introduced to the sulphur-burner as air containing 21 parts of oxygen and 79 parts of nitrogen per cent. Then with each $14 + 7 = 21$ volumes of oxygen there are also 79 volumes of nitrogen entering into the kilns, and thus the gas therein produced will consist, theoretically, of

14 volumes sulphurous acid
7 „ oxygen
79 „ nitrogen
———
100

Experience teaches that to get good working results an excess of oxygen is needful, which may amount to about 5 per cent.

If we represent the unknown volume of this excess of oxygen necessary beyond the 100 volumes of gas mixture by x, then the amount of nitrogen added will be $\frac{79}{21}x$. This must be added to the 79 volumes of nitrogen which are introduced by the 21 volumes of oxygen necessary to convert 14 volumes of sulphur into sulphuric acid. Therefore the united volume of nitrogen and oxygen required to be admitted to the kilns for every 14 volumes of sulphurous acid so as to have an excess of oxygen, will be :—$79 + \frac{79}{21}x + x = 79 + \frac{100}{21}x$.

As x represents 5 per cent., or $\frac{1}{20}$ of this volume, we have then :—

$$x = \frac{1}{20}\left(79 + \frac{100}{21}x\right) = \frac{79}{20} + \frac{5}{21}x.$$

Hence follows, $x - \frac{5}{21}x$, or, $\frac{16}{21}x = \frac{79}{20}$, then $x = \frac{79 \cdot 21}{20 \cdot 16} = 5 \cdot 18$ volume. That is to say, besides the before-mentioned theoretical volume of gases, there is an excess of 5·18 volumes of oxygen needed, together with its equivalent of nitrogen, which will be $5 \cdot 18 \,.\, \frac{79}{21} = 19 \cdot 50$ volumes of nitrogen.

The volume of gases formed in the burner and conducted thence into the chambers will be then composed as follows:—

For every 14·00 vols. sulphurous acid—
$7 + 5 \cdot 18 = 12 \cdot 18$ „ oxygen, and
$79 + 19 \cdot 50 = 98 \cdot 50$ „ nitrogen
———
Total .. .. .. 124·68 volumes.

Accordingly we may reckon that 1 litre of the gas has the following composition :—

0·1123 sulphurous acid
0·0977 oxygen
0·7900 nitrogen
———
Total .. .. .. 1·0000 litre.

In conformity with the previously given table of the weights of the various gases at 0° C. and 760 mme. pressure, we have in one litre of the gas:—

$$0\cdot1123\,;\ 2\cdot8731 + 0\cdot0977\,;\ 1\cdot4298 + 0\cdot7900\,;\ 1\cdot2562 = 1\cdot4547 \text{ gramme.}$$

The volume of the gases increases, however, with the rise of temperature in the ratio of about $\frac{1}{273}$ of the volume for every 1° C. Therefore a litre of gas at 0° C. becomes at $t°$ C. (the pressure remaining the same) $1 + \frac{t}{273} = \frac{273 + t}{273}$ litre.

If we take the temperature of the gases in the vertical shaft at 100° C., which is certainly too low, we have $\frac{273 + 100}{273} = 1\cdot3663$ litre from each litre at 0° C. and under the same pressure, which will weigh, according to the above calculation, $\frac{1\cdot4547}{1\cdot3663} = 1\cdot0647$ gramme.

For comparison we will now take the weight of one litre of air at 760 mme. pressure and a temperature of 20° C. One litre of air at 0° C. and 760 mme. weighs 1·2932 grm., and will measure at the same pressure, and a temperature of 20° C., $\frac{273 + 20}{273} = 1\cdot0733$ litres. Hence 1 litre of air at 20° C. and 760 mme. pressure gives a weight of $\frac{1\cdot2932}{1\cdot0733} = 1\cdot2049$ gramme.

Atmospheric air is therefore much heavier than the hot gases in the kiln. Even if we take the temperature of the air at an unusually high figure, for example, 35° C. we still find that the kiln gases are much lighter than the air. The weight of the latter may be taken as $\frac{273 + 35}{273} = 1\cdot1282$ for 1 litre, or $\frac{1\cdot2932}{1\cdot1282}$ gramme.

In this calculation it is not necessary to take into consideration the varying proportion of moisture contained in the atmosphere, because, by its great expansion in the hot kiln, it can only increase the difference between the weight of the kiln gases and that of the atmospheric air.

In consequence of the fact that the gases in the vertical channel are lighter than the air outside, this air will rush into the kilns at a speed corresponding with the pressure exercised from below. This speed or draught increases in proportion to the height of the vertical shaft or channel, and it is thus advantageous to allow the latter to embouch into the chamber at as great a height as possible. As a superabundant draught is thus secured, the amount of air admitted to the kiln is regulated by suitable ventilators according to need.

A second cause producing a draught is the formation of the sulphuric acid itself, for the space but lately occupied by the gases forming the acid cannot remain a vacuum, but will be immediately refilled with new gases. The condensation of the sulphuric acid takes place during the circulation of the gases.

A third promoter of the draught is the chimney or stack-pipe, through which the uncondensed gases from the last chamber escape into the air. As these gases contain the nitrogen collected in the chamber, and only 5 per cent. by volume of the heavy oxygen, and as these are saturated with steam, which lessens their specific gravity, and are generally much warmer and can, at any rate, never be colder than the atmospheric air, they are necessarily much lighter than the latter.

If none of the processes hereafter to be described be employed for recovering the nitric acid, then that gas will form an important constituent of the escaping volume, besides a small proportion of sulphurous acid, by which the specific gravity of the mass will be somewhat increased. Their influence is, however, exceedingly slight, and may be altogether disregarded.

A chimney or stack-pipe, as shown in Fig. 38 (K), with a height of 50 ft., will give a more than sufficient draught. In cold regions it is advisable to wrap non-conducting materials about that portion of the pipe which reaches above the roof of the building, so as to check, as much as possible, the evil effect of the cold. In some works the above-described chimney is replaced by putting the chamber-flue into connection with the main chimney-stalk of the works. But many manufacturers prefer to have a distinct flue-pipe opening into the free atmosphere, and furnished at the top with an open-ended cylinder for protection against the influence of the winds, because in this way it is much easier to regulate and measure the draught than is the case when the chamber exit leads into the common stalk. At one time the gases will rush through the chamber system far too fast, and thus create an enormous waste. Besides, the draught is subject to much greater vacillation in the common chimney than in a special pipe, because the temperature in a chimney can never be maintained at one degree. When, for any reason, the draught, which means the amount of air admitted, is not sufficient, it may be increased by opening the dampers which regulate the diameter of the passages through which the air has to pass.

We have already said that it does not suffice to admit the exact quantity of air necessary for the conversion of the sulphur into sulphuric acid, but that to get good working results there should be an excess of oxygen amounting to 5 per cent. beyond that theoretically needed. We have also already seen that every 14 parts of sulphurous acid containing 14 volumes of oxygen, and needing a further 7 volumes of oxygen for conversion into sulphuric acid, besides the 5·18 volumes of oxygen in excess, will need,

$$14 + 7 + 5{\cdot}18 + = 21 \quad 5{\cdot}18 = 26{\cdot}18 \text{ volumes O}$$
$$79 + 19{\cdot}50 = 98{\cdot}50 \quad \text{,,} \quad \text{N}$$

Or together 100 + 24·68 = 124·68 volumes of atmospheric air carried into the chamber system. Hence for each volume of sulphurous acid $\frac{124{\cdot}67}{14} - 8{\cdot}906$ volumes of air are necessary.

Now 1 litre of sulphurous acid at a temperature of 0° C., and a pressure of 760 mme., weighs, as we have seen, 2·8731 grammes, and the sulphurous acid stands as,

1 equiv. sulphur .. = 16
2 ,, oxygen.. .. = 16

1 equiv. sulphurous acid = 32, therefore 1 litre of sulphurous acid at 0° C., and 760 mme. =

$$\frac{2{\cdot}8731}{2} = 1{\cdot}43655 \text{ grammes sulphur}$$

and 1·43655 ,, oxygen

Total 2·87310 grammes.

There are consequently for each 1·43655 grammes of sulphur used 8·906 litres of air required at 0° C. and 760 mme. Hence we find from the proportion, 1·43655 : 1000 = 8·906 : x, that for each 1000 grammes, or 1 kilogramme of sulphur, $\frac{8906}{1{\cdot}43655} = 6199$ litres or 6·199 cubic metres of air at 0° C. and 760 mme. pressure, must be introduced into the sulphur-burner, which = 6199 ; 1·2932 = 8017 grammes, or 8·017 kilos.

In order to calculate the volume of air introduced at other temperatures and pressures upon the bases given above, we must remember that 1 volume of the gas at 0° C. gives at t° C. (the pressure remaining the same) $\frac{273 + t}{273}$ volume, and makes at V volume $\frac{(273 + t)\text{V}}{273}$ volume.

Further, it is known that the volumes of such gases stand in inverse proportion to the pressure; accordingly the pressure of b mme. on the volume $\frac{(273 + t)\text{V}}{273}$ gives the volume $\frac{(273 + t)\text{V} ; 760}{273 ; b}$, according to the proportion $b : 760 = \frac{(273 + t)\text{V}}{273} : x$, whence it follows that $x = \frac{(273 + t)\text{V} ; 760}{273 ; b}$.

With the aid of the above formula it is easy to reckon the volume assumed by any volume of air at 0° C. and 760 mme., under any variation of temperature and pressure. It shows, for example, that the 6199 litres of air at 0° C. and 760 mme. necessary for 1 kilo. of sulphur, have a volume at 20° C. of $\frac{(273 + 20)\,6199 ; 760}{273 ; 760} = \frac{293 ; 6199}{273} = 6654$ litres.

The above proportions refer, however, to dry air, whilst the atmosphere is never free from moisture, which has a distinct influence upon the volume. In order to arrive at the correct figure, we must also take this moisture into consideration.

When a gas under b pressure is saturated with water, its tension is lessened by that of the moisture, or $b - c$, when the tension of the moisture is c, so that now the mixture of gas and moisture has the same tension which the gas alone had formerly. As the moisture reduces the gas the latter changes its volume in the inverse proportion of the tension. Then, from the volume $\frac{(273 + t)\text{V} ; 760}{273 ; b}$, when V is the original volume of the dry gas at 0° C. and 760 mme., we derive the new volume $\text{V}' = \frac{(273 + t)\text{V} ; 760}{273\,(b - c)}$, through the saturation with moisture.

Then from the formula wherein the increase of temperature and moisture makes the tension 17·391 mme., we get $\frac{(273 + 20)\,6199 ; 760}{273\,(760 - 17{\cdot}391)} = \frac{293 ; 6199 ; 760}{273 ; 742{\cdot}609} = 6809$ litres.

The foregoing calculations show then that for each kilogramme of clean sulphur burnt for the manufacture of sulphuric acid, the admission of the following air is necessary :—

6199 litres dry air at 0° C. and 760 mme., or
6199 + 454 = 6653 ,, ,, 20° C. ,, ,, or
6653 + 156 = 6809 ,, air saturated with moisture at 20° C. and 760 mme. pressure.

The last 156 litres increase allowed for the moisture of the air is greater than is really ordinarily necessary, as the atmosphere is often not saturated with moisture. But as this increase is only 2·34 per cent. of the volume of dry air, whilst about 24·68 per cent. (or more than ten times as much) of excess air is introduced beyond the theoretical requirements, the changes in the moisture of the air and the differences in its volume resulting therefrom, have little effect upon the practical working. No further discussion therefore is necessary concerning them.

From the foregoing observations it is self-evident that the volume of air required on the average for a certain consumption of sulphur will depend also upon the altitude of the works, which affects the B pressure. For example, the quantity of air will occupy $5\frac{1}{2}$ per cent. greater space at Munich than at Marseilles.

The admission of the minimum of air necessary is therefore easily managed. The fulfilment of this condition alone, however, is not enough to ensure good working, for harm may be done by the introduction of more than the above-indicated excess as well as by the want of air. The evils arising from an excess of air are not so great as those caused by a want of it, but still they are sufficiently important to warrant every care being taken to avoid them. Primarily, an excess of air does harm by reducing the heat of the gases, and thus interfering with the process. Then it fills a part of the chamber space unnecessarily and renders it useless. Finally, it acts injuriously on the formation of the acid by thinning the gases and weakening the energy of their chemical action. The regulation of the draught is one of the greatest difficulties in a sulphuric acid works, because of the daily changes in the condition of the atmosphere. Hence it is of primary importance for the manufacturer to take note of these changes, and immediately to lessen their effect on the process by opening or closing the dampers in the connection pipes, &c., and by regulating the doors and ventilators in the kilns.

Though the admission of air will be reduced by shutting the outlet damper as well as by closing the kiln ventilators, still the two things are not quite synonymous. By the first means the pressure inside the chamber will be increased for the moment, by the last it will be diminished. If the kiln ventilators be shut too much, the chambers will draw in air from the other end, unless the dampers there be correspondingly closed.

The sectional area of the exit flue must always be in direct proportion to the size of the ventilators which admit air. In general the former is made equal to $\frac{2}{3}$ of the latter. No rule can possibly be given respecting the allowances to be made for the changes of the atmosphere, their degree can only be ascertained by actual experience with the works. In all well-administrated factories the escaping oxygen is measured as we shall indicate further on.

The Steam.—The amount of steam admitted to the chambers must be regulated quite as carefully as the air. We have already mentioned that in very hot countries it is not imperative that all the water introduced should be as steam in order to keep up the heat. Experience teaches us that the best results are obtained when the amount of steam injected is just sufficient, or but a trifle more than sufficient, to form $4\,HO\,SO_3$ or acid of 1·55 sp. gr. (110° Tw.), at which strength chamber crystals do not form, and which absorbs far less nitric acid than does acid containing more water. To form the tetrahydrate 4 equivs. of water are necessary for every 1 equiv. of sulphur, forming 1 equiv. of sulphuric acid, or for 16 parts of sulphur, $4 \times 9 = 36$ parts of water, as the atomic weight of sulphur and water are 16 and 9 respectively.

From this it may be estimated that for each kilogramme of sulphur 2·25 kilos. steam must be introduced to the chambers. It is of the greatest importance for the success of the process that the steam should only condense in the mass of the gases existing in the chambers in order to form the tetrahydrate, for by the condensation of great quantities of simple water an unnecessary thinning or weakening of the acid is caused, and part of the nitrogen compounds withdrawn from action. Hence arises the question, how much water can exist in the chamber gases as steam? This can be ascertained by the following calculation.

On a previous page we have shown that from the volume V of a gas at 0° C. and 760 mme. pressure, when saturated with water b mme. and at temp. t C. arose the volume $V' = \frac{(273 + t)\,V\,;\,760}{273\,(b - e)}$. We have also seen that for each kilo. of sulphur burnt there are required 6199 litres of air at 0° C. and 760 mme. pressure, the volume of which will not be altered by the formation of sulphurous acid. On saturation with moisture at the same pressure and at a temperature of 50° C., which may be taken as the ordinary temperature of the gases entering the first chamber, these 6199 litres of gas with a difference of pressure of 92 mme. will give the volume $\frac{(273 + 50)\,6199\,;\,760}{273\,(760 - 92)} = 8345$ litres of gas with a tension of 668 mme. Now 1 litre of steam at 0° C. and 760 mme. weighs 0·804343 grms., and gives, according to the formula $\frac{(273 + t)\,V\,;\,760}{273\,;\,b}$ at 50° C. and 92 mme. pressure, a volume of

$$\frac{(273 + 50)\,760}{273\,;\,92} = 9{\cdot}7739 \text{ litres.}$$

According to the proportion 9 7739 : 0·804343 = 8345 : x, we get

$$x = \frac{0\cdot804343;\ 8345}{9\cdot7739} = 686\cdot8 \text{ grm.}$$

Therefore the steam needed for 1 kilo. of sulphur, yielding 8345 litres of chamber gases, which steam they at 50° C. and 760 mm. can take up, is 686·8 grm. or ·06868 kilo.; while according to our former calculation altogether 2·250 kilos. of steam are necessary for this quantity of sulphur. From this it might be thought that for every kilo. of sulphur only $\frac{686\cdot8}{2250}$ grm. of steam, or about 30·5 per cent. of the necessary quantity, should be introduced at the commencement of the process. This conclusion would, however, be erroneous, because the excess of steam beyond the saturation point does not immediately condense in drops, but is conducted in great part through the chamber system in the form of mist, in which state it probably assists in the formation of the acid. The amount of steam which spreads through the chambers in this state is not known. In the figures of works which we have given, the greatest part of the steam is introduced at a single spot near the entrance of the gases into the large chamber. In many works on the other hand there are several steam pipes leading to the large chamber. Occasionally they are not placed in the most advantageous spots, but only a little above the bottom of the chamber, and without taking into consideration the direction in which the gases are passing. The influx of the steam should always be regulated in accordance with the directions pursued by the gases.

In those works where the nitrogen compounds leaving the chamber system, are not recovered in the Gay-Lussac apparatus, hereafter to be described, the steam is introduced generally into the individual chambers in such proportions that the last small chamber receives considerably more than is necessary for the formation of tetrahydrate, the acid being there produced at 32° Tw., and in the last chamber but one at 52° Tw. When working in this manner the steam that would be necessary for the formation of the acid in the large chamber must be reduced in proportion to the amount replaced by the superfluous water contained in the acid flowing in from the small chambers. The object of this mode of procedure is to decompose the nitrous or hyponitric acid obtained from the small chambers, and to form the greatest possible amount of nitric acid, which is again brought into use by the action of the sulphurous acid in the large chamber. It is by no means claimed that a great saving is effected by this plan; it possesses rather a great defect, to wit, that the weak acid containing nitrogen compounds attacks the lead very energetically. Hence the strength of the acid in the last chamber should never be allowed to get below 32° Tw.

Taking all things into consideration, it is probably more profitable so to distribute the steam among the chambers as to produce in each of them an acid containing not more, or very little more, water than the tetrahydrate.

The introduction of the steam is far easier to regulate than the amount of air admitted, especially when the chambers are worked with a slow draught. When once the steam has been raised to the proper pressure, and the taps have been carefully adjusted, it is only necessary to keep the head of steam at a constant point. Much greater disturbances of the regularity of the process are likely to arise from an excess of steam than from a lack of it, because in the former case the gases oxidize a large quantity of the nitrous and hyponitric acids, which condense as nitric acid. This may become so serious as to cause stoppage of the works.

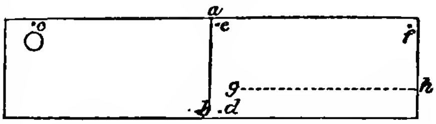
Want of steam, which acts injuriously by permitting the formation of chamber crystals, may continue for a long time without causing an actual interruption of the process, because they will be decomposed, and their nitrogen compounds recovered for use so long as there is acid on the floor of the chamber. The want of steam may continue until the sulphuric acid has become so strong that it will no longer effect their decomposition.

The Direction which the Gases follow through the Chambers.—It is evident that upon the manner in which the chambers are arranged will greatly depend the passage and distribution of the gases through the chamber system, and that any tendency to check or hinder their flow must be guarded against. The gases rising through the substantially built flue from the kilns enter the chambers in a heated condition and gradually cool during their passage through them until they escape into the atmosphere at about its own temperature. As the gases become cooler according to the time they have remained in the chambers, one method of estimating the rate at which they are passing through presents itself in the form of temperature observations at regular intervals. Observations of the temperature in the first chamber (D) of the series already described showed, at a point immediately under the ceiling at the end where the gases enter from the kilns, 53° (127° F.), and at the opposite end, where they leave to enter the second chamber, 49° (122° F.). In the horizontal layer of gas at about 6 ft. above the bottom of the chamber an even temperature of 47° (116° F.), prevailed throughout the whole length, while at a level of about 4 ft. 6 in. a constant temperature of about 45½° (114° F.) was noticed.

According to these observations, then, the moment that the gases enter the chamber they spread along under the ceiling and afterwards sink evenly over the whole expanse. We may therefore picture to ourselves the contents of the chambers as being so many horizontal layers of gas sinking slowly as their temperature falls, and being constantly replaced by new supplies.

Following out this line of reasoning, a chamber was divided, as shown in Fig. 47, by a vertical partition *a b*, rising from about 18 in. from the floor quite up to the ceiling. In the two compartments thus formed the following temperatures were observed. Under the ceiling of the first half, and just over the inlet pipe *c*, the gases had a temperature of 60° (140° F.), and at about 18 in. above the floor, and near the partition *b*, they were 52½° (126° F.). At the same height in the second part, and 18 in. from the partition, or say at *d*, they were only at 50° (122° F.), while at the top of this half, close to the partition, say at *e*, they reached 51½° (125° F.); but at the opposite end, at *f*, only 48° (118° F.). In the level 5 ft. above the bottom, shown by the dotted line *g h*, at more than 5 ft. from the partition, a constant temperature of 46½° (115½° F.) was found.

47.



From the foregoing we must deduce the fact that as soon as the gases which have descended to the floor of the first part have passed under the partition into the second part, they ascend alongside of the partition directly to the ceiling, then spread themselves anew along the under surface of the ceiling, and thence descend regularly, so that in the neighbourhood of the partition there are two currents, one ascending, the other descending. The nature of gaseous bodies does not admit of the two streams being sharply divided, but where they impinge on each other they doubtless commingle to some extent, which is also shown by the fact that at the point *d*, 18 in. from the partition, a medium temperature of 50° (122° F.) was observed.

It is evident, then, that the gases must be introduced just under the ceiling of the chamber, and they must escape at a point as near the bottom as is convenient. When the first condition is neglected, and the gases are admitted near the bottom, a great loss of draught is caused by the reduction of the height of the vertical kiln flue, and consequently a waste is incurred, because the gases are so slow in passing through the chamber system. When the gases from the first chamber are not drawn out below, but at the top, a very great loss is unavoidable. With such an arrangement the gases in the first chamber do not sink regularly, but a great part of them will stream just under the ceiling into the connection pipe and immediately into the second chamber, whilst in that part of the first chamber space lying below the exit, stagnation takes place, as it becomes more and more filled with nitrogen. An opportunity of observing how great this loss might actually be in practice was presented in a works in Tuscany, wherein the connection pipe left the first chamber near the ceiling and took the gases into the top of the second chamber. The working results obtained for a long time were so unusually bad as to amount to only 150 parts of monohydrated acid from every 100 parts of sulphur burnt during the period that the connections were left in this way; yet the moment that a change was made in this respect, and the gases were withdrawn from near the bottom of the first chamber and admitted near the top of the second, the product was increased to 285 parts per 100.

It is therefore unnecessary to say that the lead-saving plan adopted by some manufacturers, in which lead curtains were suspended reaching alternately to the bottom and to the top of the large chamber, was built upon false principles. We cannot, however, recommend the arrangement of curtains in any disposition, on account of the rapid corrosion to which they are subjected.

It is found more profitable in practice not to attempt to produce all the acid in one chamber, but rather to be content with allowing the majority to condense in a first chamber, and to convey the gases from the first chamber before they have become exhausted into a second chamber, and from this into a third, both of much smaller dimensions than the first, because they have to receive a much less volume of gas. With such chambers, also, the gases should always be allowed to enter above and escape below, and this is still more necessary when, as is usual, fresh steam is admitted at each step, whereby their temperature is increased and their density diminished, so that during their stay in the small chambers they undergo a new reduction in temperature and increase in density.

The above-described manner of conducting the gases through the chambers is based on the increase of their density through cooling, and which is modified in many ways by the condensation of parts of the gas and of the steam. It will therefore be interesting to compare the densities of the gases entering the first chamber and escaping from the last, in order to satisfy ourselves whether the increase of their density really has anything to do with the course of the process.

We have already seen that 1 litre of the dry gas, composed of sulphurous acid, oxygen, and nitrogen, found in the first chamber, weighs 1·4547 grm. at 0° C. and 760 mm. B. Further, we have found that the volume derived from V at 0° C. and 760 mm. B., when saturated with steam at t° C. and b mm is $V' = \frac{(273 + t)\,V;\,760}{273\,(b - e)}$, when e is the tension caused by saturation with steam at t° C. Finally, we have shown that the temperature of the gases immediately after entering the first chamber is at 50° C., and that this temperature is equal to 92 mm. Whence we know that each 1 litre of the gas at 0° C. and 760 mm. B. in the first chamber will be increased by the saturation with steam at 50° C. to $V' = \frac{(273 + 50);\,1;\,760}{273\,(760 - 92)} = 1{\cdot}346$ litre.

As 1 litre of steam at 0° C. and 760 mm. (weighing 0·804343 grm.) produces at 50° C. and 92 mm. a volume of $\frac{1;\,(273 + 50)\,760}{273;\,92} = 9{\cdot}7739$ litres. Then, according to the proportion 9·7739 : 0·804343 = 1·346 : x, each 1·346 litre of steam at 92 mm. weighs 0·1108 grm. The total weight, therefore, of 1·346 litres of gas at 50° C. and 760 mm., and saturated with moisture, is 1·4547 + 0·1108 = 1·5655 grm., or 1 litre of the gas mixture weighs $\frac{1{\cdot}5655}{1{\cdot}346} = 1{\cdot}163$ grm.

We have now to reckon in the same way the weight of the gases which leave the last chamber, containing the superfluous oxygen and nitrogen in the dry proportion of 0·05 litre oxygen and 0·95 litre nitrogen in each litre, but saturated with moisture. To be sure that we do not make their specific gravity too high we will take the temperature at 20° C., as it is generally lower. As at 0° C. and 760 mm. 1 litre of dry oxygen weighs 1·4298 grm., and 1 litre dry nitrogen 1·2562 grm., then 1 litre of the mixed gases at the same temperature and pressure will weigh 0·05 ; 1·4298 + 0·95 ; 1·2562 = 1·26488 ; 1·2649 grm. But taking into consideration the tension 17·391 derived from the saturation with steam at 20° C., we have $\frac{(273 + 20);\,1;\,760}{273\,(760 - 17{\cdot}391)} = 1{\cdot}098$ litre. Also 1 litre of steam at 0° C. and 760 mm., weighing 0·804343 grm., becomes at 20° C. and 17·391 mm. $\frac{1\,(273 + 20)\,760}{273;\,17{\cdot}391} = 46{\cdot}902$ litres. Then, according to the proportion

$$46{\cdot}902 : 0{\cdot}804343 = 1{\cdot}098 : x,$$

each 1·098 litre of steam weighs, at 17·391 mm., 0·0188 grm. Then the combined weight of 1·098 litre of the gas at 20° C. and 760 mm., and saturated with steam, = 1·2649 + 0·0188 = 1·2837 grm., or 1 litre of this compound weighs $\frac{1{\cdot}2837}{1{\cdot}098} = 1{\cdot}169$ grm. It is therefore heavier than the 1 litre of steam-saturated gas mixture on its entering the first chamber, whose weight, as we have seen, was only 1·163 grm.

There are a few points bearing on the above calculations which must not be overlooked. It has been taken for granted that the gaseous mixture leaving the chambers contains no longer any sulphurous acid, whereas in practice that gas is never completely converted, and some small proportion always remains uncondensed. This fact, the influence of which is trifling, can only increase the density of the escaping gases, for each of the gases forming the compound is far lighter than sulphurous acid. This cannot therefore in any way disprove the foregoing conclusion.

Further, the nitrogen compounds cannot be correctly estimated, because as yet we do not know for certain whether nitrous or hyponitric acid is contained in the chamber gases, and because no reliable examination of the density, &c., of the vapours of these acids has hitherto been made. But it must be observed that, theoretically, the nitrogen compounds are not consumed, but should escape unchanged from the chamber process; in that case, in consequence of the cooling to which they are subjected in their passage through the chambers, they could certainly only effect an increase of the difference between the densities of the entering and escaping gases. It is an absolute certainty, however, that one portion of the nitrogen compounds is lost and withdrawn from the gaseous mixture during the process, and this may be thought to exercise an opposite influence upon the conclusion arrived at. The following remarks will, however, show that the maximum effect possible from that source is much too small to throw any doubt upon the correctness of the conclusion stated.

In good working, the proportion of nitrate of soda used per 100 parts of sulphur burnt never exceeds 7 parts. This means 3·79 parts of hyponitric acid per 100 parts sulphur. For each kilogramme of sulphur there are then 37·9 grms. hyponitric acid, which, as vapour at 0° C. and 760 mm., make 18·3 litres, because the ascertained weight of one litre of this vapour is 2·0715 grms. Now we have seen that for each kilogramme of sulphur burnt, the mass of gas produced at 50° C. and 760 mm., and saturated with steam, is 8345 litres, and in this volume there are 18·3 litres of hyponitric acid. It is evident therefore that no contradiction nor modification of the above conclusions can be produced by the action of the nitrogen compounds.

Division of the Labour.—As it is most important that the conduct of the process should be made as constant and regular as possible, the daily consumption of sulphur is divided into

24 portions, one of which is added every hour. If the nitric acid be derived from the decomposition of nitre with sulphuric acid in the sulphur burner, this is apportioned in the same way.

The sulphur and nitre should be weighed out by the foreman daily, and be placed in suitable vessels, within handy reach of the kilns ready for use, but the sulphuric acid may be left to the judgment of the "kiln man," to be added as required by means of a leaden cup of the proper capacity. It is advisable that the acid used should be about 110° Tw., in order that it may thoroughly liberate the gas.

We have already suggested that the sulphur should be damped a little, so as to prevent its volatilization. The workman spreads the charge of sulphur next to be used on a board floor and then sprinkles over it an amount of water in proportion to its weight. It should be turned over once or twice so as to become well moistened. This is done just before charging, and then the nitre-pot is prepared as already described, so that everything is in readiness for charging.

As one hour is not always enough to completely liberate the nitric acid from the nitre, the nitre-pot is left in the burner during the combustion of two charges of sulphur, so that there are constantly two nitre-pots in the oven. Before the introduction of each charge the nitre-pot which has been longest in the oven is withdrawn, and the sulphur ashes are cleaned out with a rake from the bed of the furnace. As soon as the kiln is cleaned a new portion of sulphur is introduced on a broad iron shovel. Then the fresh pot containing nitre and sulphuric acid is put in and the door closed. The sulphate of soda formed is taken out of the pot, while yet warm and soft, with an iron spatula or spoon.

When ready-made nitric acid is used, and, as described, is allowed to run directly into the chambers, the labour at the kiln is reduced to cleaning out the kiln, preparing the sulphur, and charging it.

In the works we have particularly described, the "kiln man" had also to look after the steam boiler. Care must be taken that the pressure of steam be not allowed to get down. The augmentation or diminution of the steam admitted to the chambers may be easily managed by simply varying the pressure in the boiler, instead of regulating the taps throughout the whole series. When, however, it is necessary to alter the steam admitted to an individual chamber, the tap leading to it must be the means employed, while the pressure is allowed to remain unchanged. The work is carried on day and night, two workmen changing shifts with each other, and each working 12 hours. Certain modifications of the process will be necessary until such time as the chambers have reached the correct temperature and are working well. In order to bring things into their normal condition as soon as possible, the sulphur-burner is first heated by fire, which is easily done by the fireplace *z*, shown in Fig. 39. When no such fireplace is provided, the fire is placed in the burner itself, and the smoke is conducted away by an opening made for the purpose, as during the heating the vertical connection between the kilns and the chambers is discontinued.

When the kiln is hot enough, the proper communication is remade, the hole walled up, and the operation commenced. It is as well, at first, to give the kiln double charges of dry sulphur, in order to raise the temperature more quickly. The process is also brought much more rapidly into good order if a double quantity of nitre be used for the first day or so. At the commencement of the process, the moisture contained in the ordinary atmospheric air admitted is allowed to suffice for assisting the formation of the acid, and no steam is admitted, as while the temperature of the chambers is so low it will condense very fast without forming any corresponding amount of acid, and will at the same time cause the condensation of a certain amount of nitric acid. For this reason steam is not admitted until the commencement of the formation of chamber crystals. At first only very little is introduced, and gradually more and more until the correct limit is arrived at. Whilst expecting the formation of chamber crystals, the little stoneware plug placed in the wall of the first chamber opposite the gases entrance, is taken out and examined from time to time, as the crystals settle on it immediately they begin to be produced.

Manufacturers are agreed that at the commencement of the process the bottoms of the chambers should be covered with acid of a certain density in order to bring the working into good order. This holds good especially when it is necessary to have a certain amount of liquid on the floors of the chambers in order to cut off their communication with the outer air, for which purpose water should not be used, but acid of such a strength that it will not decompose the nitrous and hyponitric acids. When the sides of the chamber are "burnt," or fastened to the bottom, there is no need for covering the floor with any liquid at all, but we strongly disapprove of this plan.

Until the apparatus has reached the proper temperature, the formation of the acid and condensation of the gas proceed slowly, and in consequence the draught is slow and the sulphur requires longer to burn than under the normal conditions. At first, therefore, the outflow damper and the ventilators which admit air are put wide open, and only reduced to the proper adjustment as the process of the burning improves.

It is of the highest importance that in each of the working processes—burning the pyrites, the introduction of the steam and nitrous acid into the chambers, the regulation of the draughts and the working of the towers—the utmost possible uniformity be attained. All defects and irregularities of workmanship should therefore be detected and remedied at once, and in order to effect this, the five following points require careful and unremitting attention ;—

1. The strength of the acid produced.
2. The amount of nitric acid contained in it.
3. The escaping gases.
4. The amount of sulphurous acid in the gases.
5. The oxygen contained in the escaping gases.

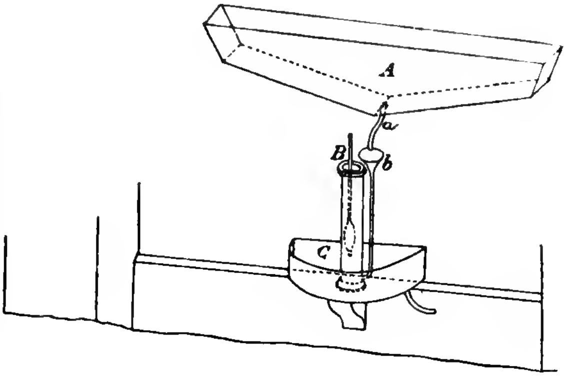
The three first receive attention in almost every works, while the two last are only attended to in the best managed establishments.

1. *The Strength of the Chamber Acid.*—The strength of the acid on the chamber floor is tried daily in order to see whether it remains constant. Changes taking place in the process, however, cannot be noticed in this way until long afterwards, since the amount of the newly-formed acid is so small as compared with that already lying there. In order to check variations as rapidly as possible, the strength of the acid dripping from the connection pipes is regularly noted four or six times daily. From the strength of these drips the changes taking place may be very readily seen. These are not due solely to alterations in the steam, but also to such causes as the want of air or nitric acid.

In the ordinary manner of working, when the amount of steam admitted to the large chamber is only sufficient to form tetrahydrate, an acid will condense in the pipe connecting it with the second chamber containing less water and more nitrogen compounds, and consequently several degrees stronger than the acid formed in the chamber. If the acid made in the first chamber is at 112° Tw., in the second at 52° Tw., and in the third at 32° Tw., the liquids condensed in the pipe connecting chambers 1 and 2 will, as a rule, be at 133° Tw., or 21° higher than in the first chamber. The acid formed in the connection between chambers 2 and 3 will show about 63° Tw., or 11° stronger than in the second chamber. The strength of the acid flowing from chamber 2 back to chamber 1 has something to do with the difference observable between the strength in No. 1 and in the connection between Nos. 1 and 2. So also the acid in the second chamber is weakened by the acid flowing in from No. 3. The acid formed in the pipe leading from the third chamber is never stronger, and is often several degrees weaker, than the acid in that chamber, as it is not thinned by the influx of weaker acid from another chamber. The strength of the acid condensed in the escape flue can only be stronger than that formed in the last chamber when a great quantity of uncondensed sulphurous acid is escaping, and thus maintaining the formation of acid in the flue.

If the acid in the small chamber also be made at 112° Tw., then it is evident that the acid formed in the connection of these chambers will be some degrees stronger, and, like the acid dripping from the connection of Nos. 1 and 2, will contain dissolved chamber crystals.

48.



With large chambers it is not sufficient to have drips only in the connection pipes, but the chambers themselves must be provided with what are called "drip-trays," as shown in Fig. 48. A is a leaden vessel inside the chamber, 2 ft. 6 in. from the bottom, and "burnt" on to the chamber wall. The acid caught in it flows by the pipe *a*, which pierces the chamber wall and is burnt to it, into the cylindrical leaden vessel B, where a hydrometer is floating. The vessel is fitted with a side pipe *b*, entering near the bottom, rising higher than B, and provided at the top with a leaden funnel for catching the acid. In accordance with the laws of hydrostatic pressure the acid flows continuously in at the bottom of B, and away again at the top by a little spout, falling into the cistern C, from whence it returns to the chamber through a small tube.

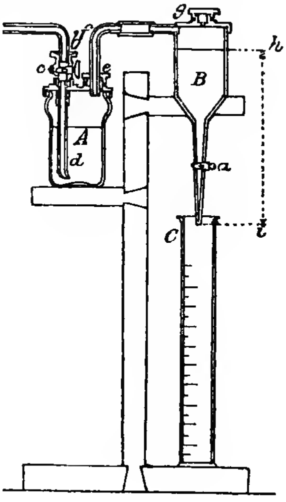
These drip-tests show the strength of the acid actually being formed in the chamber itself to which they are attached, and in good working their degree of strength ought to differ only to a trifling extent from that of the acid on the floor. The usual small differences noticed generally occur in proportion to the distance from the gases inlet, and as a matter of course vary in every different works, therefore it is necessary to find out in each case what is the proper strength for each individual drip, in order to keep the working process at the best possible grade.

2. *The Nitric Acid in the Sulphuric Acid.*—Besides trying the strength of the acid in the drips and in the chambers, it is necessary to observe how much nitric acid it contains. This may be done by a solution of indigo in sulphuric acid, the blue colour of which is destroyed if the amount of nitric acid present be large. The test is not very sensitive, and a very small proportion of nitric acid will not show itself at all, or only after a long time; still it is sufficiently good for the purpose. When, however, it is desired to estimate very trifling proportions of nitric acid or nitrogen compounds, as for instance in connection with concentration in platinum vessels, to which we shall presently come, a much more delicate test must be used, such as the following;—Some of the acid to be tested is poured into a glass test-tube held sloping, and then a little of solution of sulphate of iron is added. Concentrated sulphuric acid is now carefully and slowly poured down the inside of the vessel so that it shall float. Its great specific gravity soon causes it to sink bodily to the bottom of the vessel. If the acid contain nitrogen compounds, a hyacinth-red layer will be formed at the point of contact between the acid to be tested and the concentrated acid, and will become brown-red, and even black, according to the quantity of nitrogen compounds present.

Under proper working, the acid formed in the first chamber should contain no nitric acid, but rather an excess of sulphurous acid, as may be ascertained by its smell. On the other hand, the acid in the small chamber, especially in the last, should hold nitric acid. If the acid on the floor of the large chamber smell strongly of sulphurous acid, the consumption of nitric acid must be increased, and it should only be diminished when the acid contains nitric acid in such quantities that the indigo solution is discoloured after some time.

3. *Examining the Gases.*—A valuable means of controlling the operation is presented in the observation of the gases, which may be done by allowing small portions of them to escape at intervals through the luted openings made in the chambers for the purpose. The colour of the gases also may be distinctly seen through windows or glass cylinders in the chambers and connection pipes. From the appearance and smell of the gases, presence of nitrous and hyponitric acids may be judged as easily as the sulphurous acid. The gases of the first chamber must be sulphurous, while in the others a relative proportion of nitrogen compounds will be easily recognized by the red colour. When the gases are colourless in the exit pipe, but appear red on escaping into the atmosphere, they contain nitrogen oxide, and oxygen is wanting in the apparatus. If, however, they look colourless or white on escaping to the air, the nitric acid admitted is not sufficient or there is some disturbance taking place in the process.

49.



Besides the foregoing observations it is well to pay attention daily to the small stoneware plug in the chamber wall opposite the entrance of the kiln gases, in order to note their composition. On this plug any sublimation of sulphur or formation of chamber crystals will be immediately noticed.

4. *The Sulphurous Acid in the Gases.*—We have already seen that the gases entering the chamber should contain 0·1123 litre of sulphurous acid, 0·0977 litre oxygen, and 0·7900 litre nitrogen in each litre, or about 11 per cent. by volume of sulphurous acid. This holds good in practice, and should be daily controlled. In some works a simple apparatus is used for examining the gases. In order to put it into communication with the interior of the chamber, the chamber wall is pierced and the orifice fitted with an indiarubber plug through which is passed a glass tube.

Fig. 49 shows this apparatus as consisting of three principal parts fitted to an easily movable wooden frame.

An ordinary sugar-glass A acts as an absorbing vessel, a cylindrical metal vessel B, funnel-shaped at the bottom and furnished with a long narrow exit tube and tap *a*, serves for an aspirator, and a glass measure C permits the admeasurement of the water escaping from B.

The glass vessel A is tightly closed by a metal cover in which are two openings. Through one is inserted a brass tube *b*, bent towards the left at the top and furnished with a tap *c*, for the purpose of making communication between the interior of the vessel and the outer air or the other mouth of the pipe, or to disconnect altogether the interior of the vessel. Into the lower part of this brass tube a glass tube *d* is cemented, reaching almost to the bottom of the vessel, but somewhat bent on one side and drawn to a fine point at the end. The second opening *e* admits a short glass tube bent towards the right at the top. It is very important so to arrange this that the stopper may be easily taken out and put in, and it is better to make it air-tight by means of a screw, as this stopper must be withdrawn at each test, and will very soon wear out if it fits so tightly as to make an airtight joint of itself. The metal vessel B has a lateral tube, which may be connected with the tube *f* by means of indiarubber tubing. In the upper part is an opening *g*, closed with a cork and also with a screw cover to make it air-tight.

When it is desired to make a test of the sulphurous acid contained in a volume of gas, a glass or other tube is inserted into the chamber and joined to the pipe *b* by indiarubber tubing. It is most important that these joints be air-tight, so that no air may enter from without, for there is no means of discovering any accidental error in the test. The vessel A is $\frac{1}{2}$ or $\frac{2}{3}$ filled with water through the opening *e*, and the vessel B is similarly filled moderately full through *g*. From an ordinary Mohr's burette some solution of iodine (containing 1·27 grm. iodine as iodide of potash in a litre) is added to the water in A, as well as some starch solution by which the water is rendered of a deep blue colour. When all the openings have been closed and the tap *c* so regulated that no air can draw into A, the tap *a* is opened and the water flows out until the vessel B is emptied. The tap *a* is then shut and the tap *c* opened, so that a communication is formed between *b* and *d*; then *a* is opened, so that the water can only flow out very slowly, and the gas volume to be tested bubbles in through *d*, and rises through the coloured water. As soon as the sulphurous acid mixes with the water it turns the free iodine into hydriodic acid, and in time the liquid will be decolorized, which may be very well seen towards the end of the process when it proceeds with great rapidity. The tap *a* is then shut as well as the inlet of the decolorizing matter. The passage *e* is opened and a measured volume of the iodine solution is admitted to the vessel A, which also assumes a blue colour. After closing *e*, *a* is cautiously opened and so much water allowed to escape that the fluid in the pipe *d*, which had been reduced to the level of that outside by the opening of *e*, is drawn to the point of the tube; *a* is then quickly shut, all the liquid hitherto caught in C is thrown away and the empty vessel replaced. Thereupon *a* is reopened, and the water flowing away causes the gas to be slowly sucked through A till decolorization again ensues, when the tap *a* is shut and the volume water run into C is measured.

The risk of sulphurous acid going away unabsorbed is certainly so small as not to enter into the calculation.

If it be desired to make a further test, a new measure of iodine solution can be introduced without trouble, and the operation recommenced immediately. When several repetitions have been made it will be observed that the liquid in A when decolorized will colour itself anew after a time, because it has then come to contain so much hydriodic acid that it decomposes of itself and free iodine is liberated. The liquid must then be poured out of A, and the vessel be refilled with clean water containing a little starch. Such a test can be made in a very short time when the gas is rich in oxygen.

When the volume of gases is found to contain much more than 11 per cent. of sulphurous acid, the draught must be increased, and in the opposite case it must be reduced.

5. *The Oxygen in the Escaping Gases.*—We have already seen that the gases escaping from the chambers should contain about 5 per cent. by volume of oxygen and 95 per cent. of nitrogen. Fixing the amount of this proportion in practice may often assist very materially in regulating the process, and will serve as a check upon the estimation of the sulphurous acid, and to some extent even render it unnecessary. A very simple arrangement is in use for absorbing the gases which gives results sufficiently accurate for all ordinary purposes, though not absolutely so. The volume of gases to be tested, which consist, besides oxygen and nitrogen, of some steam and a small proportion of sulphurous acid and oxides of nitrogen, is generally aspirated from the exit flue of the last chamber by the agency of a vessel alternately filled and emptied with water. A small gasometer may be conveniently used for the purpose, and should be furnished with a tap for regulating the outflow. In lieu of this, in some works a small bellows made entirely of indiarubber is used, holding an exactly ascertained volume of the gas, which it is made to give up by closing the inlet, opening the outlet, and squeezing the bellows together. A simple hollow indiarubber ball fitted with tubes and which may be squeezed in the hand, answers just as well. In using this it is first tightly compressed in the hand so as to eject all the air, then it is put into connection with the interior of the flue by passing the indiarubber tube over the glass tube in the flue, and the hand is opened. The moment the pressure is removed the ball fills with the gas. The ball is filled and emptied several times in succession in order to be sure that no air remains, but that it is entirely filled with gas, and finally the tubes are shut with pinchcocks.

The inclosed gas is now put into a graduated glass cylinder surrounded by water in a pneumatic trough for examination. By the passage of the gas through the water, the small portion of sulphurous acid and the traces of the nitrogen compounds contained in it will be absorbed. The volume of the remaining gas is then noted, and a small stick of phosphorus on a wire is introduced into the cylinder above the water level. After twenty-four hours the phosphorus remaining unoxidized by the oxygen is removed, and the volume of the gases is estimated anew. The difference is the volume of oxygen. As the absorption of the oxygen by the phosphorus only takes place at 12° C., and under certain conditions not till a temperature of 15°–20° C. is reached, it is necessary to notice at the commencement of the operation whether the phosphorus becomes coated with a film of phosphorous acid, and, if needed, the water must be warmed.

A concentrated alkaline solution of pyrogallate of potash is now more generally used than phosphorus. Such a solution absorbs a considerable amount of oxygen. According to Döbereiner 1 grm. of pyrogallic acid in an ammonia solution absorbs 260 cc. of oxygen. In the process, the gas to be tested is collected in a graduated cylinder over mercury and the solution added.

When estimating the oxygen by pyrogallate of potash, it is advisable to allow the gas to be for some time previously in contact with a solution of bichromate of potash, whereby the sulphurous acid is turned into sulphuric acid, and the binoxide of nitrogen and the nitrous and hyponitric acids are converted into nitric acid and completely removed from the volume of the gas.

By employing such tests as these in conjunction with a constant regulation of the draught and temperature it is possible to render the process almost exact, and in the event of irregularities occurring they can be checked immediately they commence. When, however, such irregularities are allowed to continue for a long time their rectification is more difficult, as by reducing the formation of sulphuric acid the relative proportion of sulphurous acid is abnormally increased. This causes an interruption of the draught and the temperature rises in the kiln in consequence, till at last the sulphur sublimes. When the mischief has once got so far, there remains no cure but to stop the working and recommence anew.

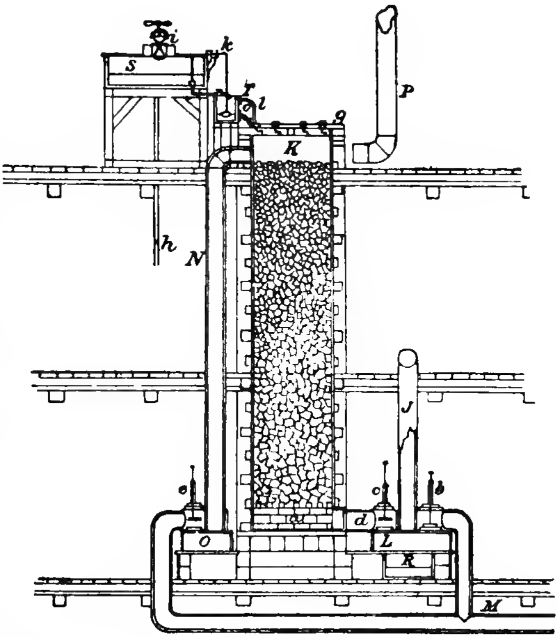
In watching the conduct of the process it must not be forgotten that various causes will show similar symptoms. Thus the reduction in strength of the acid may be caused as much by a cessation of production as by an excess of steam. A check in the draught may also be due to reduced formation of sulphuric acid as well as to atmospheric influences, or to stoppage of the pipes and connections through which the gases pass. The conversion of the sulphurous acid into sulphuric acid may be hindered as much by want of air consequent upon slow draught as by excess of air from too strong a draught. This evil may also be due not only to excess of steam causing a condensation of the nitric acid from the volume of the gases, but likewise to a lack of steam permitting the combination of the nitrous acid with the sulphuric acid to form chamber crystals. All these causes may reduce the strength of the chamber acid.

Recovery of the Nitrogen Compounds.—The fact that nitrogen compounds are absorbed by sulphuric acid of a certain strength, furnishes us with a means of recovering a portion escaping unused in the exit gases, and which may be re-used in the process. For one method, and that by far the most generally used, of applying this fact we are indebted to the celebrated Gay-Lussac.

Fig. 50 shows a vertical section, and Fig. 51 a ground-plan, of the Gay-Lussac "absorbing" tower. It consists principally of a leaden tower K, 25 ft. high and 5 ft. 6 in. in diameter, placed in a wooden frame in the same way as the chambers. The cover or roof is not, however, burnt to the sides, but is made movable. It is composed of a board frame covered with sheet lead, and having a border burnt on all round. This border fits into a gutter which is made in the topmost joist of the framing of the tower, and over which the side lead is drawn. This gutter is filled with acid and the joint thus luted. At the bottom of the tower a sort of grating of fire-bricks is erected. These are arranged in parallel rows, and form channels about 1 ft. 6 in. high. They are crossed by others at right angles, leaving spaces of about 2 in. broad through which the ascending gas and descending acid can freely pass. The tower is packed with pieces of hard coke, resting upon the grating and reaching close up to the inlet pipe N, these pieces being largest at the bottom and gradually decreasing in size towards the top. Three manholes are made in one side of the tower, in order that the coke may be more easily introduced. These are closed with wooden doors covered inside with sheet lead and made tight with putty. The gases pass from the last chamber through the pipe J into the tower, traversing the damper box L, which is provided for the purpose of deflecting the gases through the pipe M, so that when repairing or refilling the tower the work need not be stopped. In that case the damper *b* is opened while *c* is shut. On the other hand, when *b* is shut and *c* is opened, the gases pass through the short pipe *d* under one side of the tower, and spreading themselves among the channels in the grating rise up through the coke in the tower, while at the same time acid of about 149°–150° Tw. flows down and absorbs the nitric acid from the gas, and flows out at the bottom of the tower, having the same composition as a solution of chamber crystals. The denitrated gases escape at N and M, passing another damper box which is only intended to be used while the damper *e* is closed to cut off communication between the tower and the pipe M, when the gases are to be conveyed directly into the air and not through the tower. The nitro-sulphuric acid flows from the tower through the pipe *f*, seen in the ground-plan, into a cistern R, whence it is taken to the so-called "denitrating" tower, when the nitric acid is re-eliminated, as we shall presently describe.

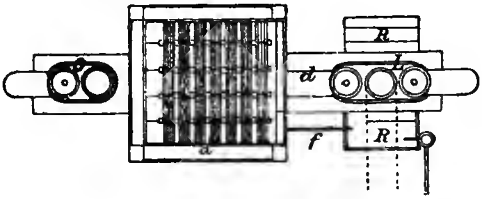
In some works the absorbing tower is placed quite close to the denitrator, which stands near the first leaden chamber into which the nitric acid is introduced. This necessitates the gases from the last chamber being taken through a very long pipe to the tower. The check thus created to the draught is probably the reason why it has been found necessary with this arrangement to have the pipe M in connection with a chimney. We have already stated that such an arrangement is sometimes adopted, and is, in fact, almost universal in this country. In the other case, it is better to put the absorbing tower in the immediate vicinity of the last chamber, so that the gases have only to pass a short pipe. With this arrangement it is not necessary to take the gases into a chimney, they may be conveyed away simply by the pipe which is seen at P.

50.



In order to observe the colour of the gases as they enter and leave the tower, glass windows are placed opposite each other in the two damper boxes L and O, or a part of each of the two pipes J and N is fitted with a glass cylinder. Before entering the tower the gases should appear orange-coloured, afterwards colourless. It is of importance in the foregoing process, that the supply of acid for absorbing the nitrogen compounds shall be precisely regulated so that it may be distributed evenly over the coke, otherwise with even an excessive supply of acid, the gases may still escape without surrendering their nitrous acids. A special apparatus therefore is required. This apparatus consists of two leaden cisterns S and T, and a delivery vessel *g* at the top of the tower. The acid is generally forced into the cistern S by an air force-pump. The acid is collected below in an air-tight iron cistern lined with lead, and upon it air is forced until the acid rises up an escape pipe from the bottom. A part of the ascending pipe is seen at *h*. The acid enters the cistern S through a leaden rose, which detains all solid bodies which may have accidentally got into the acid, and can be removed for cleaning. The acid passes from S through a leaden pipe into the smaller cistern T. The inflow to this second cistern corresponds with the outflow by means of an automatic arrangement, consisting of a leaden float hanging from one arm of the balance *k*, by the rising of which the other arm is depressed and closes the exit pipe. The pipe *l* is only to prevent any chance of the acid overflowing in consequence of an accident to the balance. The acid runs from T to the coke-packed tower K, through the intervention of the delivery apparatus.

51.



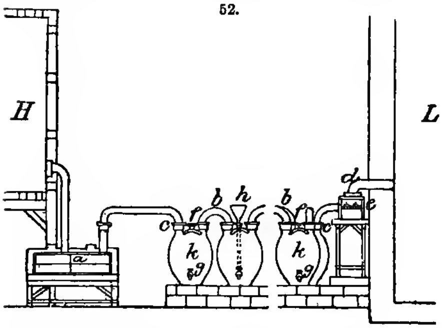
Formerly this delivery apparatus consisted of a simple tumbling trough, such as we have already described. The quantity of acid required is so small, however, that the intervals between the discharges from the trough were found to be too long, and too much acid was delivered at a time. The apparatus also easily becomes disarranged. For these reasons it is now discontinued in most works.

Another plan, shown in Fig. 50, consists of four rows each of four drip pipes, equidistant from each other and fastened securely into the cover of the tower. These pipes are furnished at top with a funnel, and underneath are bent up and down so that the suspended liquid cuts off communication with the outside air. The acid is conveyed from the cistern T through the pipe *o* to the drip tubes, the pipe *o* being divided into two branches, each passing between two rows of the drip tubes and provided with branches and taps, so that each drip tube is supplied with acid from a special tap. Thus the supply of acid depends upon the adjustment of sixteen taps. It is, however, very difficult so to regulate each tap that the amount of acid received by each drip tube is exactly correct. The tubes also are very liable to become choked.

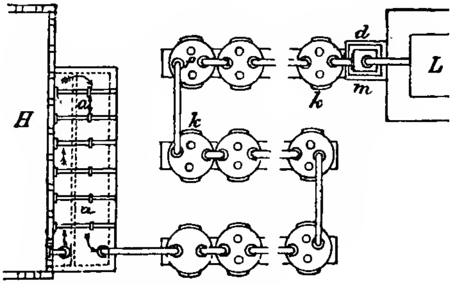
The method now in common use, alike in this country and on the Continent, is an adaptation of the principle of the turbine. The top of the tower is divided into low-walled compartments, each furnished at bottom with a luted exit pipe. Two pipes descend from a small hopper and are bent round in such a way that the acid flowing from them causes them and the hopper to revolve. The acid falls on fireclay tiles inside the tower and then splashes over the coke.

Instead of the tower packed with coke in many Continental works, another arrangement is adopted, shown in plan and elevation in Figs. 52 and 53. It consists of thirty to forty stoneware jars *k*, about 3 ft. high. They are connected with pipes of the same material placed in the necks *c* and plastered with putty. In order that the gases may be acted upon as much as possible, they are led through the jars, where they come into contact with acid of about 150° Tw., with which the jars are one-third filled. After giving up their nitrogen compounds to the sulphuric acid they escape at *d* into either the draught pipe or the chimney, as the case may be.

52.



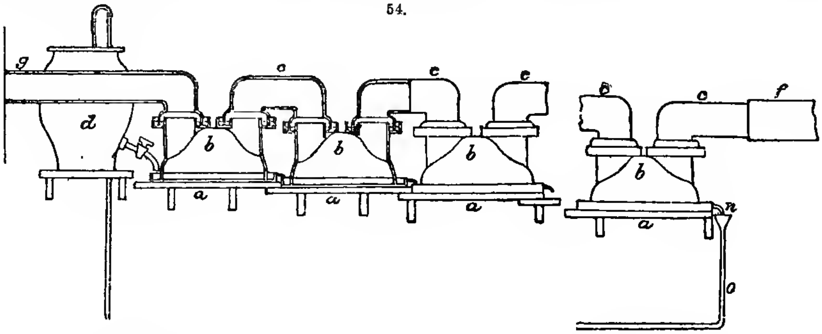
53.



For convenience in filling the jars, funnels *h* can be inserted into their necks *f*, descending almost to the bottom of the jars and thus preventing the escape of gas by the acid lying there. The acid is drawn off at the taps *g*. In order that the acid may absorb as much nitrous gas as possible, it is allowed to remain twenty-four hours on each row of jars. The first row is emptied daily, and refilled with the acid taken from the second row, the second row is supplied from the third and into the third fresh acid is put. It is convenient to put the second row at a higher level than the first, and the third higher than the second, so that the acid may flow from one row to another without trouble. The jars of the highest row are filled from a cistern standing above them.

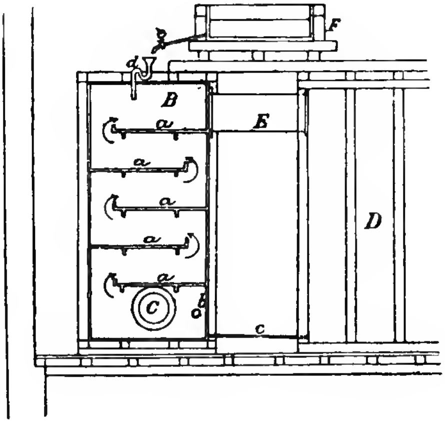
A modification of this plan is comprised of large saucers *a*, Fig. 54, covered with bells *b* and joined together by pipes *c*. This arrangement possesses the advantage that each portion of the apparatus is lighter and cheaper, and that the acid can run from one to another, terrace-like, in a direction opposite to that of the gases.

54.



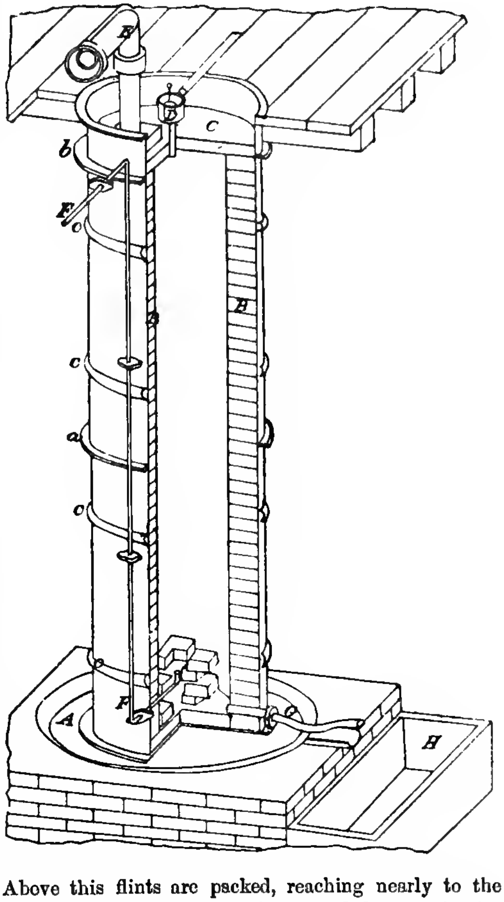
In order to procure for further use the nitrous acid thus entrapped, it must be liberated from the sulphuric acid. Formerly this was done by letting the mixed acids flow into the largest chamber near the gases entrance. The operation is now more effectually performed in a small chamber, as shown in Fig. 55 (B). The mixed acids are first placed in the cistern F and run thence through the tap *c*, which regulates the outflow, and then through the funnel-topped bent tube *d* into the chamber, which is furnished with horizontal leaden shelves over which the acid flows. These shelves are burnt to the walls of the chamber on three sides, and on the fourth, where the acid flows over, they are furnished with low rims about 4 in. high to detain the acid. The gases rush immediately out of the sulphur burner into the small chamber through the pipe C a little above the bottom, near which at *b* the necessary steam is introduced, and escape from the top along with the nitrous acid fumes liberated from the nitro-sulphuric acid through the pipe E into the large chamber, whilst the denitrated acid flows into the basin of the chamber by the pipe *c*.

55.



The above-described apparatus is useful when the nitrous acid supply is derived from the decomposition of nitre in the kilns. It is, however, almost entirely gone out of fashion. A more common form of denitrator is the following, known in this country as a "steam tower."

56.



In Fig. 56, representing such a tower, part of the side wall is removed, in order to show the interior of the apparatus. It consists of a cylindrical-shaped tower, of strong sheet lead, put together in three pieces, which are burnt together at *a* and *b*, the whole being 12 ft. high and about 3 ft. in diameter, and standing on a solid foundation. The bottom A is also of sheet lead. Four strong iron bands *c* help to hold the structure firmly together. In order to protect the lead from the effect of the hot acid, it is provided with a casing of hard-burnt fire-bricks, so formed and arranged that they lie quite close one upon another. The joints are made with fine pipe-clay cement. On the top of the cylinder a basin C is fixed, resting close down upon the uppermost tier of the brickwork. The nitro-sulphuric acid flows through the leaden feed-pipe D, placed in the middle of the basin. The disengaged sulphurous acid finds its way to the chambers through the stoneware pipe E, which is fixed tightly in the basin. Sometimes this pipe is covered with an outside coating of lead to prevent the mischief which may arise from a breaking of the pipe from any cause. The steam is admitted at the bottom of the cylinder by the pipe F at such a height that the mouth of the pipe remains higher than the level of the sulphuric acid which collects at the bottom. The pipe is supported, surrounded, and covered with fire-bricks in such a manner that spaces remain for the free passage of the steam and the acid. Above this flints are packed, reaching nearly to the summit of the tower. Those at the bottom are about as large as a man's fist, and decrease in size as they rise till they are no larger than nuts. Instead of flints sometimes broken remains of hard burnt stoneware vessels are used.

The nitro-sulphuric acid flowing in from above, trickles down through the flints and is decomposed by the steam which it meets, while the liberated sulphurous acid streams in a gaseous form through the pipe E into the chamber. The sulphuric acid, weakened by the condensed water, flows away at the bottom of the cylinder through the pipe G into the cistern H. This outlet pipe is so bent that the acid lying in it shuts in the gases.

As we have before remarked, the steam should be so adjusted that the acid made in the chambers may contain a little more water than the tetrahydrate, or 1·55 sp. gr.; when much stronger it will hold chamber crystals in solution, when much weaker it will cause a decomposition of the nitrous acid. These facts teach us that the proportion of water present has an important influence upon the process. If, for instance, the gases from the last chamber are brought into contact with sulphuric acid containing so much water as to equal more than 4 equivs. of water to 1 equiv. of acid, no nitrous acid will be absorbed, and only a little nitric acid arising from the decomposition of the nitrous and hyponitric acids. With perfectly dry gas the acid may be tetrahydrate or 1·55 sp. gr. Generally acid of 150° Tw. is now used, because it can be concentrated to that degree in leaden pans. As it has been found, however, that acid of 170° Tw. absorbs nitrous acid far more readily and to a greater extent, viz. three times as much as acid of 145° Tw., it becomes a question whether the extra cost of concentration to that strength in glass or platinum would not be repaid. At any rate it is advisable so to regulate the conduct of the manufacture when working with a Gay-Lussac tower that the gases from the last chamber shall be as dry as possible. In this case the steam to the last chamber should be so reduced that the acid made in it too will show 110° Tw. If, however, the steam be admitted to the last chamber in such a degree as to produce acid of only 52° Tw., the gases must be dried as much as possible before leading them into the tower. This may be effected by allowing them to circulate in a long channel J, as shown in Fig. 37, in which a great part of the moisture will condense as weak, somewhat nitrous, sulphuric acid, which may be run into the last chamber.

To perfectly carry out the idea of the Gay-Lussac tower, the amount of steam must be very carefully regulated, and further success depends greatly upon the proportion of oxygen in the chamber gases, which must be so great that the nitrous acid cannot possibly be reduced to lower oxide which is not absorbed by sulphuric acid. To fulfil these requirements the excess of air we have already indicated must not be diminished. But even when both the preceding conditions are fulfilled the success of the process is not ensured; in fact, so many small trifles need rigorous attention, that the process is extremely difficult of accurate adjustment, so much so that many manufacturers hesitate about erecting the expensive plant necessary.

We have already said that it is still doubtful whether the nitrogen combinations in the chambers are as nitrous or as hyponitric acid, as we know that either of them may be formed, and even both may exist in the gases at the same moment, and their state probably depends upon the proportion of the sulphurous acid to the oxygen. Even if hyponitric acid be absorbed by the sulphuric acid, still we have seen that it forms a very weak chemical combination with it, and that the hyponitric acid is given up very freely on subjection to heat, and even at ordinary temperatures it escapes rapidly in red fumes. The affinity between nitrous acid and sulphuric acid is, on the other hand, very great, and these two acids form, as we have seen, a definite and fixed form. It is therefore easy to understand that the Gay-Lussac process will not succeed when the gases contain only hyponitric acid, which does not admit of reduction to nitrous acid. This may happen when, in the desire to work the chambers well, the escaping gases having only the normal excess of oxygen are quite free from sulphurous acid. In proof of this it is found that in each case when the Gay-Lussac tower works well, the escaping gases still contain a small proportion of sulphurous acid, which either prevents the oxidation of the nitrous acid to hyponitric acid, or the already existing hyponitric acid is reduced to nitrous acid by the action of the sulphuric acid despite the presence of oxygen.

From these observations it will readily be believed that the saving of nitre effected by the Gay-Lussac towers varies considerably in different works. With first-rate manipulation the nitrous sulphuric acid should contain 3½ per cent. of nitrous acid. Winkler found at one works, when the acid was used at 145° Tw., that it contained about 2½ per cent. of nitrous acid. The analysis shows the following composition:—

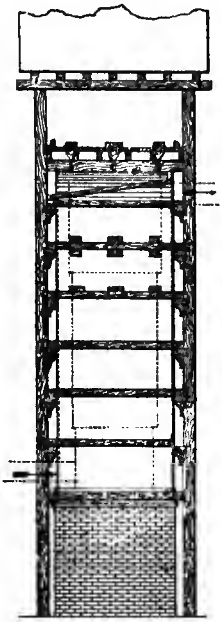
Sulphuric acid	60·200
Water	37·191
Nitrous acid	2·550
Nitric acid	·256
Organic colouring matter	·022
	100·219

In order to find out with ease and approximate correctness the amount of nitrous acid contained in the nitro-sulphuric acid, according to one plan the nitro-sulphuric acid is poured from a burette into a titrated solution of chromate of potash, until the pure green colour of chromium oxide is produced by the decomposition of the chromic acid. The known quantity of oxygen which the chromic acid thus gives up serves to convert the sulphurous into sulphuric acid, and at the same time, from the amount of nitro-sulphuric acid used, the proportion of nitrous acid can be readily calculated.

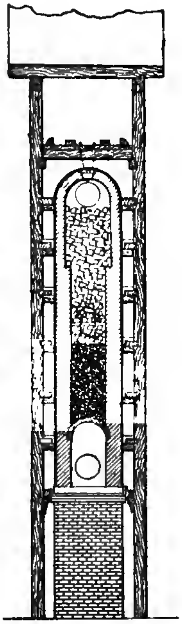
Many of the drawbacks attending the use of the Gay-Lussac absorbing tower are removed by having a Glover's denitrating tower working in conjunction with the Gay-Lussac tower.

Figs. 57 and 58 show such a tower of the smallest size for which plans are furnished, the dimensions being increased in accordance with the amount of work required to be done. This tower is the invention of Mr. John Glover, Newcastle-on-Tyne, who first tried to denitrate, and at the same time concentrate, the acid from the Gay-Lussac tower along with the acid from the chambers, in the year 1859. It has been gradually perfected until it has reached its present state. It has been generally adopted since 1869 and 1870, and no acid works can now be considered complete without it. The Gay-Lussac tower was of course in use long before the above dates, and the acid from that tower, after having absorbed the nitrogen compounds leaving the chambers, was denitrated by being run down the small leaden towers packed with coke, and into the bottom of which steam was injected, as we have already described. This of course at once reduced the acid in strength, consequently the nitrogen compounds were given off and taken into the chambers. This plan compelled the reconcentration of the acid, which was done in leaden pans by surface heat at a large expenditure of fuel and heavy wear and tear of the pans, to say nothing of the annoyance of the acid fumes given off during the process. This plan became so costly, and such a nuisance, that the Gay-Lussac tower fell into disuse, the expense of upholding the pans and cost of fuel far exceeding any benefit derived from the saving of nitre. With the Glover tower, however, *all* the acid is easily and economically concentrated to a density of 145°–155° Tw., and at the same time all thoroughly denitrated, thus saving the whole of the fuel formerly required for concentrating acid for the Gay-Lussac tower, besides that used in the decomposition of salt for making sulphate of soda, as hot and strong acid is thus always at hand for the decomposing pans. All fumes given off in the tower of course go into the chambers. Objection is taken to the tower, in that some of the nitrogen compounds are reduced in it by the hot gases from pyrites burners to the lower oxides, and even to nitrogen. The fact, however, remains that no works having any pretensions to being worked scientifically are without the towers. Works in the Tyne district are working with 2 and 3 per cent. of nitre on the sulphur actually converted into oil of vitriol 1·845 sp. gr.; the latter is the outside quantity. Wear and tear of chambers is also saved by the gases entering so much cooler. The gas from the pyrites burners enters the tower at about 700° Fahr., and leaves the tower at 160°–180° Fahr., taking with it all the steam due to the concentration which has taken place in the tower. The figure shows a leaden tower of oblong shape, lined with hard silicious fire-brick, and packed with flints or flints and coke. It is placed, of course, at the end of the pyrites burners, between them and the chambers. The hot sulphurous acid from the kilns enters, as shown, below a perforated arch, which carries the packing and meets the descending current of mixed nitro-sulphuric acid from the Gay-Lussac tower, and chamber acid which had previously been introduced at the top of the tower; the gaseous constituents of the pyrites and sulphuric acids passing through a pipe to the chambers, along with all the steam and volatilized acid which are formed during concentration. The acid issuing from the tower is sufficiently strong to be used again on the Gay-Lussac tower, and so on. The towers give no trouble, and are easily worked. Cases have, however, occurred where they have not done so, but whenever this has happened it has been owing to ignorance in proportioning the apparatus to the work required, and as the invention is not patented, this has sometimes happened when towers are erected by incompetent persons..

57.



58.



Under certain conditions, it may be convenient to use other bodies than concentrated sulphuric acid for absorbing the nitrogen compounds. Kuhlmann uses the ammoniacal liquor from gas-works, which is allowed to flow down a tower filled with coke, such as we have already described. The ammonia combines with the acid contained in the gases, and by allowing the solution which escapes from the tower to stand, the salt will crystallize out. The same manufacturer also uses carbonate of barium in jars, such as we have already described, by which is produced a white paint, known as "permanent white," sulphate of barium; the nitrogen acids combine with the barium as a soluble salt, whence they can be recovered and the residue can be re-utilized.

Working Results.—*The Proportion of Sulphur used in regard to the Chamber Space.*—We have already seen that theoretically a very small amount of nitrous or hyponitric acid is necessary for the formation of a very large quantity of sulphuric acid from a mixture of sulphurous acid, oxygen, and steam. But an absorption of this acid by the sulphuric acid constantly takes place, and there is a certain, but not as yet correctly estimated, time necessary in order to completely change a fixed volume of the gas mixture into sulphuric acid through the agency of the nitrogen compounds. The amount of sulphuric acid which forms in a certain time, or the volume of gas condensed into sulphuric acid in that time, is proportioned, up to a certain point and under equal conditions, to the increased consumption of nitrogen compounds. The time necessary for the conversion of a certain volume of gas into sulphuric acid will thus be diminished by increase of the nitrogen compounds, and augmented by their reduction.

In a chamber space of certain size, constantly filled with a mixture of sulphurous acid, air, and steam, and to which a certain quantity of nitrogen compounds is added, only a small amount of the volume of gas can condense in a certain time to sulphuric acid, and this increases up to a certain point with the increase of the nitrogen compounds. The quantity of sulphuric acid made in a given time depends therefore as much upon the amount of chamber space as upon the nitrogen compounds provided. Other conditions being unchanged, it stands in direct proportion to the space or to the amount of the volume of gas with which that space is filled. It can be increased by an increased consumption of nitre up to a certain point, and similarly, this consumption can be reduced to a certain degree if the chamber space be increased. There are limits to these points in practical working, based as much upon technical as upon financial grounds.

In the chambers we have described there are about 33,435 cubic feet (974 cm.) space, and with these it was found that the best working results were got when the amount of sulphur burnt in 24 hours was not more, but not much less, than 3 lb. per 100 cubic feet (·5 kilo. per 1 cm.), under which conditions for each 100 parts of sulphur there were needed 6 parts of clean nitre, or 4·45 parts of monohydrated nitric acid, or 8·24 parts of nitric acid, of 1·340 sp. gr. at 15° C., or containing 54 per cent. of monohydrated acid. This daily consumption of sulphur could be increased to 3½ lb. per foot without ill effect. In larger works generally much more sulphur is burnt in the same time and space. In this country it reaches, and sometimes exceeds, 5 lb., while in Germany and France it is seldom higher than 4½ lb.

Theoretically the 3 lb. per 100 cubic feet in 24 hours, or ·5 kilo. per 1 cm., is arrived at by the following calculation. We have already seen that for each kilo. of sulphur burnt, 8345 litres of gas at 760 mm. and 50° C., and saturated with moisture, are conveyed into the chambers; then ·5 kilo. sulphur produces 4172·5 litres of gas per cubic metre, or 1000 litres space—that is to say, the formation of the sulphuric acid from the gas introduced at the above rate of consumption will occupy about 5¾ hours.

The following calculations may serve to show the influence of the nitrogen compounds upon the production of the acid. One hundred parts of sulphur require for their conversion to 200 parts of sulphurous acid 100 parts of oxygen from the air. These 200 parts of sulphurous acid need a further 50 parts of oxygen for their conversion to sulphuric acid, from which is lost by the reduction of the 3·812 parts of anhydrous nitric acid (derived from 6 parts of nitre) to 3·247 parts hyponitric acid, only ·565 part, and but 1·129 part is lost in reducing this to 2·683 parts of nitrous acid.

On the supposition that the nitrogen compounds exist in the chambers as hyponitric acid, the amount of oxygen taken from the air for the conversion of each 200 parts of sulphurous acid to sulphuric acid $= 50 - 0{\cdot}565 = 49{\cdot}435$ parts, while each 3·247 parts of hyponitric acid only contain 2·259 parts of oxygen. The hyponitric acid therefore permits the combination of the sulphurous acid with a volume of oxygen from the air which is $\frac{49{\cdot}435}{2{\cdot}259} = 21{\cdot}9$ times as great as its own contents of oxygen.

On the supposition that the nitrogen compound exists as nitrous acid, the 200 parts of sulphurous acid will take $50 - 1{\cdot}129 = 48{\cdot}871$ parts of oxygen from the air, whilst the 2·683 parts of nitrous acid only contain 1·695 part of oxygen. Then the nitrous acid enables the volume of oxygen taken from the air to be $\frac{48{\cdot}871}{1{\cdot}695} = 28{\cdot}8$ times as great as its own volume of oxygen.

Consumption of Nitre, or Nitric Acid.—When the consumption of sulphur takes place in the proportion we have indicated, and the process is well conducted, the amount of nitre necessary per 100 parts of sulphur will be about 6, or 3·812 per cent. of anhydrous nitric acid. If the sulphur consumption be increased, or the conduct of the work be irregular, this percentage may easily be increased to 7·5.

Market fluctuations and other causes sometimes necessitate an increased production, or that the chambers be "forced." But it is never advisable to exceed the limits mentioned above, because, beyond a certain limit, the increased consumption of nitre, which bears a direct proportion to the increased product of acid, will have the effect of creating a rapid corrosion of the lead without any corresponding augmented yield of acid. On the other hand, it is not good to let the consumption and product fall too low, because the process then becomes retarded in several ways, especially through the cooling of the apparatus.

When the nitrogen compounds are produced by the decomposition of nitre with sulphuric acid in the kiln, it is essential to take care that all the nitrogenous gas be liberated. To ensure this there must be an excess of acid. Generally the proportion is 2 equivs. acid for 1 equiv. nitre, by which the alkali is formed into a bisulphate. So large a proportion of acid is not absolutely necessary, however, for all the nitre will be decomposed by 1¼ part of acid when the right temperature is maintained. Hence 1 equiv. nitre requires ·72 equiv. monohydrated sulphuric acid, or 1·12 equiv. tetrahydrate acid, or at 1·55 sp. gr., which is the strength at which it is commonly used, as it may then be drawn direct from the chambers. With this proportion ¾ of the base will be made into simple sulphate and ¼ will be bisulphate. Nitre 1 part gives theoretically mixed sulphate of soda ·95 part. This corresponds pretty well with the practical result, as 100 parts nitre give 90–93 parts. The difference is owing to mechanical loss.

Commercial nitre nearly always contains a quantity of common salt. This, as well as the moisture, should always be estimated, and a corresponding increase of nitre be used. The salt must always be ascertained, which may be easily done by a titrated solution of silver. The best brands of nitre contain less than ½ per cent. of salt; often 2–3 per cent. is met with, and sometimes the article offered in the market is so impure or adulterated as to consist of 30 per cent. of salt. Nitre containing much more than 3 per cent. must be purified before use by recrystallization, because the chlorine which is otherwise formed attacks the lead of the last chamber when present in large quantities.

In the neighbourhood of alum works, it is sometimes possible to get nitrate of potash instead of nitrate of soda. Of this an increased proportion must be used, 1 part of nitre being equal to about 1·19 part saltpetre.

When great care is exercised in passing the gases from the last chamber through a Gay-Lussac absorber, one half of the nitre consumed may be recovered, thus reducing the percentage by weight from 6 to 3.

Three parts of nitre equal 1·34 part nitrous acid, and as we have said, sulphuric acid at 150° Tw. takes up 3½ per cent. by weight of nitrous acid. Therefore 38·29 parts of sulphuric acid at 150° Tw. are necessary for the recovery of 1·34 part nitrous acid, or 3 per cent. on the sulphur burnt. Often, however, this acid only reaches 112° Tw., though it appears highly probable that the extra cost of concentration to 170° Tw. would be repaid.

The Make of Acid.—When the chamber system is well arranged, the steam accurately adjusted, and the working regularly managed, only about 3 per cent. of the acid which can be made theoretically is lost. From 100 parts of sulphur are obtained 297 parts monohydrated acid instead of 306¼, the possible maximum. These 297 parts exist in the chambers, however, in a weak state, viz. as 460·65 parts of tetrahydrated acid, or at 1·550 sp. gr., with slight modifications, being sometimes made a little stronger, sometimes weaker. These 460·65 parts tetrahydrated acid = 319·35 parts of acid at 1·845 sp. gr. containing 93 per cent. of monohydrated acid.

According to the figures we have given above, the daily consumption of these chambers will be about 9½ cwt. of sulphur, and 88¼ lb. of nitric acid at 68° Tw. = 8·24 per cent. by weight of the sulphur, and the production will be about 44 cwt. of sulphuric acid at 150° Tw. or 30½ cwt. at 170° Tw.

When the nitrogen compounds are not derived from nitric acid, but from nitre and sulphuric acid in the kilns, 64 lb. of nitrate of soda (or 6 per cent. by weight of the sulphur) and 72 lb. sulphuric acid at 112° Tw. will be required; and about 58 lb. of sulphate of soda, of which ¼ is as bisulphate, will be formed as a bye-product.

By thoroughly good management of the Gay-Lussac process, one half of these nitrogen compounds can be saved. The daily consumption will then be reduced to 44 lb. of nitric acid at 68° Tw. = 4·12 per cent. of the weight of sulphur, or to 32 lb. of nitre (3 per cent.) and 36 lb. of sulphuric acid at 112° Tw. On the other hand, 29 lb. less sulphate of soda is produced. The operation needs, however, 410 lb. daily of sulphuric acid at 150° Tw.

For raising the necessary steam about 5½ cwt. of good coal will be needed. When, however a much larger chamber system is supplied from one boiler, the consumption of fuel will not be proportionally increased.

It is hardly necessary to state that the raw materials are always sold upon the basis of the proportion of useful matter which they contain.

Acid from Sulphides.—We have already remarked that in comparatively recent times sulphur has been to a very great extent displaced by various metallic sulphides in the manufacture of sulphuric acid. Principally iron pyrites is used; but in many places copper pyrites also, and even zinc-blende is so roasted that the sulphurous acid evolved may be utilized for acid-making.

In the manufacture from iron pyrites the acid is often the only product of value, and even when the resulting oxide of iron is economized the acid remains the chief product. Iron pyrites is now mined in many places simply for acid-making, where formerly it was altogether neglected. But there are many pyrites beds, especially in Spain, Portugal, and Norway, which contain a considerable proportion of copper. In many works this pyrites is used first as a source of sulphur for acid-making, and the copper is afterwards recovered from the cinders by the wet process.

For the modification, or more properly the extension, of sulphuric acid making by the use of pyrites, we have to thank a king of Naples, who in 1838 gave the monopoly of the trade in Sicilian brimstone to a French company at Marseilles. Through the rapacity of the king and the company the price of brimstone was put at such an exorbitant figure that consumers immediately sought a means of relieving themselves of the burden. In consequence of this, the use of pyrites, which had already been inaugurated both in England and several continental countries, came to be very quickly and generally adopted in the manufacture. When the threats of England had caused the withdrawal of the monopoly, and brimstone had returned to its normal price, the pyrites was in many cases given up again; but in other places where the brimstone cost much on account of transport the use of pyrites was continued. The utilization of the sulphurous acid liberated in copper-smelting was not attempted till some years later.

The sulphurous acid generated in the roasting of zinc-blende is utilized in few places for the manufacture of sulphuric acid, principally because the zinc-blende burns with considerable difficulty, and the heat generated by its combustion is not sufficient to roast it completely. Hence a considerable additional heat must be supplied, and the roasting must be carried on in kilns which do not admit of such convenient economy of the liberated sulphurous acid as the ordinary form of pyrites kilns.

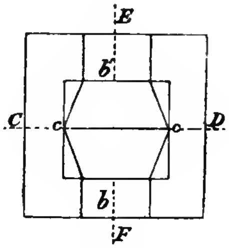
The sulphur in pyrites costs so much less than native sulphur that it would probably have become the only source of sulphuric acid making were it not that all pyrites contains a certain proportion of arsenic, which finds its way into the sulphuric acid as arsenious acid. The elimination of this arsenic from the acid is very difficult, and therefore acid which is required to be free from arsenic is made in large quantities from native brimstone. Probably about $\frac{6}{7}$ of the total product of sulphuric acid is from pyrites. The same apparatus may be used when pyrites are employed as with brimstone, except the kilns, which need to be especially constructed.

In the mining of metallic sulphides, besides the large pieces, a great deal of dust is formed, and also in wet workings a large quantity of mud. These different grades require various forms of kilns for their treatment, or the dust ore may be burnt in the same kiln with the lump ore, if it be first made into balls or cubes about 2–4 in. in diameter. Sometimes it is necessary to separate all the dust from the lump ore by sifting, and the former is then worked up with soft clay. The plastic mass is formed into balls or cubes in the hand or in moulds, and these are then dried by the waste heat of the kilns. Occasionally the dust is moistened with weak sulphuric acid and a less proportion of clay used. The balls may be dried on iron plates placed on the top of the kiln flue. In this way they are rendered so hard that they crumble little more than the lump ore. The admixture of clay has a great drawback, however, inasmuch as the decomposition of the clay towards the end of the process retards the burning so much that some of the sulphur is necessarily lost.

The burning of the lump ore of iron and copper pyrites may be performed in small shaft kilns, first invented in this country. Their shape and size vary very much according to the nature of the ore they are intended to roast. Figs. 59, 60, and 61 show a kiln without a fire-grating, about 10 ft. high and 3 ft. in diameter. In the vertical view to the left of the line A B is seen the outside view of the kiln, and on the right of the same line a vertical section of the kiln on the line C D of the plan. Fig. 61 gives a vertical section of the lower part of the kiln on the line E F of the plan. The moulded and lump ores, which latter are previously reduced to about 1½ in. in diameter, are inserted through the opening *a* fitted with an iron cover, and after being completely burnt they are drawn out at the bottom at *b b′* with iron rakes.

In order to lighten the labour, the sole of the kiln is formed as a cone rising in the shape *c c*, and down which the ore easily runs. The air necessary for the combustion enters partly at *b b′*, and partly at the holes *d* in the side wall of the kiln, which are closed according to need by pieces of brick. These openings also serve for the introduction of iron pokers when the mass needs stirring or breaking up. This happens especially with copper ores which very easily sinter together. The height to which the kiln is filled depends upon the quality of the ore to be burnt. The more difficult of burning, the greater the quantity of ore necessary at a time. It is very important to be sure that sufficient air is admitted to fully burn off the sulphur of the upper layers. The gases pass through *e* into the leaden chambers. In many works they are taken first through a brick chamber where much of the dust mechanically carried in the gas is deposited. When the nitric acid is derived from nitre and sulphuric acid, the pots containing the mixture are put through a close-shutting door into the channel *e*, where the temperature is high enough to produce decomposition.

60.



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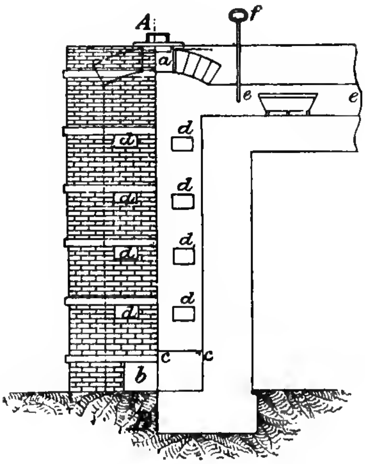
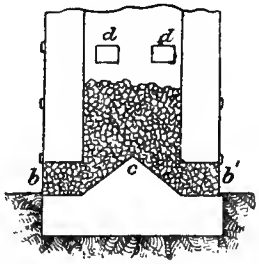


61.



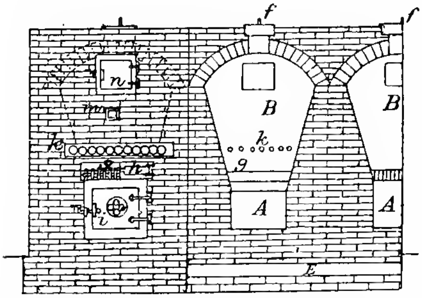
When starting the kiln it must first be made red hot by means of an ordinary fire. Coal or coke may be used for the purpose, and these are introduced like the ore at *a*. During the combustion of the coal, the hole *a* remains uncovered to give a draught to the fire, while the channel *e* is shut by the damper *f* to prevent the coal smoke, &c., from entering the chambers. When the kiln is sufficiently hot, it is cleaned out, put again into communication with the chambers, and then fed gradually with ore in such a manner that each successive charge becomes thoroughly hot before the next is admitted. When the kiln has in this way been filled to the proper height with glowing ore, the work continues regularly, and the new charge is introduced every 12, 6, or 4 hours.

The amount of ore which can be properly burnt in such a kiln depends upon the physical and chemical properties of the ore. To feed such a chamber system as we have described with sulphurous acid, from two to six such kilns will be necessary, according to the amount of sulphur in the ore used. They are then built all together, so that one channel serves to conduct all their gases into a vertical shaft leading to the chambers.

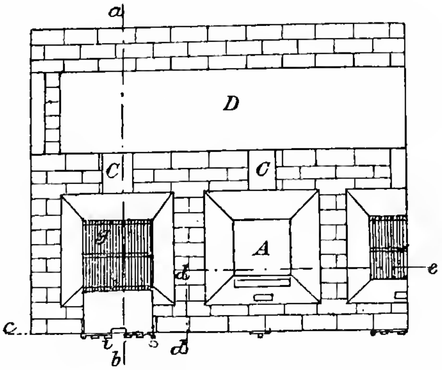
Ore which crumbles readily settles into such a compact mass in perpendicular-walled kilns that the draught becomes choked. In order to check this evil as much as possible, kilns for burning such ores are built with two walls sloping together towards the bottom, these walls being much longer than the other two. The great height of these kilns affords considerable advantages in burning ores of slow combustion; but they always possess the fault that the great mass at the bottom makes the draught very difficult to regulate and to supply in sufficiency. To overcome this defect, they have recently been provided with gratings under which is an empty space or ashpit, into which the necessary air is admitted through a tight-fitting iron door furnished with holes.

Fig. 62 shows a view as well as a vertical section (through the line *cd*, *de* of the plan, Fig. 63) of such a kiln, and Fig. 64 is a vertical section of the same through the line *a b* of the plan. The shaft B of this kiln is of much less height than that of the kiln shown in Figs. 59, 60, and 61, and is much larger above than below. This kiln is well suited for ores which burn rapidly. The mineral is introduced from above at the opening *f*, which is fitted with a close-shutting cover. The withdrawal of the burnt ore through the door *h* is facilitated by having the grate *g* which carries the ore, arranged to be in a sloping position. Small fragments fall through the grating into the ashpit, and are removed from time to time through the door *i*, which is furnished with ventilation holes. About 10 in. above the grating the front wall of the kiln is provided with a row of holes *k*, in which are boxes fitted with round iron bars *l*. These can be used in breaking up the mass, and also serve to prevent the falling of the overlying mass while the spent ore is being withdrawn. The opening *m* provided with a door is useful for watching the process and for inserting an iron bar to stir up the mineral when that becomes necessary. The larger opening *n* (also shut with a door) can be used for the same purpose, and also for introducing the nitre pot into the channel C, when the nitrogen compounds are derived in that manner. The gases next pass from the channel C into the wide channel D, which in some works is made 300 ft. long, and in which the dust as well as a great portion of the arsenic contained in the pyrites will settle. Any required number of kilns may be put into communication with this flue, and their collective gases thus be taken to the chambers. The gutter E lying below the sole of the furnace is for protecting the kiln from wet.

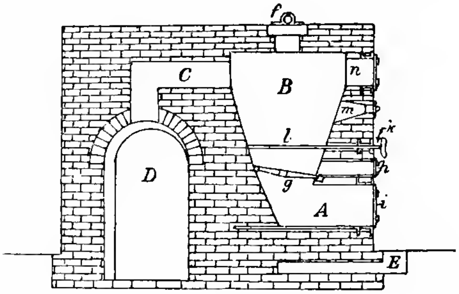
62.



63.



64.



More recently, this kiln has been improved by letting the spent pyrites fall into the ashpit. For this purpose, four-sided iron furnace-bars are used to support the mineral. These are 1–1¼ in. in diameter, and have circular pieces turned on them at each end lying in semicircular hollows so that they may be made to revolve. In order that they may be turned easily by an iron key, their ends project somewhat from the kiln wall. The space between each two bars is naturally greater when they lie square to each other than when at an angle. Thus the pyrites is crushed through by the revolution of the bars. With this arrangement the ashpit is made very deep in order to accommodate a great mass of spent ore at a time. Its mouth is closed with an iron plate pierced with holes for admitting the air. The plate is fixed and luted into the wall at each operation.

In many French works such kilns are fitted at top with leaden pans for concentrating acid to about 140° Tw. by the heat of the gases. With this disposition the ore must be introduced at a lateral opening. Such a kiln, with a grating area of 6 ft. × 3 ft. 9 in., is charged every three hours, or eight times daily with 1 cwt. of ore.

At Chessy, near Lyons, in France, a great deal of copper pyrites is smelted, and the sulphurous acid is utilized by means of a kiln consisting of a hollow vault, 4½ ft. long, 3 ft. wide, and 3¼ ft. high, enclosed by strong walls. Low down in one of the long side walls are four holes, equidistant from each other, each 8 in. wide and 11 in. high, shut by cast-iron doors, provided with numerous holes, of less than ½ in. diameter, for admitting air. An opening is left in the upper part of one of the short side walls through which the gases escape into the channel or flue leading to the chambers. This can be shut at will by a damper.

For feeding each chamber system sixteen kilns are needed, the gases from which are conveyed to the first chamber by a single flue, as the kilns are grouped into one body. This flue is fitted with a cast-iron pipe that takes to pieces for convenience in removal, and is only used for carrying away the smoke, &c., when lighting up the kiln.

To start the kilns each partition is furnished with such an amount of broken ore as will evenly cover the grating surface from the doors, up to a level of about 21 in.

After disconnecting the kilns from the chambers they are heated to redness with an ordinary fire. The ashes, &c., are then quickly raked out, each kiln is supplied with 1 cwt. of ore, and communication with the chambers is re-made. Three hours later, another 1 cwt. is introduced, and this is continued regularly, so that each kiln receives 8 cwt. per twenty-four hours. This quantity can be roasted daily with proper working. After the kilns have been brought into condition the charge is only made once in twelve hours, each time with 4 cwt., and the spent ore is drawn out at the same time. As the mines yield ores varying considerably in the proportion of sulphur they contain, the rich samples are mixed with the poor, so that the mass burnt may be as uniform as possible. Until the kiln is going well it is good to use only rich ores.

Much the same form of kiln is used also in Belgium, but they are larger and are furnished with grates. These are 22 ft. long, 6 ft. 6 in. wide, and 11 ft. 4 in. high; the grate, formed of iron bars about 1 in. apart, has a surface of 113 square ft. and lies at about 6 ft. 6 in. above the sole of the kiln, so that it divides into two portions, an upper of about 5 ft. in height and a lower of about 6 ft. 6 in. Into the lower space the air is admitted, and thence also the spent pyrites is withdrawn by means of a rake. The spent ore lies in the lower part till it ceases to glow, and is then withdrawn. In the top of the kiln are several holes through which the ore is introduced and is spread over the surface of the kiln with iron tools to an equable depth of 8 to 12 in. The gases leave the kilns through a broad flue in which the nitre and sulphuric acid are put for decomposition, and thence the mixed gases pass to the chambers. In such a kiln from 40 to 60 cwt. are burnt per twenty-four hours, introduced in charges from four to eight times daily.

Fig. 65 shows a large set of kilns fitted with a nitre oven in the main flue, as devised and manufactured by Messrs. R. Daglish and Co., St. Helen's Foundry, Lancashire. The long iron pipe is for the purpose of coolnig the gases before they enter the chambers.

66.

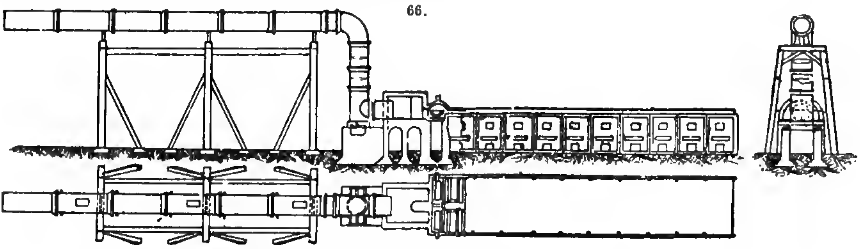
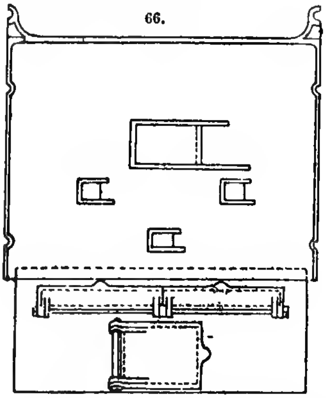


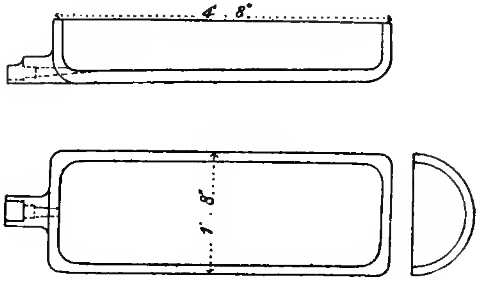
Fig. 66 shows the front of a pyrites kiln as most commonly constructed; these fittings are, however, subject to endless variation, as few manufacturers employ kilns of the same height and shape. The size and position of the charging and working doors are also widely different in different works.

Fig. 67 shows in detail the construction of the nitre pot, which remains stationary in the oven, it being periodically supplied with nitre and warm acid through a hopper, as seen in the preceding figure. The plug in the bottom of the pot admits of the sulphate of soda being run out, the acid supplied being always somewhat in excess, so as to ensure the sulphate of soda being sufficiently soft to flow out easily.

66.



67.

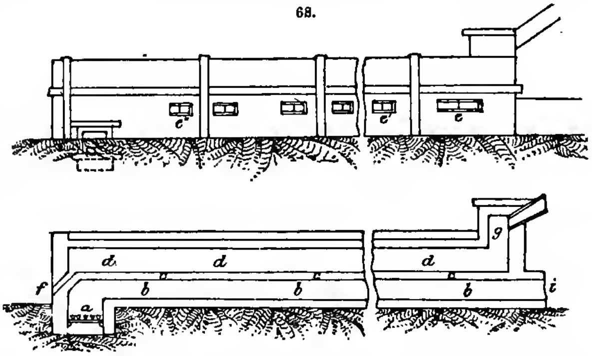


We now come to kilns for burning dust pyrites. As the dust prevents the passage of air when disposed in thick layers, it must be spread in a thin coating over which the draught can pass. The heat generated is so much lessened under the circumstances, however, that the combustion can only be maintained by the assistance of additional heat from without. With this object the dust has been, till recently, burnt in so-called muffle furnaces, having an enclosed roasting space, heated by fire on the outside. Such were also formerly used for roasting copper pyrites, and are still employed for zinc-blende; but they are no longer in use for treating iron pyrites dust for sulphuric acid making, as other and better plans have been devised. Muffle furnaces therefore are no longer to be found in works where sulphuric acid is the chief product, but only where the sulphurous acid from the smelting of ores is applied to the manufacture of sulphuric acid as a bye-product.

A plan common in Germany consists in dividing the kiln into two parts by a low wall, in each of which are placed four fire-clay plates 6 ft. long, 1 ft. 7 in. wide, and 4 in. thick, ranged at 8 in. distance one above another. Each of the eight portions of roasting surface is provided with a door 12 in. wide and 6 in. high, fitted with holes for the admission of air, by which the charge is introduced, and at the back is an opening, 4 in. square, through which the liberated sulphurous acid escapes into a vertical flue, 3 ft. long and 8 in. wide, in connection with the chambers. The nitre pots are inserted in this flue. The whole roasting surface is made red hot by a coal fire; the flame branches into all the flues, but re-unites at one, and escapes by a shaft.

In many Belgian works the dust pyrites is roasted in muffle furnaces having a single fire-bed 30 ft. long × 8 ft. broad. This is made of fire-clay slabs, 3 in. thick, supported by the side walls of the kiln and by several subsidiary walls, 4½ in. thick, and heated from below. In one of the long sides of the kiln three fireplaces are made, the heat from which is divided and spread under the whole of the bed-plate. An arch is turned over the bed-plate so that the roasting space is 16 in. high at the walls and 2 ft. 4 in. in the centre. At one end of the kiln is a pipe which conducts the gases to the chambers. Near this is an opening, that may be closed at pleasure, through which the kiln is charged, and at the opposite end, in the sole of the furnace, is a second opening, 8 in. square, through which the burnt pyrites is withdrawn from the ashpit into which it has fallen. This is shut by an iron door, perforated with holes for the admission of air. In one of the long sides of the roasting chamber four holes are made, at which the workman inserts the tool for raking out the spent dust before inserting each new charge. About five tons of dust can be burnt in this kiln per twenty-four hours, divided into six or eight charges daily, and spread about 3 to 4 in. thick over the surface of the bed-plate. The withdrawal of the burnt ore and the introduction and spreading of the fresh charge occupy about one hour. Besides this the dust must be turned over about every half hour, which occupies ten minutes. It requires two workmen.

68.



In this country Spence's kiln, as shown in Fig. 68, is chiefly used. The fire-lump bed *c*, 30 to 45 ft. long, is heated from below by a fire in the furnace-grate *a*, whilst the pyrites is spread out in a layer about 2 to 3 in. thick on the sole of the chamber *d*. The necessary air enters at the passage *f* (by which also the spent dust is withdrawn) into the roasting chamber, and the gas formed passes at *g* into the leaden chamber. The charge is introduced at the lateral hole *e* farthest from the fire, as the charge immediately before is turned over towards *f*, and thus leaves a space. The tools used for this purpose are inserted at the holes *e*, *e'*, *e''*. By this process the ore is pushed, as it gets poorer in sulphur, always into a hotter part of the kiln, where also the air is richer in oxygen. Thus the burning of the last portions of the sulphur, which is generally so difficult, is greatly assisted, and with due care very little sulphur is left in the ore.

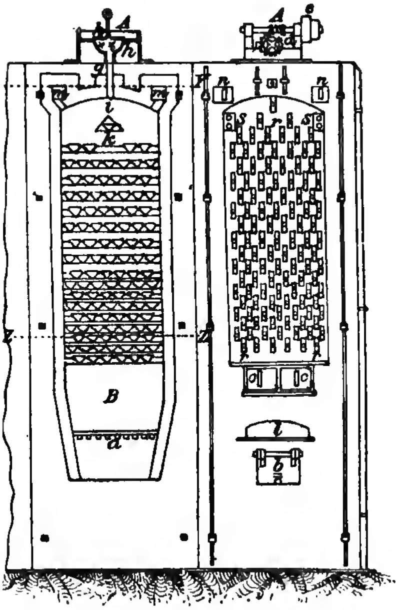
At Swansea these kilns are generally about 30 ft. long, and are charged every two hours with about 10 cwt. of copper pyrites dust, which remains twelve hours in the kiln, thus daily 6 tons of ore are roasted.

Among the newest forms of kiln for roasting dust ores is Gerstenhoefer's, consisting of a tall shaft, while Olivier and Perret's furnace is intended for treating lump and dust ores at the same time.

The former kiln is shown in Figs. 69, 70, 71, and 72. Fig. 69 is partly in elevation and partly in section along the line V V of Fig. 70, the latter being a part plan and a part horizontal section of the former along the line Y Y. Fig. 71 is a vertical section along the line X X of Figs. 70 and 72, the latter being a horizontal section along the line Z Z of Figs. 69 and 71. The main shaft of the kiln, formed of fire-bricks, is about 17 ft. high, 4 ft. 3 in. long, and 2 ft. 9 in. wide.

Before charging the kiln it must be made white hot. For this purpose fire-bars must be put into the furnace *a*, Figs. 69 and 71, and the hole *l*, which will have been opened for this purpose, is re-closed, and a strong fire is made in the grate. The necessary fuel is inserted at the openings *c*, which may be closed with cast-iron doors. The lowest door *b* remains open to admit air. The connection of the kiln with the chambers is shut while the kiln is being heated, and on the other hand a side flue is opened through which the combustion gases escape. When the kiln is white hot the charging is slowly commenced. To keep the burning regular, the ore must be supplied as a dry powder of constant grade, and for this reason it is sifted before use. It is poured into the cast-iron box A, fitted with a wooden hopper, and which contains the apparatus for regulating the admission.

69.



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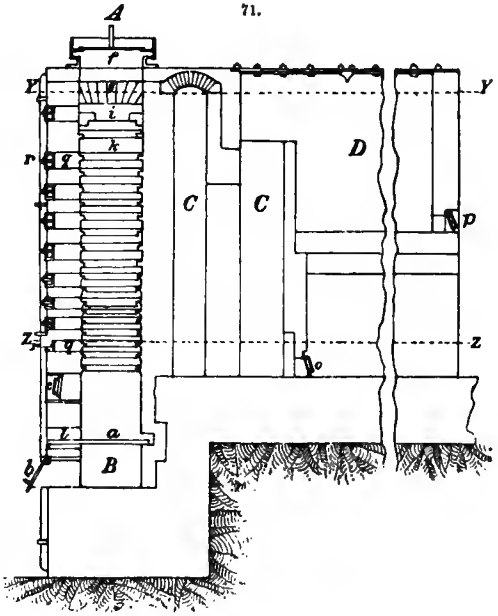

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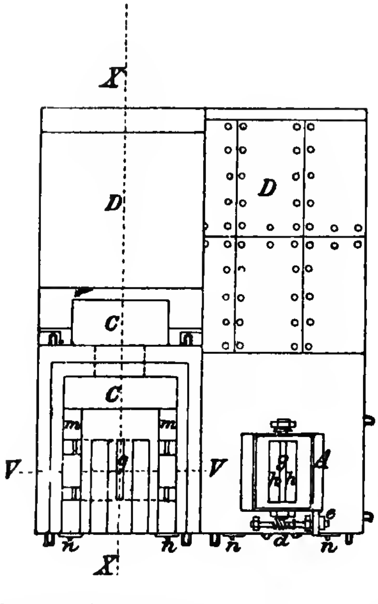

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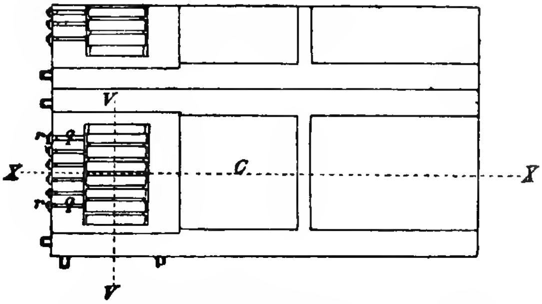
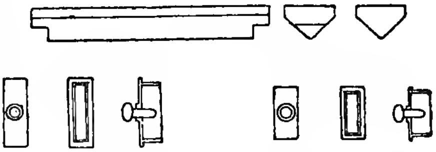


This consists of two corrugated rollers, with ribs about $\frac{3}{8}$ in. broad, 2 in. in diameter in the hollows, and $3\frac{1}{8}$ in. in the ribs, made to revolve regularly by the worm *d* on the pulley shaft *e*. By the pace of these rollers, which at first is only one revolution in five minutes (thus taking seven hours to feed the kiln), the supply is regulated. The cover *f*, above the rollers, can be shut or opened at pleasure, and serves to protect them from the weight of the superincumbent mass of mineral. The ore taken in by the rollers is dropped into the slit *g*, which is shut by the ore lying in the half-cylinder *h* above the rollers, so that no kiln gas can escape. From the slit *g* the ore falls on the fire-clay prism *i*, and thence on both sides to a row of four prismatic fire-clay bars *k*, whence it falls again on to seven such bars lying immediately below. Beneath are fifteen such rows, alternately six and seven bars, and so arranged that the bars above always correspond to spaces below, and the spaces above to bars below. The ore thus falls gradually to the bottom of the kiln B, which serves as a collecting space. As soon as the ore begins to fall upon the fourth row of bars counting from the bottom, the fire is suspended in the furnace *a*. Then the fire-bars are drawn out one by one, the holes left are walled up, the ashpit is cleared out, and the kiln completely closed, save the openings necessary for supplying air. The gases are still allowed to escape for a short time, then the connection between the kiln and the escape flue is altogether closed, and that leading to the chambers re-opened. Formerly *hot* air was forced into the kiln, but now cold air only is used in the roasting of iron and copper pyrites. For sulphides which burn with great difficulty, as zinc-blende, it is preferable to have hot air. The falling ore comes into contact with ascending air in such a way that, in consequence of the oxidization and desulphurization, it constantly finds air richer in oxygen, by which its complete roasting is much assisted.

The sulphurous acid formed and the excess of oxygen and nitrogen from the air admitted leave the kiln at the top through the flues *m* (which are furnished with closing doors *n*, for convenience in cleaning) into the main flue C, and thence through the dust chamber D into the leaden chamber. The openings *o* and *p*, shut with folding iron doors, are used when cleaning the main flue and the dust chamber. This last-named is roofed with iron plates, on which the ore is dried. In the front wall of the kiln are openings *q* corresponding with the spaces between the bars. These are fitted with iron boxes *r*, pierced by round holes furnished with fire-clay plugs. These serve for watching the progress of the roasting, and for the introduction of an iron scraper, should the spaces between the bars become clogged. It is well to see to this every three hours. Also occasionally the dust must be removed from the uppermost part of the kiln, where it accumulates. This is effected through the holes *s* (Fig. 69). The form of the boxes and bars needs no further explanation than the view shown in Fig. 73

73.

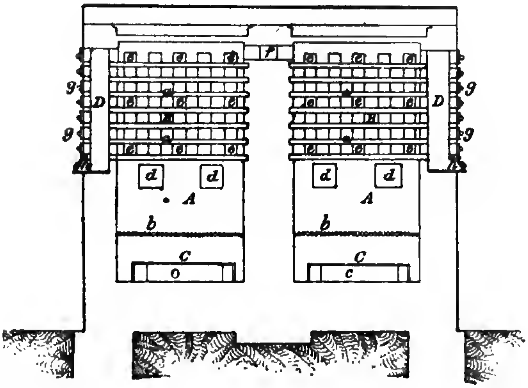


From two to five tons can be burnt daily in this kiln. At this rate the pit B must be emptied every six hours. In order to reduce as far as possible the amount of air thus perforce admitted, the scraper or rake is introduced through a little opening formed in the door *b*. In working the kiln four men are necessary, but they can manage more than one kiln at a time. The result of the working depends greatly upon the care bestowed by the workmen in cleaning the spaces between the bars. In the proper conduct of the working, the greatest heat prevails at the upper part of the shaft, lower down it decreases to low red, whilst the lowest bars cease to glow at all. When air is admitted in too great quantity the heat spreads downwards, and when deficient it retreats upwards; in the former case the kiln becomes too hot, in the latter too cold. When the heat is too great the draught must be diminished, or the supply of ore increased, by augmenting the pace of the rollers. Should fritting of the ore ensue from too rapid combustion, the fault must be checked by substituting spent ore for raw in feeding the kiln.

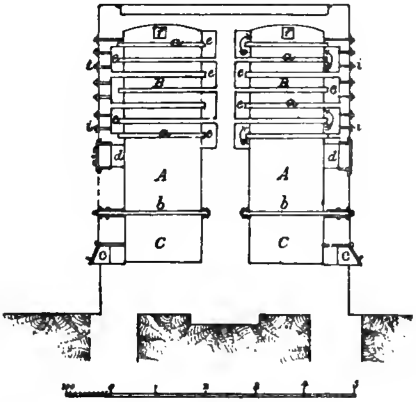
It has been complained of this kiln that a great amount of dust is produced in it, which is continually choking the flues, and that the bars soon wear out. From the latter circumstance it is necessary to fire the furnace three weeks before charging, when starting the kiln, so that the temperature may rise gradually to a white heat. Probably these difficulties account for the fact that when using pyrites simply for making sulphuric acid, manufacturers prefer Olivier and Perret's kiln, which we now proceed to describe.

Fig. 74 shows a vertical longitudinal section, and Fig. 75 a vertical cross-section of this kiln, as arranged four in a group, thus forming an oblong quadrangle. The lump ore is burnt below in the space A, while the dust is roasted above on the seven fire-clay plates, about 4 in. thick, by which the kiln is divided. The under part A is furnished with a fireplace *b*, which is made of four-sided bars that can be turned round, and through which the roasted ore falls into the ashpit C below, as already described. From time to time the ashes are drawn out at the opening *c*, furnished with a tightly shutting iron door. In this door, or better nearer under the fireplace, holes are made in the wall, through which the necessary air finds its way into the kiln, and which may be shut as required by clay plugs. The openings *d*, provided with iron doors, are used when charging the kiln. The dust is spread on the clay slabs *a* about 2 in. thick, and is burnt by the heated gases arising from the combustion of the lump ore in the fireplace of A. These gases ascend through the spaces *e* left in the walls, pass over the surface of the clay plates as shown by the arrows in Fig. 75, and then through the flue *f* to the chambers. The little holes *i*, stopped with clay plugs, allow the roasting of the dust on the slabs to be watched. The slabs are charged through the openings *g*, which can be closed with iron doors, and after perfect roasting the dust is raked into the channel D which lies at the end of the slabs, and extends throughout the whole length of the kiln. This channel D must remain filled with spent ore during the process. When a new charge is to be inserted on the slabs, the channel D is first emptied through the doorway *h*, this is then shut, and the spent ore from the lowest slab is raked into the channel D, whose dimensions are so regulated that it then becomes filled exactly up to the level of the slab. The lowest slab is now supplied with fresh ore, the corresponding door *g* is re-shut, and the spent dust from the second slab is raked into the channel D, which is thus filled just up to the level of the second slab. This is continued till all the slabs are supplied. In this kiln ores may be burnt in the proportion of thirty-five parts lump ore and sixty-five parts dust.

74.



75.



As the kiln gases have such a high temperature as to require cooling before entering the chambers, the heat thus evolved is sometimes utilized for concentrating acid in leaden pans as seen in the figures, or for heating the boiler which supplies steam to the chambers.

Regulating the Operation.—As the percentage of sulphur contained in the material used has very much to do with the conduct of the operation and forms the basis of all calculations, its varying proportions must be ascertained. This may be done in the following manner:—

Pelouze mixes 1 grm. of powdered ore with 5 grm. salt, 7 grm. chlorate of potash, and 5 grm. anhydrous carbonate of soda, fuses the mixture, and keeps it red hot for ten minutes. The sulphur will thus be reduced by the chlorate of potash to sulphuric acid, which displaces a certain part of the carbonic acid and unites with the sodium from which the carbonic acid has been evolved. The fused mass is dissolved in boiling water, and the proportion of carbonate of soda remaining is alkalimetrically measured. From the difference between the amount of carbonate of soda existing before the fusion and that formed afterwards, a simple calculation gives the equivalent of sulphur which was in the ore. When the pyrites contains quartz or silica, the solution in *boiling* water is the more necessary, because in this case the alkaline silicates are not fully dissolved in cold water, and will also interfere with the alkalimetric estimation. This process, moreover, cannot be used for pyrites containing sulphates of alkaline earths, because these will be decomposed by the carbonate of soda.

Another test consists in mixing 1 grm. of the finely powdered pyrites with 3 grm. anhydrous carbonate of soda and the same quantity of saltpetre. This is fused together in a muffle furnace at a red heat, dissolved in hot water and the solution filtered into a beaker. The acid liquid is then boiled for a short time, and the sulphuric acid estimated, whence the equivalent of sulphur can be calculated. This estimation is performed by a solution of chloride of barium, so regulated that 1 cc. of this is equal to 2 per cent. of sulphur.

Or, the sulphur may be determined by dissolving 1 grm. finely powdered ore with 4 grm. chlorate of potash in nitric acid. When the solution is completed, the liquid is diluted and filtered. The filtrate contains the sulphur as sulphuric acid, which may be determined by titrated chloride of barium solution.

The amount of sulphur contained in the burnt pyrites must also be frequently tested in order to check the perfection of the burning in the kilns. The same processes may be adopted for that as we have already indicated for the raw ore, but the sample must be larger on account of the lessened amount of sulphur. For instance, 5 grm. roasted ore may be mixed with 5 grm. carbonate of soda and 5 grm. chlorate of potash, without salt.

The total amount of sulphur contained in an ore is never utilized, even with the best possible working, but a portion always remains in the cinders unburnt. The proportion of loss varies greatly and depends upon the natural quality of the ore, the arrangement of the kiln, and the care bestowed on the roasting. In hard, close-grained iron pyrites, and in copper pyrites, more sulphur is lost than from the porous, gritty iron pyrites found in the coal measures. With the former, the air finds so much difficulty in piercing into the interior of the ore that towards the end of the roasting the further oxidation proceeds very slowly, and thus a portion of the sulphur must be allowed to remain. Under the most favourable conditions the amount of the sulphur left in the ore may not exceed 2 per cent., but as a rule 4 per cent. is wasted. When the sulphuric acid is only formed as a bye-product in the reduction of metallic sulphides, a very much larger proportion of the sulphurous acid is often allowed to escape up the chimney.

In the roasting of pyrites a slight, variable amount of sulphuric acid is formed, free from water, and this finds its way to the chambers with the kiln gases. Besides the sulphur the metals also will be oxidized, and the oxygen thus required will be admitted to the kiln as air, and the proportion required has a considerable effect upon the process.

We shall now consider the points to be observed in working, in the same order as we have already done for using native sulphur.

The Temperature.—Through the oxidation of the metals contained in the pyrites, such an amount of heat is generated that the gases will be much hotter than when sulphur is used, rising even to 200°. For this reason, instead of it being necessary to check any tendency to cooling in the connection flues, it is absolutely necessary to cool the gases somewhat before admitting them to the chambers. This is sometimes effected by passing them up a double-lined shaft formed of thick sheet lead, 30 feet high and 2 feet in diameter, into the outer casing of which cold water constantly flows at the bottom and escapes in a heated state at the top. An arrangement such as we have shown in Fig. 65 is more common, however, and nothing of the sort is needed when Glover's towers are used.

The Draught and Admission of Air.—The proportions of air required for the oxidation of the sulphur contained in pyrites vary considerably. We will see the proportion needed by bisulphide of iron or pure iron pyrites. This consists of—

1 Equivalent Iron .. .. $Fe = 28$, and
2 „ Sulphur .. .. $S_2 = 32$

1 Equivalent bisulphide of iron .. $FeS_2 = 60$, or $46\frac{2}{3}$ per cent. of iron and $53\frac{1}{3}$ per cent. of sulphur.

Though when burning hard iron pyrites all the iron is not oxidized to Fe_2O_3, seeing that sometimes magnetic iron (FeO, Fe_2O_3) is formed, still we must calculate upon the complete oxidation of the iron normally, which is a point endeavoured to be attained in order that all the sulphur may be utilized. Then 2 equivs. or 120 parts of bisulphide require 3 equivs. or 24 parts of oxygen for the oxidation of the iron, and a further 8 equivs. or 64 parts of oxygen for the conversion of their 4 equivs. or 64 parts of sulphur to sulphurous acid. In all 11 equivs. or 88 parts of oxygen are thus needful for the roasting. Besides this, 4 equivs. or 32 parts of oxygen must be introduced for the conversion of the 4 equivs. or 128 parts of sulphurous acid formed into sulphuric acid.

From the preceding it follows that—

1. For every 1000 parts bisulphide of iron are needed:—

200	parts oxygen for oxidation of the iron,
$533\frac{1}{3}$	„ „ formation of sulphurous acid, and
$266\frac{2}{3}$	„ „ conversion of sulphurous to sulphuric acid.
1000	

2. That for every 1000 parts of sulphur used in the form of bisulphide of iron, the following oxygen must be admitted:—

375	parts oxygen for the oxidation of the iron,
1000	„ „ formation of sulphurous acid,
500	„ „ conversion of sulphurous to sulphuric acid.
1875	

As 1 litre of oxygen weighs 1·4298 grm. at 0° C. and 760 mm., the above weights will equal

375	grm. oxygen	= 262·3	litres,	combined with	986·7	lit., nitrogen as air.
1000	„	= 699·4	„	„	2631·1	„ „
500	„	= 349·7	„	„	1315·5	„ „
1875	„	= 1311·4	„	„	4933·3	„ „

Theoretically each 1000 grm. sulphur burnt out of the bisulphide of iron will require the admission of 1311·4 + 4933·3 = 6244·7 litres of air at 0° C. and 760 mm.

To this an excess of oxygen must be added, and manufacturers are agreed that a greater excess is necessary with pyrites than with sulphur, and that it should amount to 6·4 parts by volume for each 93·6 parts nitrogen escaping from the chambers, or 6·4 per cent. by volume of the mixed gases in a dry state. Let x equal the unknown percentage of excess oxygen which must be admitted, and the volume of nitrogen from which it must be liberated is $\frac{79}{21}x$ litres. The amount of these two gases joined to the 4933·3 litres nitrogen introduced with the oxygen required for the formation of the sulphuric acid from the sulphur will give a volume of

$$4933{\cdot}3 + x + \frac{79}{21}x = 4933{\cdot}3 + \frac{100}{21}x.$$

But $x = \frac{6{\cdot}4}{100}$ of this volume, therefore we have $x = \frac{6{\cdot}4}{100}\left(4933{\cdot}3 + \frac{100}{21}x\right) = (x = 454{\cdot}1)$.

Besides the theoretical 6244·7 litres of air necessary for every 1000 grms. or 1 kilo. of sulphur burnt from pyrites, there are then 454·1 litres of excess oxygen necessary, which is combined with $\frac{454{\cdot}1\ ;\ 79}{21} = 1708{\cdot}4$ litres nitrogen; that is, 2162·5 litres of air or a total of 8407·2 litres of air at 0° C. and 760 mm. We have already seen that each 1 kilo. of native sulphur requires 6199 litres of air at 0° C. and 760 mm.; therefore, when the sulphur is derived from bisulphide of iron it needs $\frac{8407{\cdot}2}{6199} = 1{\cdot}356$ times as much air.

This proportion does not remain constant in the amount of gases admitted to the chambers. In burning pyrites, a part of the oxygen remains behind with the iron, while in burning brimstone the total volume of air finds its way to the chambers without any change of volume, because oxygen does not alter its volume by combination with sulphur to form sulphurous acid. The 8407·2 litres of air admitted to the kilns for each 100 grm. of sulphur from bisulphide will produce an amount of gas passing into the chambers, as follows:—

	699·4	litres sulphurous acid, having the same volume as oxygen.
	349·7	,, oxygen, for conversion of sulphurous to sulphuric acid.
	454·1	,, ,, in excess.
	4933·3	,, nitrogen, theoretically attached to the oxygen as air.
	1708·4	,, ,, ,, excess oxygen ,,
Total	8144·9	litres,

of which 699·4 are sulphurous acid, 803·8 are oxygen, and 6641·7 are nitrogen; or proportionally 1 volume of the gas consists of

0·0859	sulphurous acid.
0·0987	oxygen.
0·8154	nitrogen.
1·0000	

In many works the sulphurous acid amounts to much less than 8·59, and is even under 6 per cent. of the gas volume. It is evident that in that case the amount of sulphuric acid formed in a similar chamber space will be reduced unless at the expense of an increased consumption of nitre.

According to previously given scales, 1 litre of the above gas will weigh (at 0° C. and 760 mm.) 0·0859; 2·8731 + 0·0987; 1·4298 + 0·8154; 1·2562 = 1·4122 grm., while 1 litre of the gas which passes into the chambers from the combustion of native brimstone weighs 1·4547 grm. The gas derived from pyrites is therefore lighter, and consequently creates a stronger draught than that from native sulphur.

As the amount of gas conveyed to the chambers for each 1000 grm. of sulphur as iron pyrites is 8144·9 litres, while that from 1000 grm. of native sulphur is only 6199 litres, then a certain weight of sulphur in pyrites produces $\frac{8144{\cdot}9}{6199} = 1{\cdot}314$ times as much gas as the same weight of sulphur in a free state.

The knowledge of this proportion is sufficient to enable the conduct of the process to be regulated in the same manner as we have already described for sulphur.

The Steam.—What has already been said regarding the admission of steam in the manufacture from native sulphur holds good also in this case. The supply, however, will vary because the volume of gas produced from pyrites is 1·314 times as great as that formed by brimstone, and because under constant conditions of temperature and pressure, the amount of steam that can be contained in the gases is in direct proportion to their volume. Consequently 1·314 times as much steam may be used with pyrites. As we have seen that 30·5 per cent. of the necessary water can exist as steam in the gases, that amount will be increased with pyrites to 30·5 ; 1·314 = 40·08 per cent.

The Passage of the Gases through the Chambers.—As the gases derived from the combustion of pyrites at the time of entering the chambers are lighter than those formed in the roasting of native sulphur under similar conditions, while on leaving the chambers they are somewhat heavier on account of their holding somewhat more oxygen, it is evident that the increase of weight in the gases during their passage will be even greater in the case of pyrites than in that of brimstone. The following figures will show the proportions.

We have already seen that a litre of gas is increased in volume on its passage to the chambers to 1·346 litre as it enters the first chamber, and the weight of this 1·346 litre will be 1·5230 grm., or 1 litre will weigh 1·1315 grm. This 1·098 litre of gas leaving the chambers will weigh, according to preceding calculations, 1·2861 grm., or 1 litre will weigh 1·1713 grm.

It is therefore evident that the same rule concerning the manner of conducting the gases through the chambers will hold good in this case as in that of acid made from brimstone.

In some cases, however, where the gases are first taken through a flue several hundred feet in length, in order to deprive them of their arsenic to a certain extent, they become cooled to such a degree that, together with the loss in weight of arsenious acid, they actually become lighter instead of heavier, and in consequence it has been necessary, as at Freiberg, to construct the chambers on the opposite plan, the gases entering in each case at the bottom and leaving at the top. But the gases in this case enter the chambers at a temperature so low as 27° (80° F.), and it is a question whether the acid can be so beneficially made at that degree. Further, they cannot hold more than 10·5 per cent. of the necessary water as steam.

Division of the Labour.—This depends entirely upon the class of kiln used, and has already been sufficiently treated under each kiln which has been described.

The "observation of the process" and "recovery of the nitrogen compounds," as described for the manufacture from brimstone, remain unaltered.

Working Results.—In consequence of the fact that the same quantity of sulphur from pyrites produces 1·314 times as much gas as native sulphur, the chamber space will have to be 1·314 times as great for the former as for the latter, or what comes to the same thing, the amount of sulphur burnt in the former case must be only $\frac{1}{1\cdot314}$ of the amount of native sulphur burnt in a similar time.

The dilution of the chamber gas with nitrogen, owing to the oxidation of the metallic portions of the pyrites, has an evil effect in necessitating an augmented consumption of nitre. Instead of 6 per cent., which suffices for native sulphur, 10 per cent. upon the amount of sulphur oxidized from the pyrites will be requisite. These 10 parts of nitre are equivalent to 7·41 parts monohydrated nitric acid, or 13·72 parts of nitric acid at 69° Tw. The proportion of this which may be economized by the Gay-Lussac tower, remains the same as for brimstone.

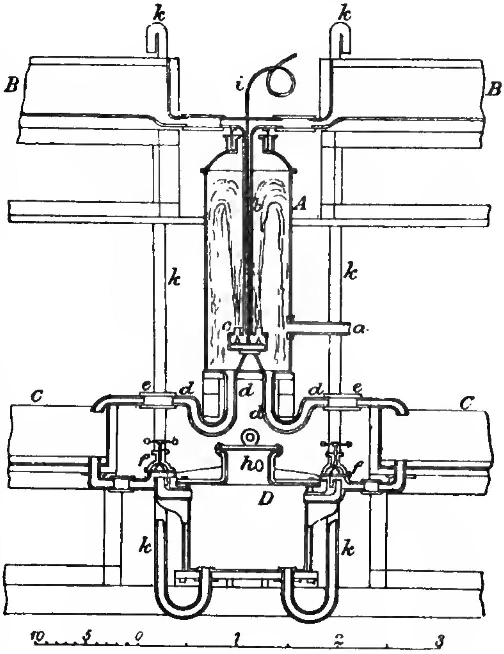
When the pyrites used contains 46 per cent. of sulphur, 4 parts of which are left in the cinders, the 42 parts of sulphur converted will yield about 128 parts of sulphuric acid at 170° Tw., that is, 100 parts of sulphur converted give 304·76 parts of acid at 170° Tw., or 283·43 parts of monohydrate. As the theoretical maximum possible make is 306·25 per cent. of monohydrate, the loss amounts to 7·45 per cent., besides the sulphur wasted in the pyrites cinders. Having already given full instructions concerning the manipulation of a brimstone acid works, and also enlarged upon all the points in which the conduct of the process with pyrites differs from that with brimstone, and the precise degrees of those differences, it will be easy to deduce the figures corresponding to any desired scale of manufactory.

REMOVAL OF ARSENIC FROM SULPHURIC ACID.—In many French works the sulphuric acid is freed from arsenic by sulphide of barium. The sulphate of barium formed falls to the bottom of the vessel with the sulphide of arsenic. In Germany, sulphuretted hydrogen gas is more generally used. At the ochre mines in the Harz Mountains, where sulphuric acid is made as a bye-product, and contains besides ·11-·14 per cent. of arsenious acid, ·02-·05 per cent. of sulphate of lead, and smaller proportions of antimony, copper, iron, lime, and potash, the following method of purification is adopted:—

The precipitation of the arsenic, lead, antimony, and copper is performed in a leaden pan about 8 ft. long by 3 ft. 6 in. wide and 1 ft. 9 in. deep, in which the acid is diluted to about 93° Tw. and heated to 75° (167° F.). The dilution of the acid to that degree is considered advisable because stronger acid decomposes more readily with sulphuretted hydrogen. At the bottom of the pan lies a leaden false bottom, or tray, perforated with small holes, whose edges are turned down about 2 in., so that the tray is suspended at about that height from the floor of the pan. The upper surface of the false bottom measures about 3 ft. 6 in. × 1 ft. Underneath it and within the down-turned edges, a leaden pipe is introduced by which the sulphuretted hydrogen gas is admitted, and which streams up through the holes and into the supernatant acid. The pan is closed by a leaden luted cover in which is a pipe for conveying away the excess of sulphuretted hydrogen. The pan holds about 2 tons of acid, whose purification will be complete in about six hours. The completion of the precipitation of the arsenic may be recognized in that the acid then commences to assume a milky appearance. Acid thus purified is said to contain but ·0003 per cent. of arsenic.

The sulphuretted hydrogen required is prepared from sulphide of iron (produced by smelting 280 parts of old iron with 115 parts of sulphur) and sulphuric acid of about 110° Tw. from the chambers. For this purpose four cylindrical leaden vessels are used, about 14 in. in diameter and 18 in. in height. In the arched cover of each vessel, besides the gas pipe for carrying the sulphuretted hydrogen to the pan, is an aperture for the insertion of the sulphide of iron which may be tightly closed by means of a screw and a funnel-topped bent tube for admitting the necessary sulphuric acid. For the purification of the 2 tons of acid which the pan holds, about 100 lb. of sulphide of iron and 110 lb. of sulphuric acid at 110° Tw. are needed.

76.



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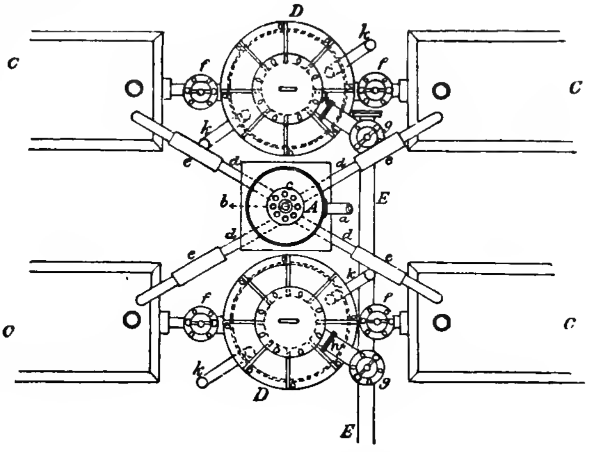


At Freiberg, the precipitation of the arsenic by sulphuretted hydrogen gas is conducted in an apparatus by which the loss of this gas is much less than in the preceding method. It is also unnecessary to dilute the sulphuric acid to be treated, as it is not subjected to heat. Fig. 76 shows a vertical section, and Fig. 77 a plan of this apparatus. A is the so-called precipitation tower formed of lead, and about 7 ft. 6 in. high and 2 ft. 6 in. in diameter. The sulphuretted hydrgen is conveyed to the tower from the generating vessel by the leaden pipe *a*. The sulphuric acid to be purified runs from the leaden chambers direct into the lead-lined cisterns D. These are in connection with the leaden tube *b* running down the centre of the tower and terminating below in a shallow box, provided with eight little holes *c*, through which the acid is forced in fine jets by the hydrostatic pressure in the pipe *b*. The great distribution thus achieved considerably assists the precipitation of the arsenic. The jet holes can be closed by raising the lead-coated iron rod *i*, which is furnished with little cones fitting exactly into the holes. The purified acid flows through the pipes *d*, which can be shut by pinch-cocks on the indiarubber parts *e*, into the cisterns C beneath. From here it is either run into the concentrating pans after having deposited the sulphide of arsenic, or it is let into the forcing apparatus D, from which it is again raised into the cisterns B, should it be found necessary to treat it once more. For this purpose the valves *f*, made of indiarubber and furnished with screw wheels, are opened. As soon as the forcing apparatus is full the valves are closed again, and air is forced into the apparatus at *h* through the pipe E, which is provided with a valve *g*, and this forces the acid up the pipes *k* into the upper cisterns. The forcing apparatus are formed of strong iron cylinders lined with sheet lead, the valves and other parts are of spelter.

More recently an improvement has been made in this apparatus, consisting in substituting horizontal prisms, such as in Gerstenhoefer's kiln, for the jets, these prisms being flat-side uppermost and formed of hollow sheet lead.

The treatment of the acid with the sulphuretted hydrogen is repeated as many times as necessary, until after remaining for some time in contact no more signs of arsenic are shown. Generally three repetitions of the process are sufficient to render the acid quite free from arsenic. The precipitated sulphide of arsenic is allowed to settle in large lead-lined tanks, and the clear liquid acid is forced by a leaden pump into the reservoir which feeds the leaden concentrating pans. The yellow sediment of sulphide of arsenic is well washed, and then sent to the arsenic smelters.

Formerly the gas generating apparatus consisted of several leaden vessels communicating with each other, and provided with an outer jacket, in which steam was made to circulate in order to warm the apparatus; now, however, a single large square leaden tank is used for the purpose. The gas passes from this tank into a leaden washer half-filled with water, provided with two little glass windows through which the process may be observed. From the washer the gas is taken direct to the precipitating tower.

Concentration of Sulphuric Acid.—The sulphuric acid made in the chambers is not strong enough for many of the purposes to which it is applied. The acid can be concentrated by boiling, however, which causes the evaporation of a part of the water with which it is combined. This may be performed in leaden pans up to a strength of 1·750 sp. gr.; but the higher the concentration the greater the difficulty in disengaging the combined water, so that the temperature at which evaporation takes place rises rapidly and an increasing proportion of acid is distilled over at the same time. The acid cannot be concentrated to monohydrate by simple evaporation of the water, but moderately strong acid will be distilled and must be afterwards condensed. As acid of more than 1·750 sp. gr. attacks lead very powerfully, and the boiling point of monohydrated acid is very nearly equivalent to the melting point of lead, the concentration is not carried beyond that point in leaden vessels, but in retorts of platinum or glass.

When the acid is to be concentrated in platinum vessels, it must first be perfectly purified from nitrogen compounds, as that metal is very rapidly destroyed by them. Nitrous acid, as we have already said, can only be present in a form of combination with the sulphuric acid in crystallizable proportions, from which it cannot be eliminated by simple heating; on the contrary, nitric acid can be so removed from the sulphuric acid when the latter contains sufficient water. Opinions have differed as to whether the sulphuric acid should be freed from nitrous and nitric acids before or during the process of concentration. A simple method consists in treating the acid with sulphurous acid during the concentration Fig. 79 shows a vertical cross-section of the arrangement of the apparatus H. It consists of a leaden vessel similar to the pan A, except that it is deeper, shorter, and narrower. A cover is formed over the vessel, and in the space above the acid the sulphurous acid introduced from the kiln through the pipe B can circulate freely. Its passage is directed by the two partitions *a*, the first of which extends from the nearer side of the pan to within a very short distance of the farther side, while the second starts from the farther side and reaches almost to the nearer side, and through these spaces the sulphurous acid has to pass. The excess of sulphurous acid finds its way to the chambers through a pipe provided for the purpose. The sulphuric acid enters the pan by the pipe E.

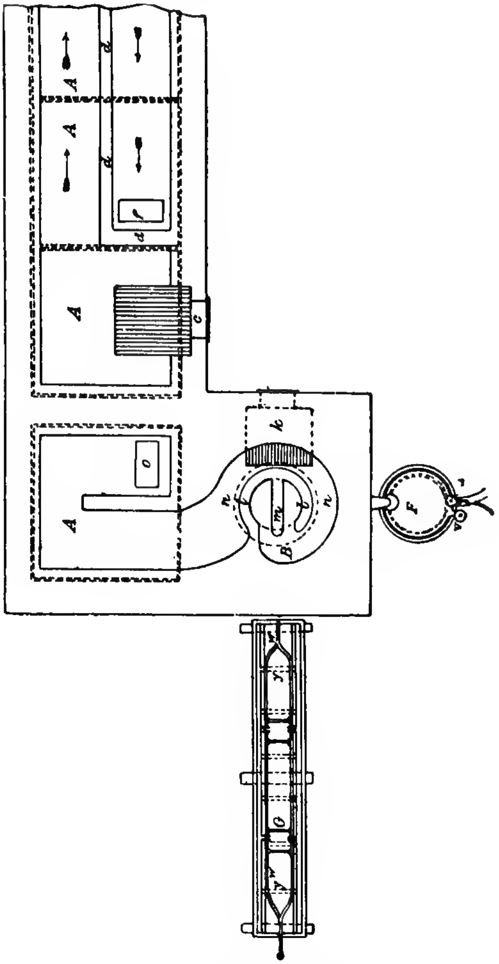
Instead of the foregoing arrangement a leaden pan may be built into the kiln flue and domed over. Into this the weak acid is run, and the kiln gases are passed over it on their way to the chambers. As these gases are very hot the acid will be considerably concentrated without the aid of any other fire, whilst the steam liberated will effect a certain economy in the consumption of fuel in the steam-boiler for supplying the chambers.

This plan of denitrating the acid by means of sulphurous acid is not worth very much, unless the acid be much weaker than that made in the chambers when the process is well conducted. The reason of this is the before-mentioned fact that the crystallizable combination of sulphuric and nitrous acids when dissolved in strong sulphuric acid is very easily decomposed by water, but that the operation by means of sulphurous acid is very difficult.

The most reliable plan of denitrating the sulphuric acid during concentration in leaden pans is by the addition of a small quantity of sulphate of ammonia. With tolerably good working the acid will contain only so much nitrogen compounds that ·1–·5 per cent. of the ammonia salt will suffice.

One authority suggests that sulphur may be used for the same end. Flowers of sulphur are best, and may be introduced in little capsules of hard stoneware into the first pan, in which the temperature does not reach the fusing point of sulphur, and where the acid is richest in water. Great caution must be exercised, however, that no sulphur finds its way into the other pans, as strong hot sulphuric acid is reduced to sulphurous acid by the presence of sulphur. As 1 part of sulphur will decompose 6⅛ parts of monohydrated acid, the loss may be very considerable. For the same reason, precautions must be taken that flowers of sulphur formed in the chambers through sublimation in the kilns shall not find their way into the concentrating apparatus. Organic substances, such as sugar, have also been proposed, but the same care must be exercised that no excess should pass into the subsequent pans. Another recommends crystallized oxalic acid.

We now proceed to describe the conduct of the concentration, and the apparatus in which it is effected. We have already referred to the cisterns into which the chamber acid may be run in order to gauge the quantity made, and which are marked M in Figs. 37 and 38. The acid is run from here by means of a leaden channel or pipe, either into the concentrating apparatus or first into the apparatus where it is to be treated with sulphurous acid. In order that the cistern M may be emptied as rapidly as possible, it is better to have a second cistern intervening from which the flow of acid is made continuous and in exact accordance with the rate of evaporation.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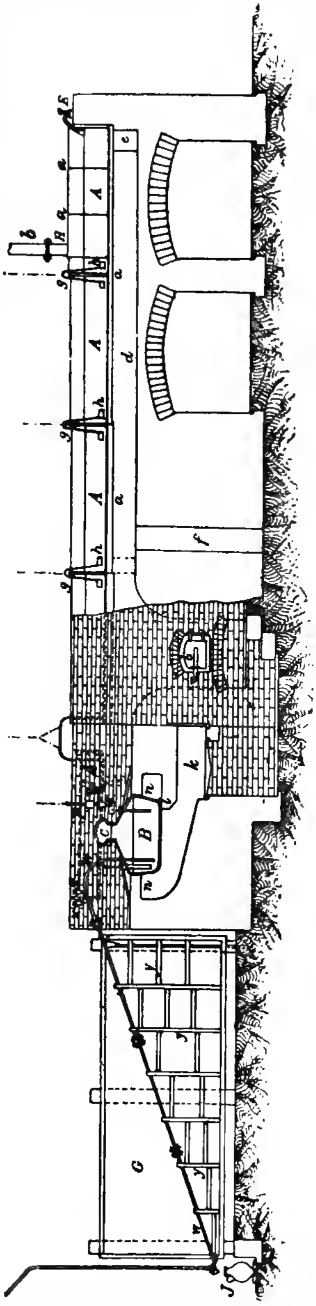
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Fig. 78 is a plan, and Fig. 79 a longitudinal section, of a concentrating apparatus, with platinum still suited to the preparation of about $1\frac{1}{2}$ ton daily of acid at 1·850 sp. gr., which is about the quantity produced by the chamber system we have described. The apparatus consists of five leaden pans A, one below the other, and a platinum still B, besides a hood and other accessories. The leaden pans are uncovered, except when the acid is to be treated with sulphurous acid in the first pan, which is then furnished with the apparatus H already described. The acid flows from one pan to the next, through the siphons *g*. These are similar to those already described in connection with the cistern M. Each pan is 5 ft. square. The first, into which the fresh acid flows, is about 15 in. deep, each lower one being a little shallower than the preceding, so that the last which feeds the platinum still is only about 11 in. deep. The pans are made of sheet lead about ¼ in. thick. They rest on cast-iron plates *a* supported by brickwork, which are generally about 2 in. thick where they lie just over the fire, decreasing to about ¾ in. as they recede from the point of greatest heat. The four first pans are heated by a special furnace, the door *b* of which is seen in Fig. 79 and the fire-bars *c* in Fig. 78. The flame spreads under the whole of the bottom of the pan lying just above the furnace, and is then conducted by the wall *d* under one-half of the three upper pans, turns at *e*, Fig. 79, round the end of the wall *d*, traverses the other half of the three upper pans, and escapes finally by the flue *f* into the chimney. These four pans lie quite close to each other, wall to wall, without being separated by brickwork. Each of the three upper pans has a lip hammered in the edge, by which the acid can run from one to another if by any accident the siphons should become stopped, or the supply of acid be admitted too fast.

From the last pan the acid flows to the platinum still B, whose greatest diameter is 33 in., and the height to the rim *i* on which the hood rests is 20 in. This size will hold about 320 gallons. The lower part is made entirely of one sheet of platinum for greater strength. The upper parts are joined by pure gold soldering with a hydrogen flame. The still is heated by the furnace *k*. Formerly the bottom was allowed to rest on brickwork, so that the flame acted only on the sides. In this manner, however, the consumption of fuel was very great and iron rods were substituted, but these were very quickly destroyed, so that finally the fire was allowed to play direct on the bottom of the still. It rests with the bottom edge on brickwork *l* and is supported in the middle by an additional wall *m*. The flame passes under the bottom of the still, round its sides by the flue *n*, and thence under the fifth pan. From there it passes by the flue *o* into the chimney. The projecting portion of the brickwork covering the flue *n*, is covered with an iron plate reaching about 4 in. over the still. This plate, and that part of the still which does not lie in the brickwork, is plastered with clay to lessen the cooling and condensation of the vapour formed. By this plan the fuel is economized and the production increased.

The still is fed with acid through the siphon *p*, one end of which dips into the last pan and the other into a little leaden vessel *q*, furnished with a spout. In order that the siphon should regulate the outflow according to need, it hangs upon a chain running over the pulley *r*, which can be raised or lowered. From the vessel *q*, the acid flows into a platinum funnel-mouthed pipe *s*, and thence into the still whose neck is fitted with a little hole for receiving the pipe *s*. The pipe itself is closed by the acid lying in the still. Besides this, a little box between the pipe and the funnel mouth through which the acid has to pass, serves to make the arrangement air-tight. This box has two partitions, one fastened to the top, and allowing communication at the bottom only, the other fastened to the bottom, and permitting communication only at the top. The acid flowing through these, cuts off the passage of gases. A platinum float indicates the level of the acid in the still. It plays in a pipe which is fixed to the still in the same way as the feed pipe.

The hood C is thrust into the wide neck of the still in such a way that a strong rim on it fits on to the rim of the still. Between the two flanges is placed a thin layer of asbestos, and the two are then brought into close contact by iron bolts. The arm of the hood opens into a leaden ball D, to which it is fastened by screw bolts on the flanges, and the joint made with putty. To this ball is secured a leaden worm, in which the weak evaporated acid is condensed, and collects in the cistern E. The worm is contained in the lead-lined vessel F, into which cold water constantly flows from below by the pipe *u*, and escapes above in a warmed state at the lip *v*.

The concentrated acid is drawn off by means of the platinum siphon *w*. The short arm of the siphon reaches fully to the bottom of the still. The long arm passes through the cooler G, into which cold water is constantly introduced by a pipe at the bottom, and flows away from the top of the other end. The portion of the siphon that traverses the cooler is split into two halves, in order to facilitate the cooling. It is closed or regulated by a tap, sometimes made of gold, but now more generally of platinum. To ensure sufficiently rapid outflow, the tap must be at least 1 ft. 6 in. lower than the bottom of the still. The siphon is set by means of the two little funnel-topped platinum tubes *x*, so arranged that their tops are higher than the highest part of the siphon.

After closing the top of the siphon and opening both the feed pipes so much sulphuric acid is poured into one of them as suffices to completely fill the siphon by which the air is expelled at the second pipe. Their stoppers are then replaced. For ease in moving and handling the siphon it is made in several, generally four, pieces fitting one into another, and provided with flanges that may be tightly compressed with screw bolts. A wooden trestle *y* supports the siphon. The concentration is carried on day and night, and by having the furnaces in juxtaposition, as we have shown, one workman can easily conduct the operation.

The surface of the five leaden pans is more than sufficient to concentrate all the acid made by the chamber system we have given from 100° to 150° Tw., at such a gentle heat that very little acid will be distilled with the water. The acid is fed continuously into the first pan, and the flow through the apparatus is so regulated that the acid leaving the fifth pan is about 133° Tw. when hot, or 150° Tw. at 15° (60° F.). The still is filled to the level of its greatest diameter, and the depth of acid is regularly maintained at this point. The concentration may be made either continuous or intermittent.

With the continuous process the siphon tap is opened to such a degree that the acid which the still is capable of concentrating flows out in a continual stream, and at the same time so much acid is supplied to the pans as will suffice to keep the level in the still at the proper height. The level of acid in the still can always be seen by the float. The strength of the distillate forms a convenient guide as to the strength to which the acid is being concentrated. If the distillate registers 90° Tw., the concentrated acid will be about 167° Tw., which is the highest grade that can be reached with continuous concentration, on account of the effect constantly exercised by the weak in-flowing acid. With continuous firing something like 34 cwt. of acid can be concentrated with this apparatus.

If it be important that the acid shall be more than 167° Tw. the intermittent process must be adopted. In this case the exit tap is closed until the distillate shows about 100° Tw. As soon as this point is reached the supply from the pans is stopped and the fire increased, and a portion of the acid drawn off as rapidly as possible into carboys. The quantity drawn off must never be so great that the level in the still sinks below the top of the flue *n*, for the still would be very rapidly destroyed if the fire were allowed to play upon parts which were not covered with acid. Probably about 2 cwt. may be drawn off each time without harm. As soon as this has been done the still is refilled from the fifth pan, whose communication with the fourth pan must at that time be suspended, or a quantity of weak acid may find its way into the still.

When the work is properly managed the still may be tapped fifteen times daily, thus producing about 30 cwt. of acid at 170° Tw. It is natural that the production by this method be much less than with continuous firing, on account of the suspension of the firing during the time that acid is being drawn from the still.

The most advantageous process is undoubtedly the continuous, by which the smallest amount of fuel is consumed in proportion to the make of acid, and by which the damage to the still is least on account of the almost constant degree at which the temperature is maintained.

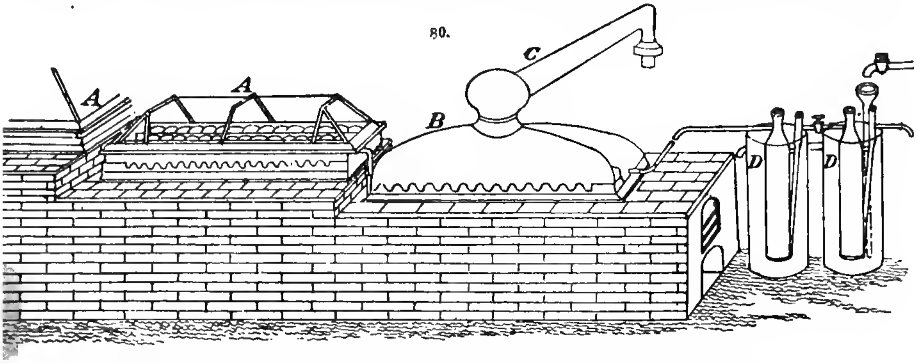
The concentrated acid flows into glass carboys holding from 1¼ to 2 cwt. These are packed in wicker baskets with straw, and closed with stoneware stoppers cemented with molten sulphur. Over these soft clay is put, and then pieces of coarse sacking are tied down round the neck. The distillate is so much purer than ordinary chamber acid that in some cases it may be conveniently used; in other cases it is run back into the basin of one of the chambers.

The total loss of acid during the operation should never exceed 1 to 2 per cent.

The amount of fuel needed will be about 11 cwt. of good steam coal.

The following illustration, Fig. 80, shows the most recent form of platinum pan and still, manufactured by Messrs. Johnson, Matthey, and Co., of Hatton Garden. A A are platinum pans, with corrugated bottoms and longitudinal or transverse partitions, exposed to the flame in the flue. They can be worked in series, replacing the thick leaden tanks now employed for concentration of the chamber acid. B is a platinum boiler, with corrugated bottom and partitions to receive the acid, at 60° Baumé, or above, from the pans A A, completing the concentration to 66° Baumé (1·845 sp. gr.). C is a head and arm for carrying off the vapour to a leaden condenser (not shown) or direct into the chamber for utilization, if required. D is a flask cooler, to receive the concentrated oil of vitriol from the boilers, and to pass it, cooled, into the carboys; the leaden water-jacket should be so arranged that the cold water may have the greatest possible amount of cooling power.

80.



This is the newest form for the concentration of sulphuric acid, securing great strength, productive power, safety and economy in working, and highest degree of purity of acid, with a minimum of platinum.

By the corrugated form of bottom (Prentice's patent) the greatest possible amount of strength, surface, and consequent evaporating power is obtained in the boiler or still, and a considerable saving in fuel is effected. By means of the pans the large and costly leaden tanks for the previous concentration of the chamber acid, which require constant repair and renewal and more or less contaminate the acid, can be to a great extent done away with. The setting of these boilers and open pans is of the simplest kind: they are placed upon an iron frame over a straight flue, and they may be multiplied or enlarged to any desired capacity of production, without sacrifice of existing plant. Pans of lead (or any suitable material) of the same form or principle employed for the first concentration of the chamber acid, are included in this patent. The cooler is of an improved economical and convenient form, easy to clean, and securing great cooling power with a minimum of water and space.

Briefly, the chief advantages of this construction are:—Great economy in first outlay and in daily expense of working: this may be estimated at about 50 per cent. each in the first weight of platinum and in the consumption of fuel. Great intrinsic value in a realizable form in proportion to the cost. Purity of acid. And freedom from danger.

In making the necessary joints, this firm has long since abandoned the use of gold; nothing but pure platinum being employed throughout the apparatus.

Fig. 81 represents the most recent Continental disposition of leaden and platinum concentrating apparatus, the novelties of which consist of compactness of arrangement, and especially the adaptation of gas as a heating medium throughout. The platinum retort or boiler is shown at A A^2, the platinum pans at B B^2 and C C^2, and the leaden concentrating pans at D D^2, E E^2, F F^2, G G^2, H H^2, and K K^2.

The chamber acid enters the leaden concentrating pan D D^2, at a strength of 91° Tw., leaves the last leaden pan K K^2 to enter the first platinum pan C C^2 at 113° Tw., leaves C C^2 to enter B B^2 at 148° Tw., and leaves this last platinum pan at 161° Tw. to enter the retort, which it leaves concentrated to 170° Tw.

The part lettered A^3 to K^3 shows the arrangement of the flues whereby the heat is led under the platinum retort and pans, and leaden pans, until it escapes into the opening M M leading to the chimney.

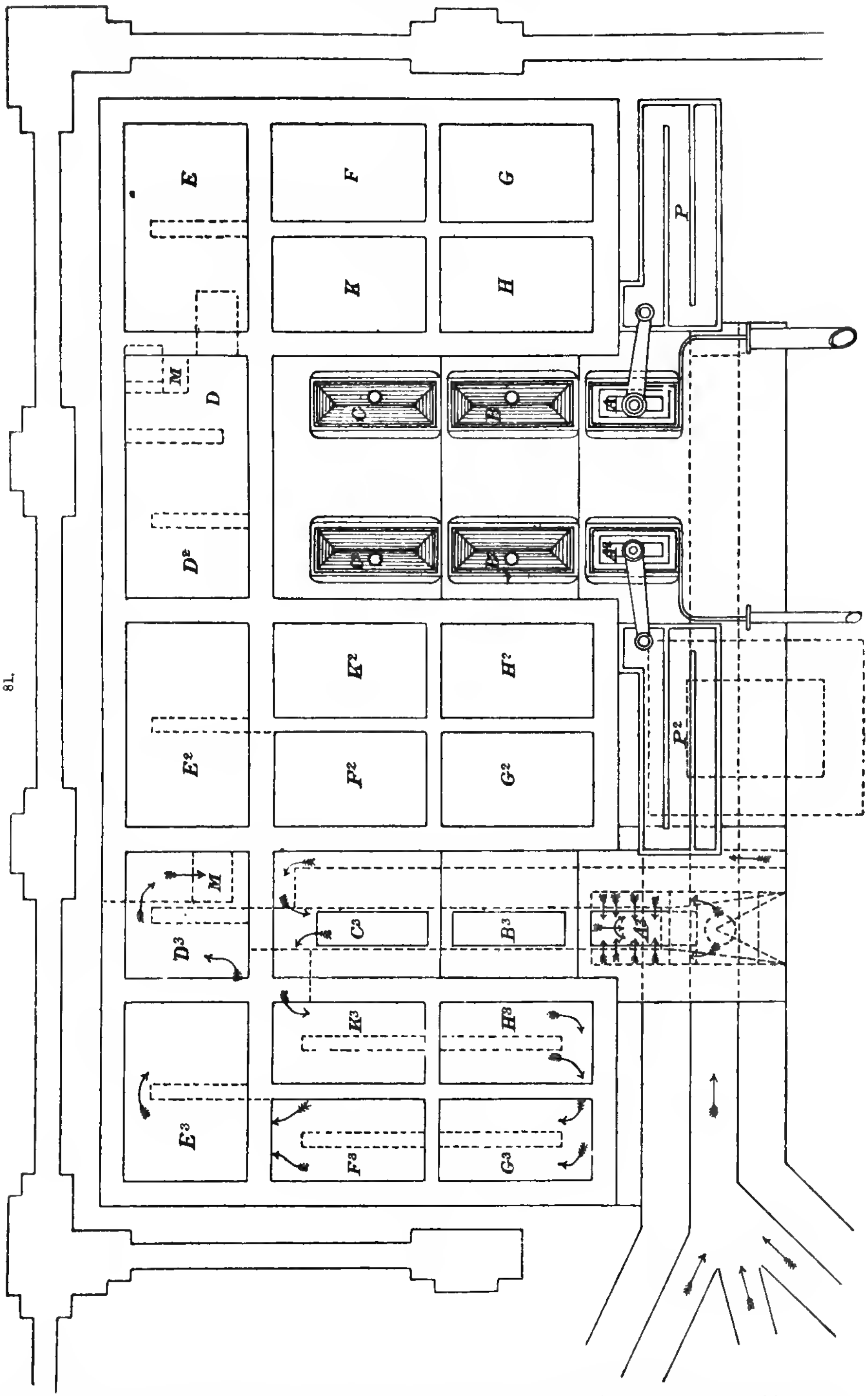
The acid vapours, escaping from the platinum retort or boiler A A^2, are condensed in the horizontal leaden worm lying in the trough P P^2, which is filled with water; this worm is about 4 in. internal diameter, and 45 ft. long.

Concentration in Leaden Pans and Glass Retorts.—Before the adoption of platinum vessels for completing the concentration of the acid, large glass retorts were used, and these are still employed in works where the glass can be bought at a low figure, or where the quantity of sulphuric acid needed in a concentrated state is small, or where the manufacturer has not sufficient capital to afford a platinum still.

The retorts may be set in two rows in a gallery furnace, and are filled with pure acid at 150° Tw. The number of retorts fed by one fire will depend upon the class of fuel used, as well as the size of the retorts. Formerly the retorts were protected against sudden changes of temperature by sand baths in iron pots, but more recently other materials have been adopted without any great benefit that we know of. The jumping of the acid during the boiling is prevented by putting some small pieces of glass or platinum into the retort. Sometimes a leaden pan is provided underneath the retorts for catching the acid in case of a fracture occurring. The glass of which the retorts are made must be free from alkali, or the acid will attack them rapidly. They are of various dimensions, but those holding about 3 cwt. are most convenient.

The steam evaporated is conducted away by glass arms fitting into the necks of the retorts, and condensed for use in the chambers in lieu of water or steam. The great drawbacks to glass retorts are that they consume very much more fuel, and that they are constantly liable to accidental breakage, on account of their necessary fragility. The retorts used in this country are cylindrical, about 33 in. high and 20 in. in diameter. Each retort is fired from a separate furnace. The top of the retort is provided with a short wide neck, into which a glass arm is fitted for carrying off the steam. The retorts are filled and emptied by means of leaden siphons, the process being intermittent. It is convenient to allow the acid concentrated during one day to remain in the retorts till the following morning, so that it may cool somewhat during the night.

SULPHURIC ANHYDRIDE.—Of late a demand has sprung up for a more powerful acid than the monohydrate, and hence sulphuric anhydride has come to be manufactured, and is applied with great advantage in the preparation of aniline dyes and in the purification of ozokerite and other similar products, but as yet the manufacture is restricted to very narrow limits, as the cost of the article as at present made is greatly in excess of that of monohydrated acid. There is no doubt



18

that with time such improvements will be introduced into the manufacture as will enable it to be sold remuneratively at a reduced price, when its employment will be vastly increased. At the present time, the manufacture of the anhydride on a commercial scale is in very few hands.

Letters patent have been granted to Rudolph Messel, of Silvertown, Victoria Docks, for his invention relating to the production of sulphuric acid, fuming sulphuric acid, and anhydrous sulphuric acid. In carrying out his invention he exposes sulphur to heat in oxygen, and prefers to pass the gases arising from this combustion into a gas-holder, either using such excess of oxygen as with the generated sulphurous acid will form equivalent proportions for their combination into sulphuric anhydride or sulphuric acid, or should these equivalent proportions not be perfectly attained he passes into the gas-holder such a proportion as may be necessary of the gas that may be deficient.

The required oxygen may be obtained by the decomposition of acidulated water acted upon by electricity, any of the well-known dynamo-electric engines being used for that purpose.

The gaseous contents of the gas-holder obtained as above are then passed over or through spongy platinum or platinized materials, such as asbestos, or the oxides of chromium, or of iron, or of copper, and either separately or in combination, which at a moderate temperature possess the property of causing the sulphurous acid and oxygen to combine so as to form anhydrous sulphuric acid. This may be condensed either alone in a suitable apparatus, or it may be dissolved in ordinary sulphuric acid, so as to form Nordhausen or fuming sulphuric acid. This process of manufacture may readily be made continuous by the employment of two gas-holders or receivers, so that whilst one is being emptied the other may be filling. The hydrogen given off during the decomposition of the water may be utilized for the purposes of heating, or, after being carburetted, for purposes of illumination.

Provisional protection has been obtained by Wilhelm Majert, of the firm of Majert and Co., of Bahnhof-Schlebusch, Germany, for improvements in the manufacture of the anhydride of sulphuric acid and of the concentrated sulphuric acid. These improvements consist chiefly in the manipulation of the retorts, their disposition and composition, and in the manufacture of the anhydride of sulphuric acid.

In arranging the retorts which are used for the splitting up of sulphuric acid they set the unburnt retorts in the furnace, and afterwards fire the furnace; or take retorts brought at least to red heat, and put them in the heat furnace. In the latter manner they prevent the retorts from being spoilt.

The aeriform products arising from the decomposition are drawn off by channels situated in the bottom of the furnace, and leading therefrom either across one or more heat retorts, or directly to the refrigerators by a tube for leading away the gases. To save the retorts they place a second inside the retort of decomposition, and into this second one the sulphuric acid (which must be split up) firstly enters by an inlet tube suitably arranged above the inner retort. The liquid obtained by the refrigeration of the gases coming out of the retorts of decomposition contains much sulphurous acid, and by making this liquid hot they liberate the sulphurous acid, and lead it back again to the mixing of gas $SO^2 + O$.

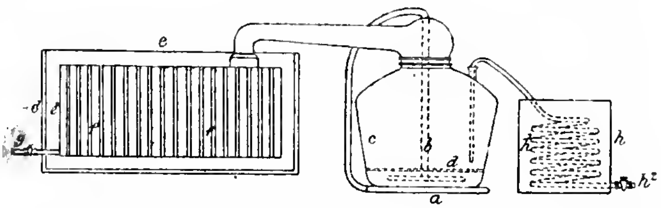
The contact action is managed in iron or copper vessels in lieu of the clay vessels hitherto used, and to ensure the stœchiometrical proportion $SO^2 + O$ they take oxide of copper, or iron, or of chromium, or mixings of these oxides one with another, in lieu of platinum or asbestos hitherto used. The mixing of gas $SO^2 + O$ escaped of the contact action, after taking from it the anhydride, will be brought anew in contact with the substance.

Mr. R. W. Wallace has secured patent rights for improvements in the manufacture of sulphuric anhydride and Nordhausen acid, and in the concentration and refining of sulphuric acid.

Fig. 82 is an elevation partly in section of the apparatus comprising a closed vessel, a condenser, and cooler, hereinafter described. Fig. 83 is a plan or top view of the said condenser. Fig. 84 is a coil of tubing. Fig. 85 is a perforated bottom for the said close vessel. Like letters indicate the same parts throughout the drawing. This invention relates to the manufacture of sulphuric anhydride and Nordhausen acid, and to the concentration and purification of sulphuric and other acids. It permits the use of retorts of cheap materials of any desired size in such manufacture. It permits the division or separation of the distillates, and the delivery and transport or removal of the anhydride in the vessel in which it is received from the still, and the process employed in the manufacture may be continuous.

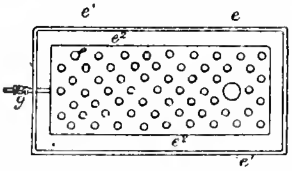
The bisulphate of soda is introduced into large retorts made of glazed plumbago or some similar preparation of earthenware, or of any other substance which will not decompose the sulphuric anhydride (SO_3), or itself be decomposed into sulphurous acid (SO_2) and oxygen (O). The said retort is heated first to dull redness, when any free sulphuric acid (H_2SO_4) and water are driven off. This water is condensed in a leaden worm, and as soon as the sulphuric anhydride commences to appear, the passage of the gases into the leaden coil is stopped by means of a three-way cock, and they then pass into a series of receivers or Woulfe's bottles, constructed to retain none of the solid sulphuric anhydride in any of the lutes. The top of these receivers is detachable, so that it can be replaced by blank plates, which are made properly tight, and the acid can thus be delivered or removed in the same receivers in which it has been collected, thereby saving the workmen from the noxious fumes which would be given off on the exposure of the acid to the air while removing it from one vessel to another. This process may be made continuous by introducing the requisite quantity of warm sulphuric acid into the retort before the neutral sulphate of soda has solidified. In this manner the bisulphate of soda is formed in the retort, and once produced therein need never be removed. And an absolutely anhydrous solid acid may be obtained without heating the Nordhausen acid (which is a combination of sulphuric acid and sulphuric anhydride) till the latter is driven off and collected, as in the usual way of manufacturing the crystals from Nordhausen acid, made from sulphate of iron, in Germany. Other bisulphates may be employed in the process, but sulphate of soda is the most manageable.

82.



Another method of obtaining sulphuric anhydride according to this invention is by the direct combination of sulphurous acid (SO_2) and oxygen (O). This object may be attained by distilling sulphuric acid (H_2SO_4), of a gravity of 1·850, in stills of glazed plumbago and passing the gas through tubes of the same material heated to redness. The sulphuric acid (H_2SO_4) is then decomposed into sulphurous acid (SO_2) and oxygen (O). Any of the acid or water remaining is then absorbed in scrubbers of chloride of calcium, or of pumice-stone moistened with sulphuric acid (H_2SO_4).

83.



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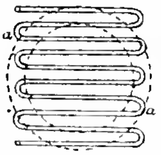

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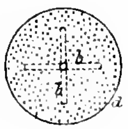


Another way of obtaining the sulphurous acid and oxygen is by burning sulphur in iron or other pans by means of an equivalent of oxygen, the admittance of oxygen being regulated by a weighted valve to ensure continuous pressure.

The direct combination of sulphurous acid (SO_2) and oxygen is also effected by passing these gases through glazed plumbago tubes heated to dull redness, and filled with platinized pumice, or asbestos, or with spongy platinum. These tubes are made of plumbago glazed on the inner side; a platinum lining is objectionable, because the great weight of the platinized pumice, asbestos, or the spongy platinum quickly causes perforations in the piping unless the latter be of great thickness, which the present price of this metal would render very costly. The sulphuric anhydride (SO_3) is finally condensed in receivers as above described.

The invention also comprises a novel process and apparatus for the concentration and refining of sulphuric acid for the above and other purposes, and the concentration and refining of other acids. The apparatus is illustrated in Figs. 82, 83, 84, and 85. According to this process air is heated to a temperature of about 700° in an iron coil *a*, and distributed by means of pipes *b*, made of platinum, porcelain, or other material, into a closed vessel *c*, made of glass, glazed plumbago, or platinum. The hot air is introduced into the sulphuric acid in this chamber by means of the said perforated pipes or a perforated false bottom *d*, and the required draught through the apparatus is produced by an air-pump or aspirator, or other suitable means. Water has hitherto been used as the medium for condensing the waste fumes and for cooling the sulphuric acid after it leaves the still, but instead of water sulphuric acid is used for these purposes.

The condenser *e*, Figs. 82 and 83, is constructed with an outer casing e^1 and an inner box or casing e^2 of lead or other suitable material. Pipes *f* extend vertically through the said inner casing, and the latter is connected with the neck of the still or closed vessel *c*. The sulphuric acid used as the condensing medium flows through the said pipes, and the air and gas from the closed vessel surround the same. *g* is a cock for drawing off the condensed liquid from the casing e^2; *h* is a cooler or vessel for cooling the liquid acid from the vessel *e*; h^1 is a coil of pipe, and h^2 is a cock in the same.

The bottom of the retort or closed vessel *c* may be heated by the flame which heats the iron coil, and the latter may serve as a support for the retort. Therefore the acid will be concentrated externally by the flame and internally by the hot air. The weak acid fumes are condensed and pumped to the top of the chamber used for the manufacture of sulphuric acid, and by means of an injector the condensed weak acid is distributed in the said chamber in the form of spray. This effects a saving of steam in the sulphuric acid chambers, and economizes the fuel used for concentration by the use of the weak acid instead of water or steam.

Other Proposed Methods of Production.—The first attempt to make sulphuric acid from a mixture of sulphurous acid and oxygen by condensation in platinum was made by Phillips. According to his plan sulphurous acid from the combustion of sulphur is mixed with an excess of atmospheric air and forced through a red-hot tube of cast iron packed with platinum, sponge, or other material by means of a blast of hot air. The gaseous sulphuric acid produced is carried with the oxygen and excess of air into the bottom of an upright leaden cylinder filled with flints, whilst water flows down the cylinder and keeps the flints constantly wet. As the gases ascend the sulphuric acid contained in them condenses and flows away from the bottom of the cylinder with the water produced, while the freed gases escape into the air.

Platinum has been found so expensive as to be partially or wholly abandoned. Piria has adopted pumice impregnated with a solution of platinum, and made red hot so that a film of platinum is formed all over it.

Schneider and Laming have patented an apparatus in which pumice causes the formation of the acid. The pumice is packed in a series of upright tubes heated to about 300° (572° F.), in which the gases circulate.

Schmersohl and Bouk pass sulphurous acid, air, and steam through horizontal stoneware or cast-iron pipes filled with asbestos, pumice, or other porous bodies, and strongly heated.

Petrie employs an upright cylinder of stoneware or enamelled cast iron heated to 300° and filled with flints constantly moistened from above.

Besides these, multifarious plans have been devised for extracting the sulphuric acid from natural sulphates, such as gypsum, but no one has been found to possess such qualities as to present any likelihood that the current system of oxidizing sulphur will be displaced. Hargreaves' method for making sulphate of soda from salt, however, will in all likelihood supplant the use of sulphuric acid in this enormous branch of chemical industry.

Uses.—The uses of sulphuric acid are more varied and numerous than those of any other chemical product.

This acid is required in the formation of sulphates, such as those of ammonium, aluminium, copper, iron, magnesium (Epsom salts), mercury (for corrosive sublimate and calomel making), potassium, sodium (Glauber's salt), and indirectly in the production of alum. It is used in the manufacture of nearly all other acids of importance, as boracic, citric, fluoric, hydrochloric, nitric, phosphoric, stearic, sulphurous, and tartaric acids. It is used in cleaning metals; in the manufacture of tin-plate; in exciting electric currents for various purposes, and for the evolution of hydrogen gas. It is further used in the preparation of ether, of ozokerite, of blacking, and of a variety of other substances of minor importance. Also in the separation of pure hydro-carbons from tars; in the purification of oils; and it is largely consumed in the removal of fats from cotton and woollen goods. Other applications of this acid are in the elimination of sugar from starch, and the precipitation of lime from molasses; in dissolving indigo; in giving a dark colour to wood; and in the preparation of aniline and madder dyes. Bleaching and dyeing consume large quantities of sulphuric acid. In the preparation of collodion, gun-cotton, nitro-benzol, nitro-glycerine, picric acid, &c., &c., it is also largely used. Enormous quantities are annually required for the manufacture of mineral waters, and still more for the conversion of mineral phosphates into superphosphates. It is also valuable in the preparation of other fertilizers, such as blood-manures and sewage, by fixing the ammonia and arresting fermentation; in the removal of bad smells from casks, &c., by destroying fungoid growths; it thus acts the part of a deodorizer. But the most important of all its uses is for the conversion of common salt into sulphate of soda, in the manufacture of alkali. In the laboratory it forms one of the most useful reagents in the hands of the analytical chemist; moreover its great hygroscopic powers make it invaluable as a desiccating agent. The uses of this acid are indeed so numerous that it would be difficult to prescribe limits to its application.

The chief seats of the industry in this country are Newcastle, Birmingham, Bristol, Lancashire, Glasgow, London, Edinburgh, and in a minor degree the counties of Norfolk, Suffolk, Hants, Devon, &c. On the Continent are many large works in Belgium, France, and Germany, and even Mexico, Finland, and Japan are not behind the rest of the world in this respect.

The principal product in all cases is the ordinary English acid. In fact, the other two varieties form but an infinitesimal part of the manufactured article, probably not one-thousandth part of the total production.

The manufacture is of comparatively recent date, it being scarcely a century since the first works were erected in this country. Yet it now stands at the head of our chemical industry, and is increasing every day in extent and importance.

The expensive nature of the plant of a sulphuric acid works, as at present constructed, necessitates the possession of considerable capital for embarking in the business, and as a consequence it is in comparatively few hands. The amount of money invested in the manufacture in this country alone is probably not less than five millions sterling.

No tax, duty, nor impost of any kind is levied on the manufacture, and no restriction is imposed by the Legislature, save the provisions of the Alkali Act prohibiting the creation of a nuisance. Practically this Act has none but a beneficial effect upon the trade, as it compels manufacturers to adopt economical measures for the prevention of the escape and consequent waste of those gases which alone create a nuisance.

The commercial value of the manufactured article varies according to its specific gravity, which is synonymons with its strength. Acid at about 1·712 sp. gr. (143° Tw.), commonly known as "brown acid" (B. A.), or as "brown oil of vitriol" (B. O. V.), is generally quoted at about $\frac{3}{4}$*d.* per lb. or 7*l.* per ton, and that at 1·850 sp. gr. (170° Tw.), called "white" or "rectified oil of vitriol" (O. V.), stands usually at 1*d.* per lb. or 9*l.* 6*s.* 8*d.* per ton. In each case a discount is remitted, fluctuating with the market prices of the raw commodities, and with the scale of the transaction, but seldom less than 30 per cent.

The price is also affected by the colour of the acid as well as by its purity. Acid made from brimstone, and containing no arsenic or other foreign deleterious matter, is worth more than "pyrites acid," which always has a certain proportion of arsenic, besides iron, selenium, and other contaminating matter.

MARKETS.—The two great markets for sulphuric acid are the manufacture of alkali and of artificial manures. In almost every instance the sulphuric acid manufacturer combines one or both of the other industries with the primary one. That which is sold as sulphuric acid goes to the smaller manure manufacturers, to gasworks, sugar refineries, mineral water factories, dyers and printers, gun-cotton, &c. makers, electro-platers, &c., &c.

India and China consume a large quantity of the concentrated acid, which is transported thither very conveniently in stoneware jars. The transport in this country is commonly conducted in large glass bottles, known as "carboys," packed with straw in well-tarred hoop-iron or withy baskets.

HYDROCHLORIC, or CHLORHYDRIC ACID. (FR., *acide chlorhydrique;* GER., *salzsäure.*) Constituents, hydrogen and chlorine; formula, HCl; molecular weight, 36·5; specific gravity, 18·25.

This most important body, the only known compound of hydrogen and chlorine, was first obtained in a gaseous state by Priestley in 1772; its solution in water, however, has been used from very early times under the names of muriatic acid—*muria*, sea salt—spirit of salt, and *acidum hydrochloricum.* The ancient alchemists were acquainted with its mixture with nitric acid, which they obtained by distilling nitre, sal-ammoniac, and vitriol together. Mention is made of "*spiritus salis,*" prepared from vitriol and "*sal communis,*" in the chemical treatises of the fifteenth century. Glauber prepared the acid about the year 1648, by heating salt with oil of vitriol, and further allusion, in the writings of Stephen Hales, about the year 1727, is made to a gas which was evolved when sal-ammoniac and sulphuric acid were heated together, and which was soluble in water. This gas Priestley collected over mercury, naming it "*marine-acid air.*"

Hydrochloric acid exists in nature in considerable quantities. It is evolved during volcanic eruptions—notably, those of Vesuvius—and probably, with this origin, is found to an appreciable extent in the hot springs of Iceland and South America, and in the streams which have their sources in volcanic regions and in the craters of extinct volcanoes.

Boussingault gives the following analysis of water taken from the torrent called Rio Vinagre, which rises in the old volcanoes of Purcé, in the Andes:—

Sulphuric acid	0·00110	Magnesia	traces
Hydrochloric acid ..	0·00091	Oxide of iron	traces
Alumina	0·00040	Soda	0·00023
Lime	0·00012		

Although the percentage of hydrochloric acid appears small upon analysis—not exceeding $\frac{1}{1000}$th part—it is worth noting that something like 12,000 tons per annum are annually carried down by the river cited.

An analysis of water from an acid spring gives the following result:—

Sulphuric acid	0·005181	Magnesia	0·000320
Hydrochloric acid ..	0·000851	Soda	0·000360
Alumina	0·000500	Oxide of iron	0·000365
Lime	0·000140	Silica	0·000183

Hydrochloric acid to the amount of 0·447 per cent. has been found in the lava flowing from Hekla. Its presence under all these circumstances is probably due to the decomposition of the chlorine compounds of the lava by the action of the silicates and steam of a high temperature.

In its gaseous form hydrochloric acid is colourless, 1·267 times heavier than air, with a strong acid taste and reaction and powerful suffocating odour.

It is peculiarly irritating to the nostrils, eyes, and skin, and, as the districts where the manufacture is carried on readily testify, extremely injurious to all kinds of vegetation. It has not been solidified but at a temperature of 10° (50° F.), and under a pressure of forty atmospheres is obtainable as a clear liquid of 1·27 specific gravity, possessing acid properties, but not so strongly marked as in the case of the ordinary commercial acid—the solution of the gas in water. Thus the anhydrous liquid is incapable of dissolving zinc, magnesium, and various metallic sulphides; it attacks sodium, lead, tin, and potassium, but no evolution of gas takes place during the operation. Hydrochloric acid supports combustion only to a very limited extent, and is not inflammable. One of the most remarkable properties of the gas is its extreme solubility in water, the enormous volume of 490 times its own bulk being taken up by the liquid at 40° (39° F.), with evolution of considerable heat. The energy of the operation may be shown by opening a cylinder of the dry gas under water; it will be noticed that the liquid immediately rushes up, as into a vacuum, the vessel becoming perceptibly warm.

The aqueous saturated solution has a density of 1·2265, and contains 44 per cent. of the dry acid. The following tables give the specific gravity at various degrees of concentration, as delivered by Ure and Davy. It will be noticed that the results differ slightly.

COMPOSITION OF AQUEOUS HYDROCHLORIC ACID ACCORDING TO URE.

Acid of 1·2 Sp. Gr.	Specific Gravity.	Per Cent. of Chlorine.	Per Cent. of Hydrochloric Acid.	Acid of 1·2 Sp. Gr.	Specific Gravity.	Per Cent. of Chlorine.	Per Cent. of Hydrochloric Acid.
100	1·2000	39·675	40·777	50	1·1000	19·837	20·388
99	1·1982	39·278	40·369	49	1·0980	19·440	19·980
98	1·1964	38·882	39·961	48	1·0960	19·044	19·572
97	1·1946	38·485	39·554	47	1·0939	18·647	19·165
96	1·1928	38·089	39·146	46	1·0919	18·250	18·757
95	1·1910	37·692	38·738	45	1·0899	17·854	18·349
94	1·1893	37·296	38·330	44	1·0879	17·457	17·941
93	1·1875	36·900	37·923	43	1·0859	17·060	71·534
92	1·1857	36·503	37·516	42	1·0838	16·664	17·126
91	1·1846	36·107	37·108	41	1·0818	16·267	16·718
90	1·1822	35·707	36·700	40	1·0798	15·870	16·310
89	1·1802	35·310	36·292	39	1·0778	15·474	15·902
88	1·1782	34·913	35·884	38	1·0758	15·077	15·494
87	1·1762	34·517	35·476	37	1·0738	14·680	15·087
86	1·1741	34·121	35·068	36	1·0718	14·284	14·679
85	1·1721	33·724	34·660	35	1·0697	13·887	14·271
84	1·1701	33·328	34·252	34	1·0677	13·490	13·863
83	1·1681	32·931	33·845	33	1·0657	13·094	13·456
82	1·1661	32·535	33·437	32	1·0637	12·697	13·049
81	1·1641	32·136	33·029	31	1·0617	12·300	12·641
80	1·1620	31·746	32·621	30	1·0597	11·903	12·233
79	1·1599	31·343	32·213	29	1·0577	11·506	11·825
78	1·1578	30·946	31·805	28	1·0557	11·109	11·418
77	1·1557	30·550	31·398	27	1·0537	10·712	11·010
76	1·1536	30·153	30·990	26	1·0517	10·316	10·602
75	1·1515	29·757	30·582	25	1·0497	9·919	10·194
74	1·1494	29·361	30·174	24	1·0477	9·522	9·786
73	1·1473	28·964	29·767	23	1·0457	9·125	9·379
72	1·1452	28·567	29·359	22	1·0437	8·729	8·971
71	1·1431	28·171	28·951	21	1·0417	8·332	8·563
70	1·1410	27·772	28·544	20	1·0397	7·935	8·155
69	1·1389	27·376	28·136	19	1·0377	7·538	7·747
68	1·1369	26·979	27·728	18	1·0357	7·141	7·340
67	1·1349	26·583	27·321	17	1·0337	6·745	6·932
66	1·1328	26·186	26·913	16	1·0318	6·348	6·524
65	1·1308	25·789	26·505	15	1·0298	5·951	6·116
64	1·1287	25·392	26·098	14	1·0279	5·554	5·709
63	1·1267	24·996	25·690	13	1·0259	5·158	5·301
62	1·1247	24·599	25·282	12	1·0239	4·762	4·893
61	1·1226	24·202	24·874	11	1·0220	4·365	4·486
60	1·1206	23·805	24·466	10	1·0200	3·968	4·078
59	1·1185	23·408	24·058	9	1·0180	3·571	3·670
58	1·1164	23·012	23·650	8	1·0160	3·174	3·262
57	1·1143	22·615	23·242	7	1·0140	2·778	2·854
56	1·1123	22·218	22·834	6	1·0120	2·381	2·447
55	1·1102	21·822	22·426	5	1·0100	1·984	2·039
54	1·1082	21·425	22·019	4	1·0080	1·588	1·631
53	1·1061	21·028	21·611	3	1·0060	1·191	1·224
52	1·1041	20·632	21·203	2	1·0040	0·795	0·816
51	1·1020	20·235	20·796	1	1·0020	0·397	0·408

COMPOSITION OF HYDROCHLORIC ACID ACCORDING TO DAVY.

Specific Gravity.	Per Cent. of Hydrochloric Acid.	Specific Gravity.	Per Cent. of Hydrochloric Acid.	Specific Gravity.	Per Cent. of Hydrochloric Acid.	Specific Gravity.	Per Cent. of Hydrochloric Acid.
1·21	42·43	1·15	30·30	1·10	20·20	1·05	10·10
1·20	40·00	1·14	28·28	1·09	18·18	1·04	8·08
1·19	38·38	1·13	26·26	1·08	16·16	1·03	6·06
1·18	36·36	1·12	24·24	1·07	14·14	1·02	4·04
1·17	34·34	1·11	22·22	1·06	12·12	1·01	2·02
1·16	32·32						

The difference in composition of the aqueous solution of hydrochloric acid at 0° and 15°, and at various densities, is shown in the following Table (J. Kolb):—

Density.	Per Cent. of Real Acid at 0° C.	Per Cent. of Real Acid at 15° C.	Density.	Per Cent. of Real Acid at 0° C.	Per Cent. of Real Acid at 15° C.	Density.	Per Cent. of Real Acid at 0° C.	Per Cent. of Real Acid at 15° C.
1·000	0·0	0·1	1·083	15·7	16·5	1·166	31·4	33·0
1·007	1·4	1·5	1·091	17·2	18·1	1·171	32·3	33·9
1·014	2·7	2·9	1·100	18·9	19·1	1·175	33·0	34·4
1·022	4·2	4·5	1·108	20·4	21·5	1·180	34·1	35·7
1·029	5·5	5·8	1·116	21·9	23·1	1·185	35·1	36·8
1·036	6·9	7·3	1·125	23·6	24·8	1·190	36·1	37·9
1·044	8·4	8·9	1·134	25·2	26·6	1·195	37·1	39·0
1·052	9·9	10·4	1·143	27·0	28·8	1·199	38·0	39·9
1·060	11·4	12·0	1·152	28·7	30·2	1·205	39·1	41·2
1·067	12·7	13·4	1·157	29·7	31·2	1·210	40·2	42·4
1·075	14·2	15·0	1·161	30·4	32·0	1·212	41·7	42·0

When a strong solution of hydrochloric acid is boiled at the ordinary temperature and pressure of the atmosphere, it gives off a gaseous acid until it is reduced to a density of 1·10, then it distils over unchanged. In similar manner, a weak solution parts with its water until a density of 1·10 is acquired, and then passes over with a constant composition, boiling at 112° (233° F.). The observation of this circumstance pointed at first to the conclusion that there was a definite hydrate of the acid with this constant composition. It has, however, been established that by varying the pressure, or vaporizing at different temperatures, other liquids with a constant composition are obtainable—liquids that distil over unchanged after reaching certain densities. The relation between the pressure under which the acid is distilled and the composition of the stable liquid is given in the following table, P *m* showing the pressure in metres of mercury, and the second column giving the percentage of real acid in the constant liquid.

P *m*.	Per Cent. of Real Acid.	P *m*.	Per Cent. of Real Acid.	P *m*.	Per Cent. of Real Acid.	P *m*.	Per Cent. of Real Acid.
0·95	23·2	0·7	20·4	1·3	19·3	1·9	18·6
0·10	22·9	0·76	20·24	1·4	19·1	2·0	18·5
0·2	22·3	0·8	20·2	1·5	19·0	2·1	18·4
0·3	21·8	0·9	19·9	1·6	18·9	2·3	18·3
0·4	21·4	1·1	19·5	1·7	18·8	2·4	18·1
0·5	21·1	1·2	19·4	1·8	18·7	2·5	18·0
0·6	20·7						

It is evident that there exists for each pressure a corresponding aqueous acid with a constant boiling point, which distils over, that is to say, under this pressure with unchanged composition.

With regard to varying temperatures, when an aqueous solution is vaporized by passing dry air through it, similar varying liquids with constant boiling points are obtained. This will be readily seen from the following table:—

T°.	Per Cent. of Real Acid.	T°.	Per Cent. of Real Acid.	T°.	Per Cent. of Real Acid.	T°.	Per Cent. of Real Acid.
0	25·0	30	24·1	55	23·2	80	22·0
5	24·9	35	23·9	60	23·0	85	21·7
10	24·7	40	23·8	65	22·8	90	21·4
15	24·6	45	23·6	70	22·6	95	21·1
20	24·4	50	23·4	75	22·3	100	20·7
25	24·3						

The powerful affinity existing between hydrochloric acid and water, to which reference has been made, is shown by the well-known white fumes which are formed when the gas is allowed to come into contact with the moisture of the atmosphere. As a pure gas it is invisible. Evolved into the air, it occupies a space several hundred times its original bulk. The aqueous solution is decomposed by all the metals which decompose water at a red heat, the metal being dissolved and hydrogen set free. The liquefied acid dissolves bitumen. Neither gas nor solution possesses bleaching properties.

A place in the arts and manufactures, only second perhaps to that occupied by sulphuric acid, must be assigned to hydrochloric acid, so largely does it enter into every-day commercial life. The great bulk is used in the manufacture of chlorine for various purposes, of the hypochlorites, and bicarbonate of soda. It is also employed to a considerable extent in the manufacture of chloride of zinc—used in the preservation of timber, &c., and as a disinfectant—of glue, the oxychloride of lead, the chlorides of tin, antimony, ammonium, mercury, &c.; in the preparation of certain freezing mixtures, in softening ivory, in cleaning tin plates, and in dissolving the incrustation upon boilers and pipes. In bleaching, hydrochloric is often substituted for sulphuric acid to make the "sours" which follow the application of chloride of lime, and it is thought to give better results, especially in cloths destined for garancine work. Finally it forms, with nitric acid, the solvent of gold, platinum, and various alloys known by the name of aqua regia, to which further reference will be made.

Hydrochloric acid is produced by the direct union of hydrogen and chlorine gases; by the action of water upon certain chlorides—phosphorus, tin, antimony, &c.; by the action of chlorine gas upon various substances containing hydrogen—water, phosphuretted hydrogen, and numerous organic bodies, such as acetic acid; by the inverse action of hydrogen upon certain chlorine compounds, such as chloride of nickel; but, chiefly, by the decomposition of common salt (chloride of sodium) by sulphuric acid. By this last method the huge bulk of the acid of commerce is manufactured.

The direct union of hydrogen and chlorine is attended by some noteworthy circumstances. A mixture of the two gases, in equal proportions, may be kept in the dark without any change taking place; but if the vessel containing the gases be exposed to the sunshine, or if an electric spark be passed through it, an immediate combination, with the formation of hydrochloric acid, will result. When the operation is conducted over mercury, no increase or diminution in the volume of gases is noticed, one volume of hydrogen uniting with one volume of chlorine to form two volumes of hydrochloric acid. This powerful attraction between chlorine and hydrogen is further shown in the second method of producing hydrochloric acid cited—the action of chlorine upon certain hydrogenized compounds. A solution of the gas in water exposed to the light becomes gradually converted into an aqueous solution of hydrochloric acid. In the case of organic compounds, one portion of the attacking chlorine unites with the hydrogen, and another takes the place of the hydrogen removed. For example, in the decomposition of acetic acid,

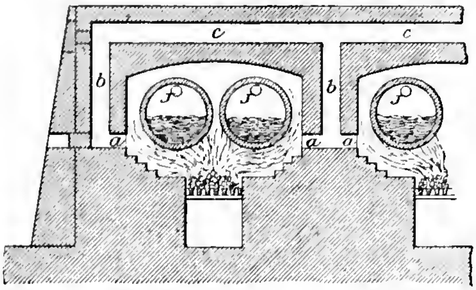
$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + \underset{\text{Chlorine.}}{3\,Cl_2} = \underset{\text{Tri-chloracetic acid.}}{C_2HCl_3O_2} + \underset{\text{Hydrochloric acid.}}{3\,HCl}$$

The decomposition of chloride of sodium by sulphuric acid is effected in two ways—in "cylinders" (retorts of iron, or, occasionally, glass), and in the ordinary sulphate of soda furnace. By the former plan the pure commercial article is obtained,—a colourless, or almost colourless, liquid (sometimes slightly tinged with a pale green, due to the presence of free chlorine), used in the production of aqua regia, the chlorides of tin and antimony, and in the finer chemical processes. This is usually designated "cylinder acid."

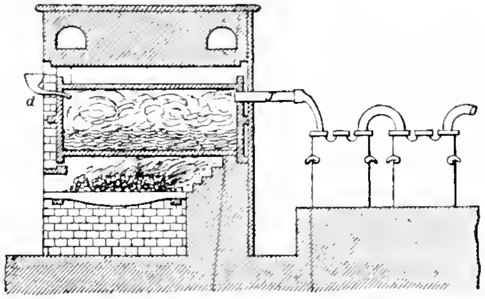
From the sulphate of soda manufacture comes the rougher commercial product, made, or used, on an enormous scale in nearly all the chief chemical industries of the day, and designated "tower acid," from the method employed for its condensation. This "tower acid" is usually of a deep yellowish brown colour, from the presence of chloride of iron and organic matter. It is utilized in all the larger chemical processes—the manufacture of bicarbonate of soda, and carbonic acid generally, of chlorine and the hypochlorites, of zinc chloride and lead oxychloride, of glue, &c., &c. The details of these two methods of obtaining liquid hydrochloric acid will now be considered.

The arrangement of iron retorts, or cylinders, is shown in sectional elevation and longitudinal section in Figs. 86 and 87. It consists of a series of cast-iron cylinders, 6 ft. long by 2 ft. 6 in. in diameter and 1 in. thick, heat being applied from an underneath fire. Each cylinder may have its separate fireplace, or, as in the drawing, one fire may serve two retorts. This latter plan tends to economize fuel. The products of combustion pass round the cylinders and escape by the openings and flues *a*, *b*, *c*, to the chimney. The ends of the retorts consist of movable lids, which are closely luted with clay when the furnace is at work. Six cwt. of salt being thrown in through the end over the fire, the door is closed, and sulphuric acid at 1·6 sp. gr. introduced by means of a funnel shown at *d*, Fig. 87, from a cistern set at a slightly higher level. The fire is then set away, gently at first, but as the end of the operation approaches, shown by the diminution of the evolution of gas, a pretty strong degree of heat must be attained. The hydrochloric acid evolved passes off through an earthenware pipe J to the condensers, and in the retort is left a white mass of sulphate of soda, which is loosened, raked out through the opened door when the furnace has cooled down, and sold to alkali makers as crude sulphate. The condensing arrangement consists of a series of Woulfe's bottles, the commencement of which is shown in Fig. 87. The first two or three of these are empty, to catch the first acid which comes over contaminated with sulphuric acid. &c. The succeeding ones are half filled with water. The range may be of the description shown in Fig. 88, the condensed acid being drawn off by cocks set at the bottom of each bottle, or it may be composed of bottles connected with earthenware and guttapercha tubes just below the water-level, as shown in Fig. 89. In the former case, the acids when withdrawn are mixed together; in the latter, by filling the final bottle, the current is made to flow in contrary direction to the gas, and so may be drawn off from the carboy nearest to the cylinder in a saturated state. The final receiver is connected with the chimney. The uppermost portion of the retorts in this process is very speedily acted upon by the acid fumes. To meet this, a custom of turning the cylinders occasionally prevails, exposing the part that was originally next the fire to the action of the gases, and *vice versâ*. A better plan is that shown in Fig. 90. The cylinder is cast in two halves, firmly bolted together, the joints being bedded with fire-clay and water, or red lead. The upper half is arranged to admit of a fire-brick casing, which can be removed from time to time, and preserves the metal from corrosion. The only objection to this plan is that it necessitates the consumption of some little extra fuel.

86.



87.



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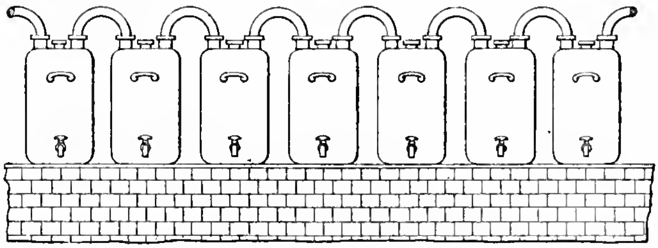
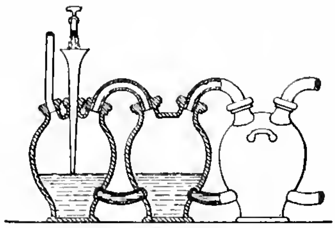


89.



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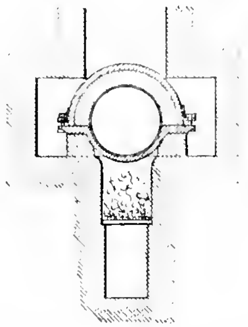
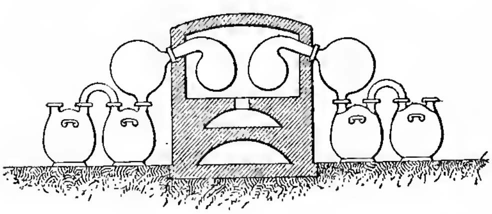
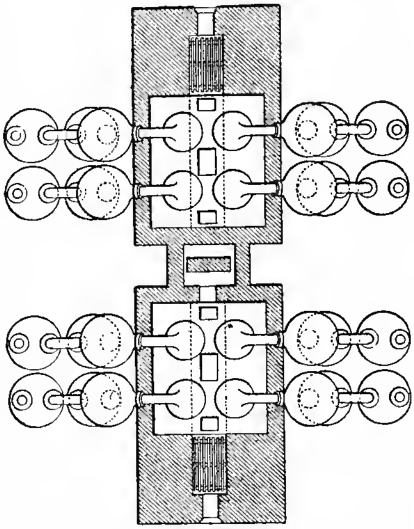


Pure commercial hydrochloric acid is also obtained by the decomposition of salt by sulphuric acid in small glass retorts. This process has found especial favour in France, where it is pursued to a considerable extent. The arrangement is shown in Figs. 91 and 92. The retorts are set, in rows of any convenient number, in brickwork, and are connected by a short arm with a glass or earthenware receiver, which again communicates with a series of Woulfe's bottles. Heat is applied from a furnace at one end of the system, and after traversing the whole range, finally passes off to the chimney. The retorts are usually coated with clay or cement, and may be arched over, or have their tops exposed to the air, as may seem desirable. The usual plan is that shown in the drawing. In Germany a somewhat similar method is adopted, the retorts being placed in metal pots or sand furnaces.

91.



92.



In these processes equivalent quantities of salt and acid may be used—two equivalents of the former to two of the latter. A mixure of bisulphate of soda, hydrochloric acid, and common salt is then first obtained, and afterwards, at a higher temperature, the bisulphate and salt react upon one another, yielding hydrochloric acid and a neutral sulphate. It is usual, however, for the sake of economizing fuel, and obtaining a sulphate which is more easily removable and of more value, to use an excess of sulphuric acid, to the amount of even two equivalents. The "salt cake" is esteemed in accordance with its more or less perfect state of decomposition—an admixture of free sulphuric acid being in no way despised.

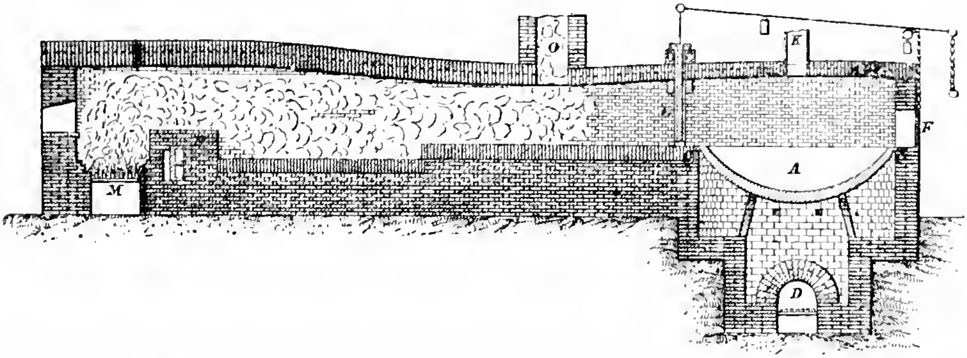
The yield of acid is somewhat variable. On an average 130 parts of a specific gravity of 1·19 will be obtained from 100 parts of salt.

The following table gives the possible yield from a ton of salt of various degrees of purity:—

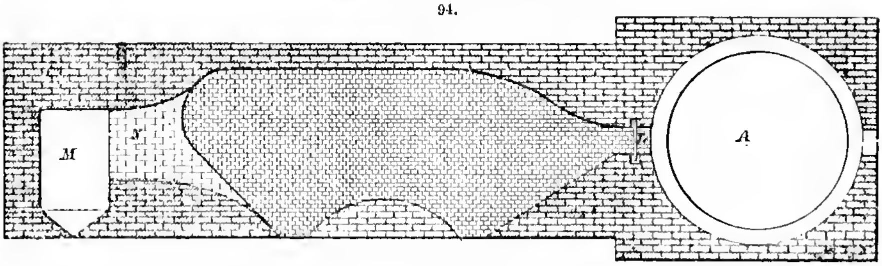
1 ton of pure salt yields	1397	lb. of acid
1 ton, containing 99 per cent. of pure salt, yields	1383·6	„
„ „ 98 „ „	1369·6	„
„ „ 97 „ „	1355·6	„
„ „ 96 „ „	1341·7	„
„ „ 95 „ „	1327·7	„
„ „ 94 „ „	1313·7	„
„ „ 93 „ „	1299·7	„
„ „ 92 „ „	1285·8	„
„ „ 91 „ „	1271·8	„
„ „ 90 „ „	1257·8	„

Fully five-sixths of the total production of hydrochloric acid is manufactured as a bye-product in the Leblanc soda process, in that section of it devoted to the obtaining of sulphate of soda. Common salt is decomposed by sulphuric acid of about 130° Tw. in some such apparatus as that set forth in Figs. 93, 94, and 95, hydrochloric acid being evolved, and afterwards condensed or dissolved in water, and a 96 per cent. sulphate of soda left behind. There are many modifications of this decomposing process, which will be described in detail under Sulphate of Soda. For the present, only one plan will be considered, that obtaining in the large majority of works at the present day. A, Figs. 93 and 94, is a cast-iron "pan" or "pot," hemispherical in shape, 9 ft. in diameter inside measurement, 2 ft. deep, 6 in. thick at the lower side or "belly," and tapering to 3 in. thick at the flanges. This pan is arched over with 9 in. brickwork, and sits upon a circular "shade" wall, shown at B, Fig. 93, 2 ft. high and 4½ in. thick. Further support is also given by resting the flanges upon the outside walls at C C. This arrangement, with an independent arch, allows of the ready setting of a new pan whenever required by accident or ordinary wear and tear. The front brickwork and shade wall are pulled down, all the rest of the apparatus being left intact, the old pan is taken out upon a bogie, a new one run in upon its seat, and the shade wall and front brickwork restored. This speedy renewal is an important consideration, as the cost of a new pan, including the stoppage of work, is about 150*l*. Heat is applied from a fire underneath, shown at D. The arch E prevents the direct playing of the fire upon the pan, the flames being conducted away through pigeon-holes at the sides and ends of the arch, and allowed to circulate freely round the flue formed by the shade wall and the outside brickwork before passing off to the chimney. The "setting" of a pan requires the greatest care and judgment to avoid breakage. A good decomposing pan will last with judicious use for fifteen months, working off 8 cwt. of salt per hour. As a great deal depends upon the care taken by the "pan men," it is usual to give them a small monthly premium as soon as the pan has lasted for twelve months. Besides accidental breakage from defects in the casting, a frequent cause of disaster is the running in of cold acid upon a pan which has been hastily heated up for its work, or allowed to get red hot between the working off of one batch and the introduction of another. Occasionally, too, the sulphate of soda, or mixture of salt and acid, cakes upon the bottom of the pan, causing that particular spot to get unduly hot.

93.

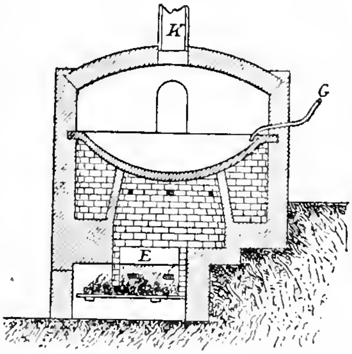


94.

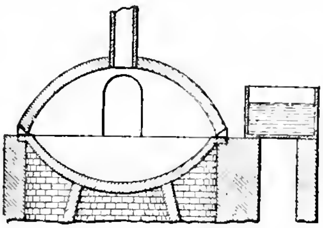


An important modification of pan setting is shown in Fig. 96. This has come into use only of late years, chiefly upon the recommendation of the Government inspectors, with a view to prevent the escape of acid gas caused by a pan boiling over. It will be observed that the arch, instead of being independent, springs from an angle iron riveted upon the flange of the pan, so that any signs of boiling over are at once observed, and the escaping liquid does not drop upon the fire arch, and by its destruction endanger the life of the pan. These advantages are, however, more than counterbalanced by the necessarily unreliable construction of the pan arch arising from its circular shape, and the fact that the work of removing an old pan and setting a new one takes twice as long as when an independent and strong arch is thrown across. In either

95.



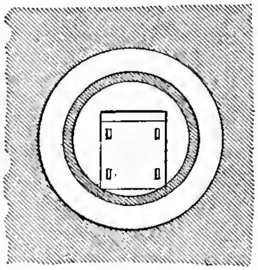
96.



case the fireplace and accessories are the same. A view of the shade wall, fire arch, and pigeon-holes, &c., is given in Fig. 97.

Referring again to Fig. 93, a charge of salt, weighing about 8 cwt., is thrown into the pan through the sliding door F, and about 8 cwt. of sulphuric acid introduced through the pipe G, Fig. 95. This acid is brought from the chambers along a leaden pipe, as required, and may be kept in a small "batch pan," as shown in Fig. 96, set alongside, and heated by the waste gases from the pan fire. The mixture must be kept thoroughly stirred up from the bottom during decomposition, and no boiling over allowed. To prevent this, it is customary to put a small quantity of tallow or grease upon the surface of the mixture as soon as the acid is run in upon the salt. All necessary working is carried on through a hole in the door, or by raising it 2 or 3 in. It is important to prevent the ingress of any considerable amount of air, or else both draught and condensation are impeded, and the escape of pungent acid fumes caused. Careful regulation of the heat must be ensured, the fire being banked down at the commencement of the operation, and only driven at all hard towards the close. The gas and steam evolved during the process escape through an opening in the arch of the pan into a range of earthenware pipes, as shown at K, Figs. 93 and 95, through which they are conducted to the condenser. After about forty minutes' boiling and stirring, the mixture,—now in a pasty state, and consisting of sulphate and bisulphate of soda, with portions of undecomposed salt and hydrochloric acid,—is transferred through the opening L into the finishing furnace, usually called "roaster" or "drier." This communication between pan and roaster is closed during the working of the batch by a sliding damper hung upon a chain and lever, as shown in Fig. 93, and under the ready control of the pan-man. The roaster is a large reverberatory furnace of brickwork, supported on the outside with cast-iron plates $\frac{3}{4}$ in. in thickness, the whole being strengthened and secured by iron rods passing over upright binders set into the ground. The bed, or sole, of the furnace is very nearly on a level with the flange of the pan. The dimensions of the "double-bedded" roaster shown in the drawing are, 20 ft. long from fire-bridge to pan damper, 7 ft. 9 in. from back to front, and 3 ft. 6 in. from sole to arch. The whole should be erected upon a good foundation of concrete to prevent yielding, or "spreading." A double-bedded furnace, i. e. a roaster with two doors and a double sole, is economical, inasmuch as it turns out more work in proportion to the plant than a single bed, and effects a certain saving of fuel. The sulphate is, moreover, worked down more finely in it, and comes out more perfectly decomposed. Heat is applied from a fireplace M. The naked flames pass over the bed of the furnace, but are kept from coming into too intimate contact with the charge by means of the bridge N, which throws the flames up towards the arch. In this roaster the mixture of sulphate and bisulphate is thoroughly turned over and worked, every portion being carefully exposed to the action of the fire, and the whole of the hydrochloric acid driven off. All the products of combustion, the gas and the steam, pass off up a brickwork flue O to the condenser. A double-bedded roaster allows of the working of two batches at once, one being newly discharged from the pan, and the other, at the fire end, nearly ready to be drawn. In many works what are called "close," or "blind," furnaces are employed. In these the fire is conducted along flues passing over and under the furnace bed, but is never allowed to come into contact with the charge. "Close" roasters give a better hydrochloric acid than "open," condensation being rendered much easier, but more fuel per ton of sulphate is consumed, an imperfectly worked article obtained, and continual risk of loss of hydrochloric acid gas incurred through leakage into the fire flues.

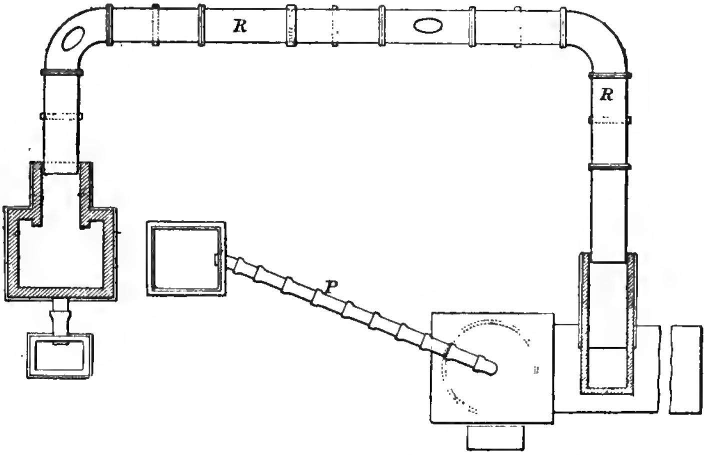
97.



Following now the gaseous products of decomposition, the reader is requested to refer to Fig. 98. The hydrochloric acid gas from the pan passes along a range of pipes P to the condenser, and from the roaster along the range R R. The former consists of 3-ft. lengths of earthenware pipes, 15 in. or 18 in. in diameter, and not less than $1\frac{1}{2}$ in. thick, the whole being laid upon a suitable wooden platform, with a narrow passage on both sides of the pipes. The joints are spigot and faucit, as will be noticed, and should be carefully "made" with a stemming of a peculiar mixture of tar and ground fire-clay. The mixing of this stemming requires attention. If there be too much tar present the heat melts it out, and the joint loosens; if too much fire-clay, the joint cannot be made at all. The best plan is to rub just enough tar into the ground clay to moisten it, and warm the mixture gently upon an iron plate over the fire. Good stemming made in this way may be kept for any reasonable length of time without in any way deteriorating. The best form of "stemmer" is shown in Fig. 99, and may be made of either wood or iron. To prevent any considerable amount of condensation and consequent leakage, before the gases reach the condenser, the range of pan pipes should not be more than about 30 ft. long, and should have a good fall towards the condenser. If the fall be the other way, the liquid acid runs back, and is liable to crack the decomposing pan.

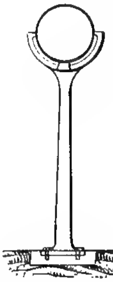
For the conveyance of the gases from the roaster many methods are employed, a brick flue being a very common one. By this plan, however, unless the flue is of inconvenient and expensive length, the gas enters the condenser too hot, and an extra amount of work and water is thereby entailed. The best method undoubtedly is a combination of cast-iron pipes and brick flue, as shown in Fig. 98. To prevent the burning of the pipes, it is advisable to carry a brick stalk and flue for about 30 ft. from the roaster, and then join into it about 70 ft. of 3-ft. diameter pipes, cast in 9-ft. lengths. The whole is supported in any convenient way, and should have a slight fall towards the condenser. The stalk should be built of fire-bricks, set in tar and china clay, and the area must not be too large. By the employment of cast-iron pipes, such radiation of heat is obtained that the gases, leaving the roaster at a temperature of about 1100°, enter the condenser cooled down to about 300°, and a ready condensation with a minimum of water is secured. A very convenient form of support for the pipes is shown in Figs. 100 and 101. It consists of an upright metal column, bolted into a stone or concrete foot set in the ground, and gripping the pipe firmly, while allowing a free current of air to pass round and underneath. One such support, weighing about 11 cwt., under every alternate 9-ft. length of pipe, is sufficient. Man-holes should be fixed in about three places along the whole range, to allow of the pipes being periodically and regularly cleaned out. The joints are made by flanges, bolted together, and bedded with the mixture of tar and pipeclay already described. It is advisable to have a short length of brick flue also at the condenser end, to prevent the metal being eaten away by condensed acid. The danger arising from contraction and expansion is provided against by the two ends of the pipes working with a certain amount of freedom in the respective brickwork terminations. An expanding joint should also be made about the middle of the range, by bringing two of the pipes together with plain, instead of flanged, ends, and securing them with a collar, as shown at A, Fig. 101. Given good metal, the flue described will last for many years, without requiring any attention beyond an occasional patch of sheet iron. The arrangement should be as far as possible in the open air; and, to secure a proper distance for both pan and roaster gases to travel, the relative positions of pipes, pan, and furnace shown in Fig. 98 should be adopted.

98.

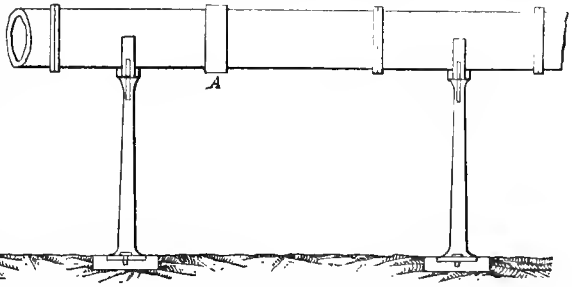


99.

100.

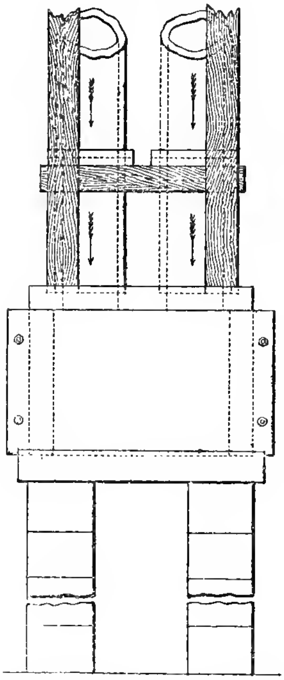


101.

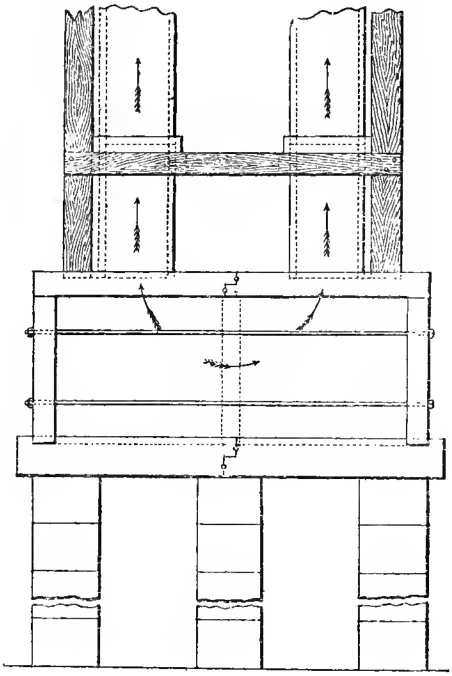


After about 80 ft. of flue, a certain amount of condensation usually takes place. To catch the acid thus formed, the gases are occasionally conducted through the cistern arrangement shown in Figs. 102 103, and 104, before entering the condenser. This consists of a large box, built of good Yorkshire flag or freestone, with sides 6 in. and bottom 12 in. thick, the whole being well bound up with 1-in. iron rods. As shown in the drawing, two ranges of pipes may be put into one such cistern; but if expense be not of any great importance, all flues and gases should be kept separate until they finally issue into the chimney flue. The direction of the gas is shown by arrows. The liquid hydrochloric acid which accumulates in the cistern is drawn off by a stopcock of earthenware, let into the side close to the bottom. Although somewhat expensive, this cistern arrangement is highly to be recommended. It is put together in a similar style to that adopted in building the condenser, details of which will be given immediately, the sides and ends being let into the bottom stone 1$\frac{1}{4}$ in., and the sides similarly dovetailed into the ends and secured with iron binders. The pipes, as they enter and leave, are supported by a wooden framework, which rests upon the cistern cover,—as near the corners as possible, to secure solid support.

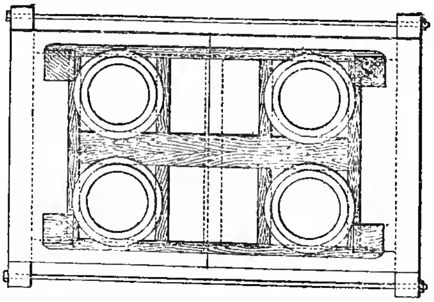
102.



103.

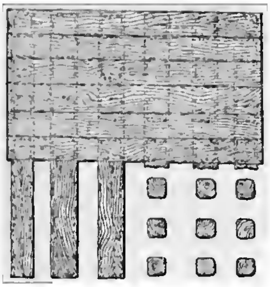


104.

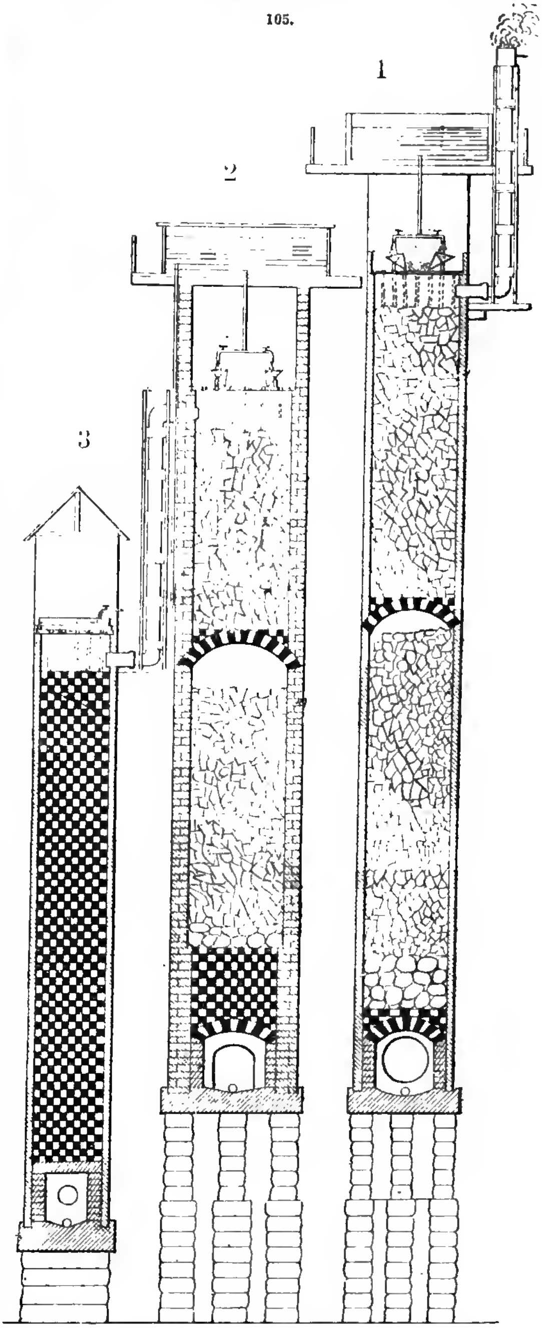


The gases now enter their respective condensers. Of these there are many varieties of form and size. The best arrangement is shown in Fig. 105, which the reader is requested carefully to study. Inasmuch as an ordinarily built condenser weighs 400 to 500 tons—which is piled up upon not more than 10 ft. of ground—and costs from 600*l.* to 1000*l.*, according to the metal used, it is of the first importance that the nature of the ground to be dealt with should be carefully ascertained, and that a sufficient and reliable foundation should be laid. The square mass of concrete often adopted is not to be recommended, inasmuch as it is only trustworthy upon a thick bed of clay or rock, even when it is kept intact, and is, moreover, constantly liable to be attacked by escaping acid. Although exceedingly expensive, the best artificial foundation—the only reliable one—consists of wood piles, about 12 in. square, driven into the ground not less than 25 ft., and standing only about 9 in. apart. Upon the heads of these balks of timber are spiked, with a flooring of 3-in. deals laid crossways, bringing the foundation level with the ground; and upon this flooring is set the stonework base of the condenser. This basement may be of the three-pillar system shown in Fig. 105, or of solid masonry, as set forth in Figs. 120 and 121. If the latter plan be adopted, the piles should be driven after the style shown in Fig. 106, the dotted lines showing the pile-heads, and the plain lines the balks of timber and flooring of deals upon which the pillars are built. This pillar system is to be recommended, not only on account of first cost, but also as allowing regular inspection of the bottom stone of the condenser. A thoroughly-piled foundation is, comparatively speaking, everlasting. It affords perfect protection against any treacherous nature of the ground, and resists any attack of leaking acid. It should be remembered that the slightest sinking of a condenser, besides entailing possible destruction, inevitably loosens the joints of the stones, causing leakage of gas and enormously increased wear and tear. Moreover, if the whole erection be not perfectly plumb, the water finds its way down one side or corner, instead of being equally distributed, and causes, first, escape of hydrochloric acid gas, and secondly, the production of a weak aqueous acid.

106.



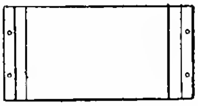
105.



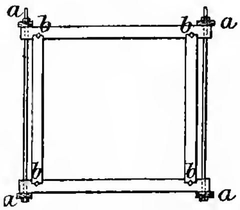
Having laid a satisfactory foundation, it is advisable to have a stonework basement some 10 or 12 ft. high, so that the acid, when it leaves the condenser, may flow freely into whatever cistern or receptacle may be provided for its reception. In estimating the height required, due allowance should also be made for the after-utilisation of the acid, without incurring cost of pumping, &c. The basement should be of stone, as being alone capable of bearing the huge weight of the condenser, and resisting the action of the acid. The reasons for preferring the pillar system to a mass of solid masonry have been already set forth. The pillars are the full length of the bottom stone, are about 2 ft. 6 in. wide, and built in "courses" of varying thickness. Immediately above is set the bottom stone of the condenser itself. If possible, this should be one solid block, not less than 18 in. in thickness, and must be laid absolutely level. A slight concavity in the centre, as shown in the drawing, forms a point of collection for the acid.

So far both pan and drier condensers are similar in construction, but as the after-details are different they must be dealt with separately. The best material for the sides of the pan condenser is stone, preferably of the description known as "Yorkshire flag," which, although very hard to work—and therefore expensive—is less liable to crack and not so porous as the ordinary freestone. These side and end stones must be not less than 6 in. thick, and are roughly quarried to the sizes required before delivery. The final accurate gauging and cutting are accomplished as speedily as possible, just before they are set in their places, that the joints may have only small chance of incurring injury. The courses vary in height from 2 ft. to 5 ft., the larger ones being placed towards the bottom of the condenser. The four stones forming a "course"—"sides" and "ends"—are cut and fitted together after the manner shown in Figs. 107 and 108. The sides are perfectly plain and fit $1\frac{1}{4}$ in. into the ends, which, to receive them, have grooves cut $6\frac{1}{4}$ in. wide and $1\frac{1}{4}$ in. deep. Every course is firmly bound together and screwed up by two 1-in. iron rods, with a head at one end and nut at the other, which pass through $1\frac{1}{4}$-in. holes drilled in the side stones. To bind the several courses together, strengthen the whole erection and prevent, as far as possible, the iron bolts coming in contact with the stone; 9 in. × 3 in. deals, as shown at *a a a a*, Fig. 108, pass down the four corners of the condenser from top to bottom. The horizontal joints of the stones are bevelled downward with a 3-in. slope, as shown in Fig. 109, and are set with a mixture of tar and very finely ground china or pipeclay. The thickness of these horizontal joints should not exceed one-eighth of an inch. The tar and clay mixture should be used as hot as possible, and is also used for bedding the sides into the ends. "Feather" drills, shown at *b b b b*, Fig. 108, are cut in the stones from top to bottom, forming a diamond-shaped interstice when the sides and ends come together, and are carefully stemmed when each course is laid with the dry mixture of tar and fire-clay, before described. A good size of condenser for a pan working 8 cwt. of salt per hour is 6 ft. square and 60 ft. high from bottom to top stone. The lowest course is let into the bottom stone about $1\frac{1}{4}$ in., and carefully stemmed to prevent any escape of acid. If it be desirable for any reason to have a larger area than 6 ft. square, it will be found necessary probably to have the bottom stone in two halves. The best method of jointing is shown in Fig. 110, in cross-section, and must be most carefully made. Two "feathers," shown at *a a*, are drilled and stemmed perfectly hard. A stout iron bar should also be let into the stones, as shown in Fig. 111, to prevent spreading. The acid as it forms is conducted away by an earthenware pipe, 3 in. in diameter, which sits on the bottom of the concavity mentioned, and passes through one of the sides.

107.



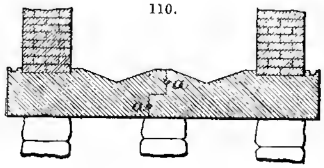
108.



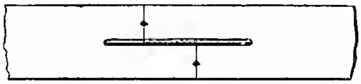
109.

Occasionally a pan condenser is built of brick instead of stone. This method, which should only be adopted in building roaster condenser, is shown in Fig. 110, and will receive further attention hereafter. Another plan of jointing the stones is shown in Fig. 112, which will readily explain itself. The corners, very carefully bevelled, are simply bedded together and secured by angles of timber, which run from the bottom to the top of the condenser, and are bound up at every four feet with iron rods, which pass through the angle irons shown at *c c c c*. It will be readily appreciated that, when simple joints of this kind are employed, any slight defect in dressing the stones is fatal. Occasionally the bevelled edges of the stone are simply screwed up by the iron binders upon a thin cord of indiarubber, running from the top to the bottom of the condenser in place of the diamond-

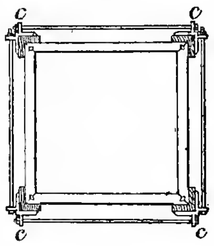
110.



111.



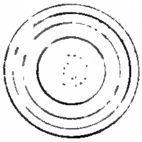
112.



shaped stemming. Upon the whole, however, the best methods of construction and arrangement are those already described, which give the results of a long practical experience.

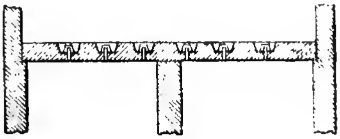
113.

114.

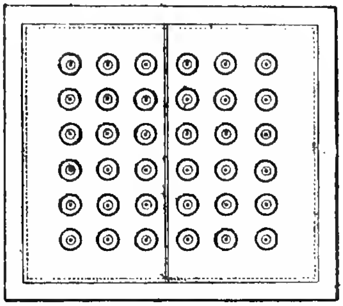


The condenser is closed at the top by a flag $4\frac{1}{2}$ in. thick, and sitting $2\frac{1}{4}$ in. upon the sides of the tower, which are cut down to receive it. A series of holes are pierced in this cover, and into them are fixed small lutes of the description shown in Figs. 113 and 114, which prevent any escape of gas from the interior of the condenser, and allow the free passage of a regulated supply of water. A plan and section of the cover, with lutes, is given in Figs. 115 and 116. If the condenser be too large for one stone, two may be conveniently used, the bevelled edges being brought together and stemmed, as shown in the drawings. In this case the stone support A should be fixed in the sides and run across the condenser exactly under the joint of the covers. The lutes should be carefully bedded with soft tar and china clay, and must be level with the surface of the stones. Upon the cover are fixed two "tumbling boxes" of the form shown in Figs. 117 and 118, by which an easily regulated supply of water from a cistern and tap arrangement above is evenly distributed over every portion of the condenser. These boxes should not be too much raised above the covers lest the dash of water when they "tumble" should throw the small and light lute caps out of their places. Occasionally larger lutes are employed, with a separate waterduct leading into each, but by this plan the distribution of the water is rendered very uneven through the constant choking of the necessarily small pipes. Many other methods are known and recommended, but the combination of small lute and tumbling box described is by far the best, admitting of easy regulation, perfect distribution, and certain work without much liability to disorganization.

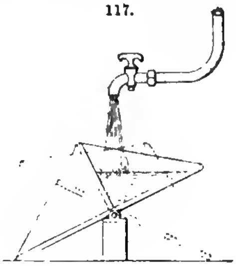
115.



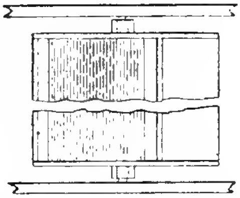
116.



117.



118.

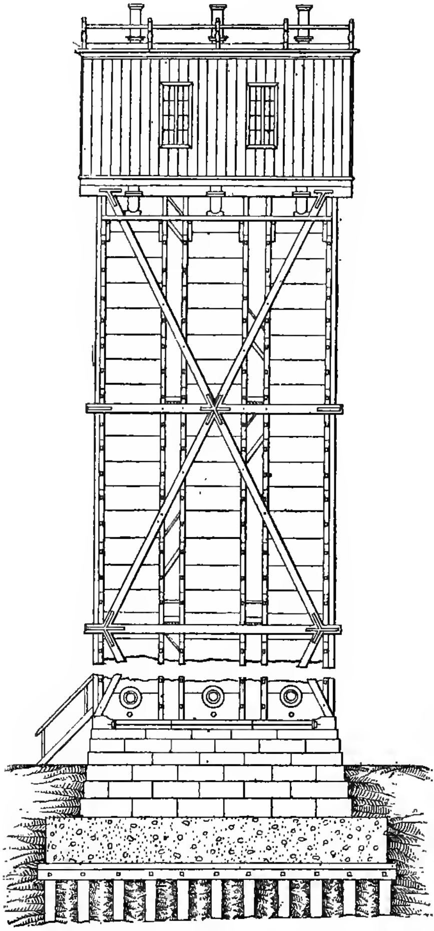


The water cistern and house arrangements upon the top of the condensers are sufficiently indicated in the figures. No special explanation is necessary. It must be noticed, however, that an unfailing supply of water must be secured and maintained, and that it is therefore important that the cistern and system of water pipes should be of the most permanent and durable character. A short or intermittent water-supply causes endless mischief to both plant and work, and allows escaping hydrochloric acid gas to work serious havoc among the surrounding vegetation.

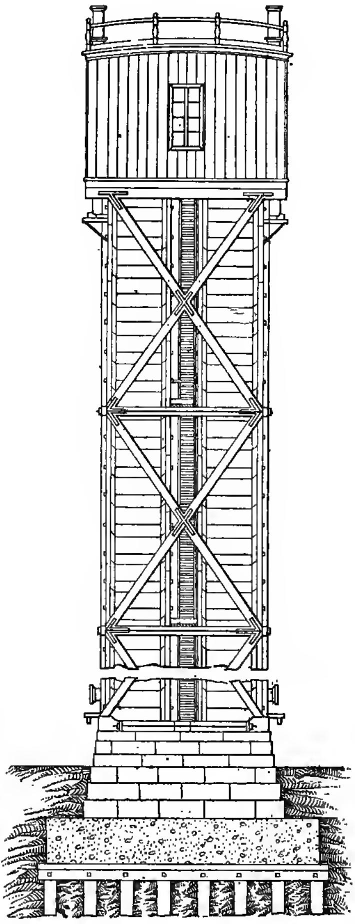
119.

Turning to the interior of the pan condenser and referring again to Fig. 105, it will be observed that the gas enters about 9 in. above the bottom stone. The conducting pipe should pass well through the side, and protrude 6 or 8 in. within the interior. About 12 in. above this ingress pipe, an open, dry, arch of firebrick, with a good crop, is thrown, to support the "packing." The method of building this arch will be readily understood from the plan, Fig. 119. The crop is levelled up with open flue work of bricks, and then flints, carefully cleaned, are thrown in to a depth of about 3 ft., to prevent the soft superincumbent coke from choking up the passages. Instead of a brick arch, stone joists, not less than 16 in. deep, may be used, supported upon $4\frac{1}{2}$-in. brick walls. They are, however, liable to crack, from the great weight resting upon them, and from constant variation of temperature. Above the flints comes a "packing" of well-sifted and hard-burnt coke, thrown loosely in to a depth of about 25 ft. The coke should be burnt for ninety-six hours, and must be free from smalls when put into the condenser, that choking may be as far as possible prevented. Rather more than half-way up the tower a second, dry, 9-in. arch of firebricks is thrown across and levelled up to the crop with open firebrick flues. Above this comes another packing of coke to within about 5 ft. of the top cover. The object of the second brick arch is to relieve the lower portion of the condenser of at least one-third of the total weight of "packing." About 12 in. below the cover an earthenware pipe is inserted in the side of the condenser to carry off the steam and whatever waste gases may be left. This final pipe arrangement is shown in the drawing as continued up the side of the cistern and issuing into the air. It may, however, be carried down and put into any convenient flue leading to the works' chimney. The plan shown is preferable, as an experienced eye can at once detect from the appearance of the gases passing away if there is any considerable amount of hydrochloric acid present. In this way so small an escape as 5 per cent. can be readily ascertained, and steps immediately taken to secure more perfect condensation. It should be stated that the employment of flints in packing is a necessary evil, and the quantity should therefore be as small as possible. They offer only a comparatively small condensing surface, and cannot be thoroughly cleansed from closely adhering impurities, which, half dissolved by the hydrochloric acid, inevitably choke up the interstices to a certain extent.

120.



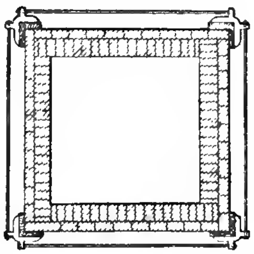
121.



In Figs. 120 and 121 are two given views of the exterior of a set of condensers, in front and side elevation. It is very desirable to adopt some such arrangement as that here shown, and not to distribute the towers about the works. Great additional strength is secured by the outside bracing, which is rendered possible, and by the enlarged foundation. The supervision and working of the towers are conducted with ease, convenience, and economy, and an actual saving in plant is effected by the concentration of cistern, pipe, and platform arrangements. Moreover, the danger and loss arising from a possible escape of acid are localized and reduced to a minimum. Some slight variations of the methods before described will be noticed, such as are rather matters of taste than necessity. One important modification, however, is shown. Between the pile-heads and basement (in this case solid masonry is given) a concrete bed will be observed. This consists of an intimate mixture of broken bricks—or any similar porous material—and pitch, or asphalte, and is higbly to be recommended if well laid. The materials must be carefully selected, freed from all dust, and a thorough mixture effected with the pitch. If these precautions be not observed, such an addition to the ordinary piled foundation, before described, is a source of weakness rather than strength.

Some details relating to the provision for condensing the gases from the roaster must now be given, attention being directed to the towers in Fig. 105, marked 2 and 3. The interior and the arrangements for distributing the water and securing a regular supply may be dismissed at once, as similar to those of the pan condenser. It will usually be found advisable, however, to carry the open brickwork above the bottom arch to a height of about 5 ft., to guard against any danger to the coke from the heat of the entering gases. The material of which the tower may be built is to a great extent a matter of choice. Brickwork, which is decidedly objectionable in the case of a pan condenser, on account of the lower temperature and consequent greater condensation and potency of acid, may be here employed with very good results. If, however, first cost be not of great consequence, the stones already described make the best and most durable condenser. If brickwork be chosen it must be carried to a height of about 10 ft., not less than 18 in. thick, and from that point to the cover 14 in. thick. Above the cover the walls may be conveniently carried up 9 in. thick for 6 or 7 ft. to form a house for the tumbling-box arrangements, and to carry the cistern. The bricks are set with a soft heated mixture of tar and finely-ground china or pipeclay, and all joints must be as thin as possible to prevent leakage of acid. The walls are let into the bottom stone after the manner shown in Fig. 110, and are bound up by strong timber corner-pieces passing from the top to the bottom of the condenser, and screwed up at every 4 ft. by the iron binders already described. The exact arrangement is shown in Fig. 122. The best dimensions of a roaster condenser are 6 ft. square interior measurement, and 50 ft. from bottom stone to cover. When all the products of combustion from the fire pass into the condenser, only a carefully-selected coke should be used, to prevent as far as possible choking of the condenser. Whether coal or coke be employed, however, it is necessary to keep a much greater draught upon the roaster than upon the pan condenser, and hence a considerable amount of hydrochloric acid is carried through the packing retaining its gaseous condition. The necessity for securing a sufficient draught also cuts down the amount of coke which can be used, as will be noticed from the drawing, and hence the escape of gas is facilitated. To meet this, and to secure perfect condensation, the small tower marked 3, Fig. 105, is usually added to the roaster condensing arrangement. This apparatus, or "flush tower," is constructed in similar manner to the pan, or drier, condenser, of brick or stone, preferably the latter. Into it are conducted by a range of earthenware pipes all gases passing off from the first tower uncondensed. The packing may be of open brickwork throughout, or a small amount of coke may be laid on the top, not more than 4 or 5 ft., that there may be no unnecessary impeding of the draught. The condensing liquid is distributed over the surface of the flush tower packing in the manner already described, and may be supplied by a pipe leading from one of the other cisterns. Good dimensions for a flush tower are the following:—35 ft. from bottom stone to cover, 4 ft. long and 3 ft. wide interior measurement. These sizes, however, may be varied to suit convenience, without entailing imperfect condensation.

122.



The working of these condensing arrangements will be already probably well understood from the description given. The gases from the pan are carried slowly up their condenser through the coke packing, and, meeting the descending water, are returned in the shape of liquid acid, fall to the bottom, and flow through the small earthenware duct to whatever reservoir may be provided.

The roaster gases are treated in similar fashion, the uncondensed portions being washed down the flush tower with whatever amount of water may be necessary to secure thorough condensation. The water supply upon the pan condenser is so regulated as to obtain an acid of about 25° Tw. *hot*. The acid from the roasters cannot be obtained of greater strength than 18° to 20°, or else a considerable loss is sustained by the large amount of uncondensed gas which has to be finally washed down. From the flush tower the water, with a slight acid taste and reaction, runs off at about 2° Tw. Condensation may be made so perfect in the pan condenser that litmus paper held in the escaping gases is not reddened. To effect this very desirable result, however, careful regulation of draught and thorough supervision are necessary. The escaping gases from the flush tower should not contain more than 1 per cent. of hydrochloric acid.

When the manufacturer estimates that the value of the available acid obtained from the roaster in the manner described does not compensate for the increased cost incurred by burning coke instead of coal, it is usual to arrange the packing of the condenser in the manner shown in the drawing of the flush tower, and wash down the whole of the gases at once with whatever amount of water may be necessary to secure thorough condensation, without regard to the strength of the acid obtained. This plan may also be adopted when the acid is intended for the evolution of carbonic anhydride from chalk or marble, as in the manufacture of bicarbonate of soda.

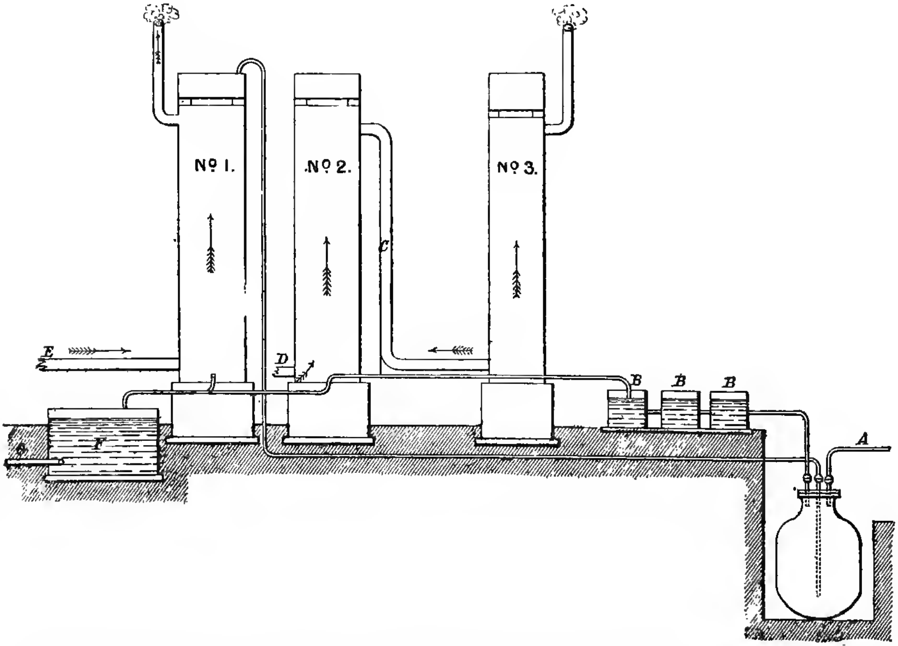
An ingenious method of condensation has been devised, and occasionally adopted, consisting in the subjection of the gases to the action of a fine spray of water, in a stone box similar in form to that shown in Figs. 102 and 103. As an appendage to the ordinary condensing apparatus, this simple device is of great service. By itself it is not sufficient for the amount of work usually required.

In place of the iron and earthenware pipes described, it has been proposed to make the gases pass from the roaster and pan through ranges of glass pipes of large dimensions. The first cost, however, and the expense of repairs and renewal, militate against the success of the system. When pipes of unglazed and porous earthenware are used, it is necessary to boil them thoroughly in tar for forty-eight hours. So prepared, they are more durable and capable than any other description of earthenware.

The octagonal form of stone condenser sometimes to be met with, while very strong and durable, is open to the objection of multiplying the number of joints, and, proportionately, the chances of leakage. The stones also require the most scrupulous care in dressing, to ensure a perfect fit. When brick is the material used, the size of the condenser should be arranged to suit the working of the courses, so that there may be as little cutting of the bricks as possible.

Mr. R. C. Clapham, having due regard to the advantages of an open packing for the roaster condenser, and flush tower, has proposed to concentrate the weak acid, which alone is obtainable from such an arrangement, by transferring it, by means of an air-pump and cast-iron egg lined with guttapercha, to the top of the pan condenser, and causing it to absorb the ascending currents of pan gas. In this way a saving of water is effected, and a uniformly strong acid obtained. The result, however, does not compensate for the extra cost of working. Mr. Clapham's arrangement is shown in Fig. 123. A is the air-pipe from the engine; B, the cooling cisterns for weak acids; C, the connecting pipe between the condensers; D, the pipe leading from the roasters; E, the pipe from the decomposing pan; F, the cistern for strong acid.

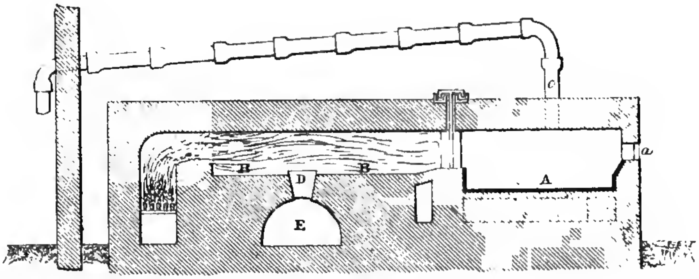
123.



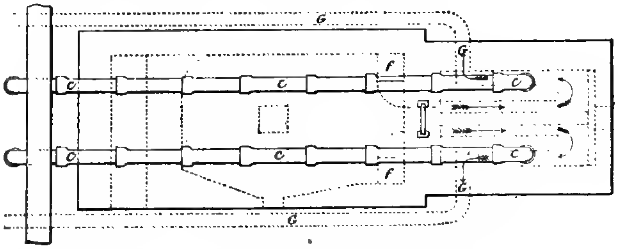
Before leaving this part of the subject, it will probably be useful to indicate some common faults in the planning and construction of condensing towers, and to draw attention to some of the most important points to be considered in the working. Perhaps the commonest fault of construction is the putting of two pans or roasters into the same condenser. It is impossible under this system to regulate the draughts properly, and a great amount of "ground" gas is necessarily allowed to escape, causing not only actual loss of acid, but serious inconvenience to the workmen and injury to the surrounding country. Moreover, at certain recurring stages of the process, an enormous accumulation of hydrochloric acid gas is forced into the condensers, which the ordinary supply of water is utterly inadequate to absorb, and a great portion of which consequently passes off into the air. Similar evils are caused when the towers are too small for their work, or when the packing becomes choked. The mischief arising from insufficient foundations has already been pointed out, and cannot be too carefully considered. No amount of care will compensate for a tower being out of plumb, or not perfectly tight. Very frequently the chimney into which the roaster gases are finally taken is no higher than the tower itself, or is overworked, and gives only an insufficient draught. Careless building, leaving wide joints between the bricks or stones, is a pregnant source of evil, as no mere bedding will withstand the action of the acid. In working the condensers, the question of a properly-regulated draught is of the first importance. Faultlessly planned and constructed towers are often spoiled in result by too great a draught being allowed. It is essential to have a carefully-managed system of dampers in both pan and roaster pipes, so manipulated that the gas in furnaces and condensers hangs back—just short of "blowing out." Inasmuch as a rapid draught enables the workman to get through his work more easily and speedily, the regulation of these dampers should be entrusted only to some competent manager or foreman, to guard against their being tampered with. The supply of water to cisterns and tumbling-boxes must be likewise under perfect control, all pipes being kept clear, or freed at once when choked. Finally, the damper between the pan and roaster must be kept as tight as possible, and well luted. The latter, having the greater draught, is apt to draw the pan gas away, and the roaster condenser is thereby overworked. On the other hand, if the heat from the roaster enters the pan pipes, the efficiency of the pan condenser is impaired, and the earthenware pipes are liable to be cracked. When the stream of water meets the stream of gas going up, the condensation is much better than when water and gas come down together. For this reason to make a double condenser, or one divided into two parts, the gas going up one side and down another, is a mistake. The packing of a roaster tower should last for three years without renewal, that of a pan condenser for five years.

The introduction of the decomposing pan now in common use in England is of comparatively recent date. Until about twenty-five years ago, the decomposition of salt and manufacture of sulphate of soda were carried on in what were called "dandy" furnaces. A somewhat similar apparatus is still in use in France, and is shown in section and plan in Figs. 124 and 125. Referring to Fig. 124, A is a rectangular pan or trough, formed of masonry, bricks, or metal, lined with lead, about 8 ft. long, 6 ft. wide, and 1 ft. deep. A damper working in a sand-bath, in similar fashion to that in use in this country, separates this pan from B, which is an ordinary reverberatory furnace, varying in size according to the judgment or experience of the manufacturer. Both furnaces are heated by a fire situated at the end of B, and one continuous arch forms the roof of the whole apparatus. The charge of salt, weighing up to 24 cwt, is introduced into A through the door *a*, and sulphuric acid of specific gravity 1·59, and in the proportion of 111 parts to every 100 parts of

124.

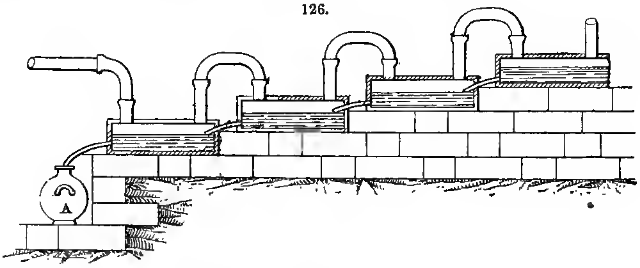


125.



salt is run in from an adjoining cistern placed upon a higher level. The door is then closed, and decomposition allowed to proceed. The hydrochloric acid evolved passes off the pipes *c c* to a series of condensing bottles. When the mass attains a pasty consistency the damper is raised and the charge transferred to the sole of the furnace B, where it is finally worked up as in an English roaster. When the operation is completed, the cover D is removed and the sulphate of soda raked down into the receptacle E to cool. The heat and products of combustion, together with all the hydrochloric acid evolved in the furnace, are carried down the holes shown in the corners at *f f*, Fig. 125, from thence under the sole of the pan in the direction indicated by the arrows, and finally pass off to a series of Woulfe's bottles, along the flues or pipes G G. By this means the necessity of having an independent pan fire is avoided. The condensation is, however, exceedingly imperfect, especially that of the heated furnace gases. An ingenious and more successful plan is adopted in the district of the Vosges, and is shown in Fig. 126. The bottles, or "dames-jeannes," are replaced by small cisterns built of hard stone, and set one above another. The interior capacity is about 2 cubic metres, and the sides 20 centimetres thick. The range is made of any suitable length, depending upon the consumption of salt, is inexpensive to build, and, comparatively speaking, indestructible. The cisterns are filled about one-third with water, and communicate by means of small leaden pipes set just at the surface of the liquid, and by larger earthenware gas pipes inserted in the covers. The gas enters the *lowest* box, or cistern, and travels upwards. Meeting the water, and exposed to a large condensing surface, liquid acid is formed, the water, or weak acid, becoming more and more saturated as it flows down from box to box, and finally passing over into the vessel A, at any strength that may be required.

126.



The chief methods for the condensation of hydrochloric acid which have been noticed, and the various apparatus described, obtain, when other processes than the ordinary decomposition of salt by sulphuric acid are employed. Of these may be cited the several plans devised for the direct action of sulphuric acid from pyrites, upon chloride of sodium, and the decomposition of salt by crystallized sulphate of magnesia, both of which processes have received a large amount of attention.

Two other plans occasionally adopted for rendering hydrochloric acid gas harmless, when its recovery as aqueous acid is not desired, are worthy of mention. The one is to pass the gas along galleries, where it meets with a constant and heavy flow of water—sea water, where its use is practicable—and is absorbed, the infinitely weak solution running off as a waste product. The second process consists of an arrangement of flue between furnaces and chimney, filled with blocks of chalk. The acid gas acts upon the carbonate of lime, producing carbonic anhydride, which passes off, and chloride of calcium. The chalk requires frequent renewal, and the flue constant supervision. This very clumsy method is adopted only in certain parts of the Continent where chalk is abundant, and obtainable at a nominal cost. Occasionally the flues themselves are cut through a chalk formation.

When due regard is had to the enormous volumes of hydrochloric acid gas that are being daily evolved from manifold chemical industries and the injurious effects of such emanations upon health and upon the surrounding vegetation, it is not surprising that stringent measures should be taken to enforce abatement of the nuisance. Indeed, the only wonder is that manufacturers, who ought to appreciate the loss of a valuable bye product through inefficient condensation, should be slow in adopting the best possible means to so worthy an end, and should require to have the necessity for a carefully organized plant, and working, so continually enforced at the point of law.

In the year 1862, a Select Committee of the House of Lords was appointed to inquire into the injury resulting from noxious vapours in certain manufacturing processes, and, after taking evidence on the subject, made their report during the same session of Parliament. They found that great injury was done to vegetation, the chief offenders being alkali and copper works, expressed no opinion on the effect of these vapours on human life or health, but stated that, in their belief, animals were indirectly affected by the poisoning of the grass upon which they fed. It was not recommended that copper works should be made the subject of special legislation, "as, unhappily, no means have yet been devised of neutralizing the effects of the vapours evolved during the manufacture of copper, consistently with the carrying on of this important branch of industry," but it was stated that upon the evidence of both scientific men and of manufacturers themselves it was not only possible but easy to carry on alkali works without causing injury to the neighbourhood. Therefore, while expressing an opinion that the legislature should not attempt to prescribe the specific process by which the nuisance should be prevented, the committee recommended that a bill should be introduced attaching a substantial penalty to the escape of muriatic or hydrochloric acid gas, appointing inspectors with ample powers wholly independent of local control and influence, and granting any person who conceived himself to be injured liberty to sue the manufacturer at Quarter Sessions, without appeal to the superior courts.

These recommendations bore speedy fruit. By the Alkali Act of 1863 (26 and 27 Vict., cap. 124), it was enacted as follows, viz.;—"The term 'alkali work' shall mean every work for the manufacture of alkali, sulphate of soda, or sulphate of potash in which muriatic acid gas is evolved.

"Every alkali work shall be carried on in such a manner as to secure the condensation, to the satisfaction of the inspector, derived from his own examination, or from that of a sub-inspector, of not less than 95 per cent. of the muriatic acid gas evolved therein: Provided always that nothing herein contained shall entitle the inspector to direct any alteration to be made in the process of manufacture, or the apparatus used therein. If any alkali work is carried on in contravention of this section, the owner of that work shall, on its being made to appear to the court before which any proceedings for recovery of a penalty may be instituted that 95 per cent. at least of the muriatic acid gas evolved in such work has not been condensed, be deemed guilty of an offence against this Act, and be subject, in respect of the first conviction to a penalty not exceeding 50*l.*, and in respect of every offence after a previous conviction to a penalty not exceeding 100*l.*; Provided always that no such owner shall be convicted of more than one such offence in respect of any one day.

"The owner of any alkali work in which any offence against this Act has been proved to have been committed, and for which a pecuniary penalty may be imposed, shall in every case be deemed to have committed the offence, and shall be liable to pay the penalty, unless he shall prove . . . that he has used due diligence to comply with and to enforce the execution of this Act, and that the offence in question was committed by some agent, servant, or workman, whom he shall charge by name as the actual offender, without his knowledge, consent, or connivance, in which case such agent, servant, or workman shall be liable to, and may be sued for, the payment of the penalty and of the costs of all proceedings . . . : Provided that it shall be lawful for the inspector to proceed in the first instance against the person whom he shall believe to be the actual offender, without first proceeding against the owner.

"No alkali work shall be carried on . . . at any time after the expiration of three months after the appointment of the inspector, until such work has been registered by the owner with the inspector. In every register hereby required to be made there shall be inserted the name in full of the owner and of the parish or township in which the work is situated, and within one month after change of ownership . . . the register of such work shall be amended by inserting the name of the new owner; and if any alkali work is carried on in contravention of this section, the owner thereof shall, on conviction, be . . . subject to a penalty not exceeding 5*l.* for every day during which such work shall have been so carried on.

"For the purpose of carrying into effect the provisions of this Act, the Board of Trade may, from time to time, appoint any fit and proper person to be inspector of alkali works under this Act.

"It shall be the duty of every inspector to ascertain from time to time that all the alkali works are carried on in conformity with the provisions of this Act, and to enforce such provisions, and to cause notice to be given to every owner whose work shall be carried on in contravention of this Act, of the commission of such offence as soon as conveniently may be after the commission thereof; and, with a view to the performance of that duty, he, or any sub-inspector, may at all reasonable times, by day and night, without giving previous notice, but so as not to interrupt the process of the manufacture, enter upon and inspect any alkali work, and examine into the efficiency of the condensing apparatus, and the quantity of muriatic acid gas condensed. And the owner . . . . shall furnish a plan, to be kept secret by such inspector, of those parts of the works in which the decomposition of salt, or other process causing the evolution of muriatic acid gas, or the condensation thereof, is carried on.

"Every person who wilfully obstructs any inspector or sub-inspector in the execution of this Act, and every owner who refuses or neglects to afford the facilities necessary for making any entry, inspection, examination, or testing, under this Act, . . . shall incur a penalty not exceeding 10*l.*"

The Board of Trade appointed an inspector, Dr. Angus Smith, and four sub-inspectors, whose head-quarters have been:—

1. Liverpool—the district including Widnes, St. Helen's, Flint, Bristol, and Swansea.
2. Manchester—the district including the eastern part of Lancashire, the country round Birmingham, Yorkshire, and London.
3. Newcastle-on-Tyne—the district including both banks of the Tyne, Middlesborough, and Seaham.
4. Glasgow—the district including all Scotland and Ireland.

Under the Public Health Act of 1872 (35 and 36 Vict.) it was directed that the powers and duties of the Board of Trade under the 1863 Act should be transferred to, and exercisable by, the Local Government Board.

The effects of this legislation were at once beneficial to the public and not unduly onerous to the manufacturer. A huge increase, however, took place in the chemical industries of the country, so that the number of escapes neutralized to a great extent the advantages gained. Moreover, the exceedingly prosperous state of the trade introduced greater laxity at a time when the work of supervising became more difficult. Dr. Smith, therefore, recommended that more stringent legislation should be initiated, and that other works than those engaged in the alkali manufacture should be brought under supervision. This was the more reasonable inasmuch as it was proved that the additional care which manufacturers were compelled to bestow upon the condensation of their gases, and the large sums of money which were spent upon the necessary apparatus had eventuated in an absolute gain—an additional profit.

Consequently, an Act (37 and 38 Vict., cap. 43), passed in 1874, further defined the term "Alkali Work" of the principal Act of 1863, as including the "formation of any sulphate in the treatment of copper ores by common salt or other chlorides," and, reciting the provision of the principal Act securing the condensation of such percentage of muriatic acid gas as therein mentioned, enacts as follows, viz.:—

"In addition to the condensation of such percentage of muriatic acid gas as aforesaid, every alkali work shall be carried on in such manner as to secure the condensation, to the satisfaction of the inspector . . . . of the muriatic acid gas evolved, to such an extent that *in each cubic foot of air, smoke or chimney gases escaping from the works into the atmosphere, there is not contained more than one-fifth part of a grain of muriatic acid.*" By this Act it was also ordained that under certain penalties the owners of alkali works "shall use the best practicable means of preventing the discharge into the atmosphere of all other noxious gases arising from such work, or of rendering such gases harmless when discharged." The penalties attaching to the contravention of the Acts were ordered to be the same as those set forth in the 1863 Act, with the additions referred to for securing the better condensation of gases other than muriatic acid gas. "Noxious gas" was defined as meaning sulphuric acid; sulphurous acid—except that arising from the combustion of coals; nitric acid, or other noxious oxides of nitrogen; sulphuretted hydrogen, and chlorine.

This Act came into operation on the 1st of March, 1875, and wrought considerable improvement. Still complaints of nuisance and damage were rife, and various petitions on the subject were presented to Parliament, resulting in the appointment of a select committee to inquire into the whole matter, and to report upon the best means to be adopted for the prevention of injury arising from the exhalation of noxious gases. The Committee sat from time to time from August, 1876, to August, 1878, at Liverpool, Tynemouth, Newcastle-upon-Tyne, Swansea, and London, and received from all parties interested a voluminous mass of evidence. The result was embodied in a Report drawn up in the summer of 1878, and, in the recommendations set down, the probable legislation of the immediate future is foreshadowed. It was proved to the satisfaction of the Commission that enormous damage to vegetation and live stock was caused by the emission of noxious vapours, which was not compensated by the increased value of land in the immediate neighbourhood of the works. With respect to the question of health, the Committee stated that they were "unable to say that the statistics adduced furnish any convincing proof of the injurious effects of the vapours." It was shown that a considerable degree of laxity entered into the administration of the present regulations, that the desultory visits of the inspectors were inadequate to the work to be performed, and, especially, that it was works other than those engaged in the alkali manufacture, which now required strict supervision and regulation. The following recommendations were finally set forth:—

1. That the number of the inspector's visits to each work, and all recorded escapes, with the names of the works in which they occurred, be published in the Annual Report of the Chief Inspector, and that the inspectors be impowered to inspect plant, and be required to report defective plant to the chief inspector, such report to be published.

2. That the escape of more than one grain of sulphur, in the form of any of its acids, contained in one cubic foot of exit gases, be made an offence under the Acts.

That the escape of more than half a grain of nitrogen, in the form of any of its acids, contained in one cubic foot of exit gases, be made an offence under the Acts.

That the limitations of acid escape specified, shall not apply to the production of sulphuric acid from sulphur gases evolved from the treatment of sulphur compounds, where otherwise the sulphur gases would escape uncondensed into the atmosphere.

That one cubic foot of exit gases shall mean one cubic foot of exit gases at 60° Fahr., and under a barometric pressure corresponding to 30 in.

That the exit gases shall in each case be collected from the exit flue of the chambers before entering the chimney.

3. That the deposit of alkali waste so as to cause a nuisance be made an offence under the Acts.

That the permitting acid drainage to come into contact with alkali waste, or the drainage from alkali waste, be made an offence under the Acts.

That the permitting alkali waste, or the drainage from alkali waste, to come into contact with acid drainage be made an offence under the Acts.

4. That all works in which sulphuric acid is manufactured for sale or use be subjected to inspection under the Alkali Acts, and that the escapes of sulphur and of nitrogen, in the form of any of their acids, beyond the proportions, and subject to the exception above specified, be made an offence under the Acts.

5. That chemical manure works be subjected to inspection, and required to adopt the best practicable means for preventing escapes of noxious or offensive gases.

6. That sulphate of ammonia works, tar distilleries, and gas-liquor works be subjected to inspection, and required to adopt the best practicable means for preventing escapes of sulphuretted hydrogen.

7. That all coke ovens be subjected to inspection; and that all coke ovens erected after the passing of the new Act be required to adopt the best practicable means for preventing escapes of black smoke, and for diluting sulphur compounds.

That, on complaint of nuisance or damage established to the satisfaction of the Local Government Board, coke ovens existing at the date of the new Act be required to adopt the best practicable means for preventing escapes of black smoke and for diluting sulphur compounds; a period of three years being allowed for compliance with the requirement.

8. That arsenic works, cement works, cobalt works, dry copper works, wet copper works (so far as regards those operations which correspond to those of dry copper works), galvanizing works, glass works, lead works, nickel works, potteries where the salt glazing process is carried on, salt works, spelter works, tin plate works, and works for the manufacture of dyes from coal tar derivatives be placed under the supervision of inspectors appointed under the Act, who should have a power of entry and of inspection; and their proceedings should be reported annually to the Local Government Board.

9. That with respect to any of the above mentioned works, the Local Government Board be empowered from time to time to fix, by provisional order to be confirmed by Parliament, a standard of escape, or to require the adoption of the best practicable means for preventing escapes.

10. In all cases of nuisance and damage alleged to be occasioned by more than one individual, the court should be clothed with full powers of apportioning damages and enforcing contributions, and of awarding costs as among all or any of the alleged contributories to the nuisance or damage.

The Committee was also "prepared" to recommend that "as the infractions of the Act involve injuries to health as well as to property, the local sanitary authority should, with the consent of the Local Government Board, have power to prosecute for offences under the Act arising within their districts or affecting their districts." From this recommendation, however, certain practical members of the Committee dissent, and it is hardly likely that such a radical change of procedure will be established, considering that an important principle underlying all legislation on the subject has been the exclusion of local influence and prejudice.

The importance of examining the foregoing recommendations, and the reports of the inspectors under the 1863 Act, which have been issued annually from 1864 to 1874 inclusive, cannot be too strongly impressed upon manufacturers, or intending manufacturers, of hydrochloric acid. Careful attention to the evidence and details set forth cannot fail to convince impartial minds that the nuisance and injury resulting from defective plant, or careless working and organization, have been by no means fairly grappled with, and that further and more stringent measures will be initiated. It must be remembered also that legislation on the subject will follow very closely the recommendations of the Committee, as borne out by the results of inspection.

The first annual report of the chief inspector was issued in 1865—for the year 1864—and gives perhaps a somewhat rosy view of the state of condensation, owing to the necessarily crude system of a novel work of examination, and the efforts of manufacturers to acquit themselves well under the recently passed Act. The following summary gives the state of condensation in the four districts as far as it could be ascertained:—

Actual condensation per cent. 98·72. The average escape of muriatic acid is 1·28 per cent. over the kingdom. This number is obtained by estimating the actual amount escaping at each work.

AVERAGE OF THE PERCENTAGES AT EACH WORK.

	Condensation.	Escape.
Western district	99·763	0·237
Middle "	99·040	0·960
Eastern "	97·940	2·060
Scotland and Ireland	98·426	1·574

Average, by adding all the percentages of the escape, and dividing by the number of works, 0·9409 per cent., which number is the proper average by which the condensation may be judged.

ACTUAL ESCAPE OF MURIATIC ACID PER WEEK IN TONS AND PER CENT.

	Escape, in Tons.	Escape, per Cent.
Western district	4·2786	0·3109
Middle ,, ...	5·221	1·207
Eastern ,, ...	26·023	2·1704
Scotland and Ireland	7·195	2·1218
Total escape in tons of dry acid ..	42·7176	..

"If all the works were of the same magnitude, these two tables would give percentages entirely alike. As they stand, the difference is small. To obtain this latter table, the amount of escape is calculated from the total quantity of salt used at each work and the condensation per cent. The total amount of salt decomposed per week is 5762 tons. This gives out 3324·96 of dry acid, or about 13,000 tons of strong commercial muriatic acid in a liquid state. The whole amount would escape if there were no condensation. The effect of the condensation reduces it to 43 tons."

The state of condensation at a series of individual works—distinguished by the register number given in the first column—is shown by the following table:—

No.	HCl. entering Condenser, in Grains per Cubic Foot.	HCl. escaping, in Grains per Cubic Foot of Air.	HCl. escaping, Grammes per Cubic Metre.	HCl. escape, in Tons per Week.	HCl. escape, per Cent.
1	Where there is no escape, the amount entering the condenser is of no importance, and is not given	..	..	..	0·
2	..	..	..	0·0087	0·25
3	Stopped for alterations.				
4	..	..	..	..	0·
5	..	..	..	..	0·
6	..	..	..	..	0·
7	..	..	..	..	0·
8	..	..	..	..	0·
9	..	..	..	..	0·
10	..	..	..	..	0·
11	34·47	0·512	1·171	1·29	1·5
12	..	..	..	..	0·
13	..	..	trace	..	0·
14	34·3	0·37	0·847	1·36	1·09
15	92·05	1·62	3·706	1·45	1·75
16	..	..	..	..	0·
17	Stopped				
18	..	..	..	..	0·
19	..	..	trace	..	0·
20	781·5	2·34	5·333	0·17	0·3
23	..	..	trace	..	0·
26	..	..	trace	..	0·
27	..	..	trace	..	0·
28	..	0·1	0·228	0·055	0·16
30	..	..	..	..	0·
31	..	0·04	0·091	0·008	0·12
32	..	0·54	1·235	1·653	4·55
33	..	..	..	..	0·
34	..	0·16	0·366	0·363	0·3
35	..	..	..	..	0·
39	..	0·06	0·137	0·079	0·24
40	..	0·40	0·910	0·655	1·67
41	..	0·23	0·532	0·078	0·63
42	..	0·14	0·32	0·044	0·54
43	..	..	..	..	0·
45	..	..	..	..	0·
46	..	0·43	0·983	0·202	1·95
47	..	1·08	2·469	0·072	2·28
48					
49	..	0·48	1·098	2·012	2·79
50	..	..	..	0·66	0·1
51	..	..	..	5·79	3·24
53	Altering				
54	..	·791	1·81	2·78	4·2
55	..	2·1	4·8	1·396	4·4
56	..	..	..	1·998	3·
57	..	..	..	0·207	0·1
58	..	·316	0·724	0·704	1·42
59	..	..	..	0·207	0·1
60	..	..	..	0·207	0·1
61	..	..	..	0·207	0·1
62	..	..	..	1·961	0·1
63	..	2·2	5·	6·713	4·48
64	..	..	..	0·207	0·1
65	..	..	..	0·207	0·1
66	..	2·8	6·4	0·207	3·7
67	..	..	..	1·384	0·1
68	..	0·728	1·6	0·207	4·4
69					
70	..	..	..	0·496	0·1
71	..	0·928	2·05	0·491	1·2
72	..	..	..	..	2·4

Referring to the state of condensation before the passing of the 1863 Act, the Report says:—"It is now, perhaps, impossible to ascertain with certainty the amount of gas allowed to escape immediately before the passing of the Act. Some years ago, as is well known, the escape of the whole was allowed; but as the manufacture increased, the public complained more, and the alkali makers erected condensers. Besides this cause, the value of the muriatic acid had been gradually increasing, and its condensation had in some places become a source of profit. Nevertheless it is true that thorough condensation was known to very few, and practised by still fewer, up to the time of the passing of the Act, and it even happened that for some time after inspection had begun 40 per cent. of the gas was in some cases allowed to escape, while 16 was a very common amount. Many alkali makers believed that any very refined condensation was impossible, but an examination of the subject showed that habitual complete condensation had been already attained in several cases at the end of the year 1863, if not earlier.

"If we estimate the escape of muriatic acid gas at 1000 tons per week before the passing of the Alkali Act, or at least before the introduction of the Alkali Bill into Parliament, we may be considered as taking a very moderate view of the question. This supposes 2324·96 to have been already condensed, and is a very favourable view of the case. The 1000 tons left uncondensed are equal to 4000 tons of 25 per cent. acid, and under one-third of the total amount evolved in the process of decomposing salt by sulphuric acid in the United Kingdom. This quantity amounts to 208,000 tons per annum. The date of the introduction of the Alkali Bill into Parliament is spoken of, as it is believed that alterations began from that period, some of the manufacturers not having waited until the passing of the Act. At the same time it may be said that the changes then made referred more to carefulness in the operations than improvements in apparatus."

In the Report for the year 1873, the inspector states his belief that while the work of inspection is being done with more exactness, and becoming more certain, the Act is nevertheless unfitted for dealing with the increase of manufactures, and asserts that there are districts in which the amount of damage done is actually on the increase. Dr. Smith says:—"It will probably be sufficient, so far as muriatic acid is concerned, to allow the present Act to remain either unaltered or with little alteration, and to pass another which shall demand that the escaping gas shall not contain above a certain amount of acid per cubic foot. Abundant trials have shown that the amount at present is 0·16 grain per cubic foot on an average in chimneys. I believe the evil is done chiefly by those above this average. It might be enough to demand that the maximum shall be 0·2 per cubic foot, which might be diminished gradually by the Local Government Board as circumstances showed it practicable, by 0·02 at a time, and annually, until it reached 0·1."

The following tables give the results of condensation in the different districts for the year 1873:—

ESCAPE OF MURIATIC ACID IN No. 1 DISTRICT.

Register No.	Salt Decomposed per Week.	No. of Close Salt Cake Furnaces.	No. of Open Salt Cake Furnaces.	Muriatic Acid found in 1 cubic foot of Air in Chimney or Culvert.	Muriatic Acid escaping through the Chimney compared with that producible from the Salt Decomposed.
	tons			grains	per cent.
1	100	3	0	0·20	4·17
2	15	1	0	0 15	1·51
3	15	0	1	0·12	1·92
4	240	2	2	0·37	6·0
5	66	2	0	0·19	2·30
6	100	2	0	0·12	1·02
7	360	8	0	0·21	3·81
8	250	6	0	0·19 0·05	4·52
9	90	3	0	0·34	4·83
10	180	3	0	0·29	4·95
11	250	5	1	0·19	3·22
12	180	4	0	0·15	2·46
13	60	2	0	0·17	2 20
14	220	0	4	0·28	4·30
15	200	1	2	0·04	1·59
16	170	2	1	0·06	3·24
17	150	3	0	0·05 0·25	2·98
18	250	5	0	0·23	4·60
19	180	3	0	0·13	2·48
20	180	0	5	0·43	2·58
23	80	2	0	0·23	4·8
26	600	12	1	0·22	4·25
27	85	2	0	0·18	3·85
75	185	4	0	0·32	4·00
88	85	2	0	0·19	1·80
89	300	7	0	0·25	4·91
92	200	1	4	0·12 0·11	2·26

Escape of Muriatic Acid in No. 1 District—*continued.*

Register No.	Salt Decomposed per Week.	No. of Close Salt Cake Furnaces.	No. of Open Salt Cake Furnaces.	Muriatic Acid found in 1 cubic foot of Air in Chimney or Culvert.	Muriatic Acid escaping through the Chimney compared with that producible from the Salt Decomposed.
	tons			grains	per cent.
96	160	3	0	0·13	4·80
97	200	4	0	0·60	2·40
98	40	1	0	0·43	3·80
100	80	2	0	0·42	3·50
102	120	3	0	0·31	4·60
103	80	2	0	0·36	1·76
104	50	1	1	0·26	1·93
112	150	3	0	0·41	3·10
113	350	6	2	0·28	3·78
118	300	2	2	0·32	3·35
123	250	5	0	0·45	4·21
126	40	2	0	0·28	3·65
127		Not at work.			
131	30	..	..	0·10	0·31
124		Not at work.			
133	25	0	1	0·92	2·80
	6666	Average	.. ..	0·25	3·28

No. 2 District.

Register No.	Average Escape of Acid.	Register No.	Average Escape of Acid.	Register No.	Average Escape of Acid.
28	2·94	40	0·86	48	1·62
30	3·27	41	2·22	49	2·07
31	2·78	42	2·53	90	2·04
32	3·70	43	1·12	111	1·17
33	2·29	45	1·19	112	5·07
34	3·52	46	0·18	120	1·38
35	2·50	47	2·96	130	2·70

The whole of these figures give an average of 2·19 per cent. for the district.

No. 3 District.

In the annexed table the pan gas is unestimated, but is taken as two-thirds of the whole. Consequently the results are divided by 3 to ascertain the amount of uncondensed roaster gas. The pan condensers were never found to have an escape of 1 per cent.

Register No.	Inlet Gas, HCl. Grains per Cubic Foot.	Outlet Gas, HCl. Grains per Cubic Foot.	Escape, per Cent.		Register No.	Inlet Gas, HCl. Grains per Cubic Foot.	Outlet Gas, HCl. Grains per Cubic Foot.	Escape, per Cent.	
64	15	0·4	2·6÷3=	0·8	51 HL	24	0·4	1·6÷3=	0·5
,,	14·1	0·3	2·1	0·7	52	20	0·5	2·5	0·8
,,	20	0·5	2·5	0·8	,,	25	0·5	2	0·6
,,	15	1·5	9·9	3·3	,,	24	0·6	2·5	0·8
,,	15	1	6·6	2·2	53	20	0·9	4·5	1·5
67	25	0·4	1·6	0·5	54	22	0·2	0·9	0·3
71	24	0·5	2	0·6	56	15	1	6·8	2·2
70	22	0·6	2·7	0·9	,,	150	3·0	2	
,,	25	0·9	3·6	1·2	,,	48	6	12·5	4·1
,,	20	0·6	3	1	57	70	1·1	1·5	
94	70	0·4		0·5	55	20	3	15	5
101	70	0·3		0·4	58	30	0·9	3	1
50	25	1	4	1·2	,,	21	3·1	14·7	
,,	11	1	9	3	,,	20·4	3·3	1·6	5·3
,,	19	0·6	3	1	,,	70	1·7	2·4	
,,	12	0·6	5	1·6	59	16	0·3	1·8	0·6
51 HL	24	1	4·1	1·3	60	150	0·4		0·26
,,	22	0·4	1·8	0·6	61	13	0·5	3·8	1·2

No. 3 DISTRICT—*continued.*

Register No.	Inlet Gas, HCl. Grains per Cubic Foot.	Outlet Gas, HCl. Grains per Cubic Foot.	Escape, per Cent.	Register No.	Inlet Gas, HCl. Grains per Cubic Foot.	Outlet Gas, HCl. Grains per Cubic Foot.	Escape, per Cent.
63	40	0·3	2·1÷3=0·7	115	20	1	5 ÷3=1·6
107	20	0·7	3·5 1·1	„	18	0·5	2·7 0·9
„	20·7	1·1	5·3 1·7	116	13·3	0·3	2·2 0·7
„	15	0·9	6 2	„	14	0·3	2·1 0·7
108	20	3·3	16·5 5·5	„	22	0·3	1·3 0·4
114	20	0·5	2·5 0·8	„	20	0·2	1 0·3

No. 4 DISTRICT—SCOTLAND AND IRELAND.

Register No.	Quantity of Salt Decomposed in 24 hours.	Total Condensing Space for each Furnace.	Length of Pipes and Flues.			Average Escape of HCl. per Cubic Foot.	Area of Flue or Chimney.	Speed of Flue or Chimney, per Second.	No. of Visits.	Quantity of Acid made.
			Furnace to Condenser.	Condenser to Chimney.	Furnace to Chimney.					
	cwts.	cub. ft.	ft.	ft.	ft.	grains	sq. ft.	ft.		
72	10	960	..	..	..	This work has ceased decomposing salt.			3	
73	30	1200	20	20	80	·020	28	7	11	
77	30	Work slowly, and condense in bottles.						..	18	
79	1800	1250	130	250	200	See notes for details of condensation.			46	
80	220	1764	150	80	80	·11	25	9	5	About 1030 cub. ft. at 20° T.
81	Uncertain 20	1620	114	100	38	·02	..	..	4	
82	200	1600	180	102	70	·05	24	9·5	8	Quantity unknown. Strength at 28° T.
83	288	1420	72	40	72	·099	25	9	6	Do., 23° T.
105	222	2000	100	180	145	·08	27	8	5	About 180 cwt. at 23° T.
106	196	950	227	102	90	1·1	36	8·5	16	About 2300 galls. at 29° T.
117	84	900	187	20	100	·03	18	..	7	640 galls. at 31° T.
119	118	1778	100	48	126	·077	16	8	4	133 cwt. at 25° T.
95	9·1	1240	413	27	32	·18	20	7	20	1050 galls. at 34° T.
125	180	900	Work stopped.			·12	..	..	4	
134	120	1177	120	95	80	·088	18	Work stopped.	6	About 380 cub. ft. 28° T.
..	140	1427	630	..	120	trace	..	..	3	
128	96	1340	156	255	180	·075	20	10	8	

This interesting table will especially repay a careful study, as showing the different apparatus and condensing capabilities of the several works.

During the year (1873) some important experiments were made with a view to ascertain the action of the acid gases upon vegetation. The results are set forth in the annexed table. It was deemed that the best method of procedure was to steep the twigs carefully in water and then examine the liquid. The mode of testing must of course be delicate, as the amounts of acidity are comparatively small. After being washed with water, the twigs were crushed, and treated with dilute nitric acid for about twelve hours. It will be at once apparent that the action of the gases is to produce acidity on the outside of the plant, and to increase the amount of acid in a combined state both on the surface and internally.

WATER WASHING OF TWIGS.

Place of Growth.	Parts per 100,000 of Twigs.				Proportion of Hydrochloric to Sulphuric Acid.
	Hydrochloric Acid.	Sulphuric Acid.	Acidity calculated as Sulphuric Anhydride.	Total Acids.	
Liable to be reached by acid vapours.					
Exposed to Runcorn and Widnes smoke, 1½ miles on Moore Road from Runcorn. Old twigs ..	72·0	21·2	17·8	93·2	1 to 0·30
Ditto. Old twigs	22·2	3·6	3·7	25·8	1 „ 0·16
East of Runcorn a mile. Old elm, very black	66·0	71·8	56·6	137·8	1 „ 1·09

WATER WASHING OF TWIGS—*continued.*

Place of Growth.	Parts per 100,000 of Twigs.				Proportion of Hydrochloric to Sulphuric Acid.
	Hydrochloric Acid.	Sulphuric Acid.	Acidity calculated as Sulphuric Anhydride.	Total Acids.	
Runcorn, east of :—					
Old thorn, very black	12·6	5·7	5·6	18·3	1 „ 0·45
Old bark	6·0	5·7	3·1	11·7	1 „ 0·95
Green fir	4·8	2·6	3·3	7·4	1 „ 0·54
Near Runcorn :—					
Fir, brownish leaves	64·1	21·4	..	85·5	1 „ 0·33
Fir, green part	21·0	8·1	..	29·1	1 „ 0·39
Rotten thorn	17·4	4·1	6·5	21·5	1 „ 0·23
Fresh thorn	12·2	5·8	..	18·0	1 „ 0·47
Copse, west of Moore a mile. Old elm, very black	12·8	19·6	24·3	32·4	1 „ 1·52
Park looking to Runcorn. Raining	2·4	4·7	0·3	7·1	1 „ 2·00
Average	26·1	14·5	10·1	40·6	1 „ 0·55
From places not affected by acid vapours.					
*Bark of a tree, elm, at Walton	9·0	4·9	1·8	13·9	1 to 0·54
Walton elms	3·8	19·6	0·9	23·4	1 „ 0·54
Healthy wood, sheltered from acid vapours	9·0	6·5	1·9	15·5	1 „ 0·92
Rusholme. Old thorn	5·4	10·9	..	16·3	1 „ 2·02
„ New thorn	4·2	1·6	..	5·8	1 „ 0·38
Average	5·6	9·6	0·7	15·2	1 „ 1·71

* Not included in the average.

TWIGS TREATED WITH NITRIC ACID.

Place of Growth.	Parts per 100,000 of Twigs.			Proportion of Hydrochloric to Sulphuric Acid.
	Hydrochloric Acid.	Sulphuric Acid.	Total Acids.	
Liable to be reached by acid vapours.				
Exposed to Runcorn and Widnes smoke, 1½ miles from Runcorn	1·2	17·9	19·1	1 to 14·90
East of Runcorn a mile. Old elm, very black	0	179·5	179·5	..
Runcorn, east of :—				
Old thorn, very black	6·0	4·1	10·1	1 „ 0·68
Old bark	1·2	..	..	..
Green fir	3·0	27·2	30·2	1 „ 9·07
Near Runcorn :—				
Fir, brownish leaves	0·3	..	..	..
Fir, green leaves	0·3	..	..	..
Rotten thorn	0·6	4·9	5·5	1 „ 8·1
Fresh thorn	..	9·3	..	..
Copse, west of Moore a mile. Old elm, very black	2·4	12·9	15·3	1 „ 5·37
Park looking to Runcorn. Raining	18·0	20·4	38·4	1 „ 1·13
Average	3·1	31·2	38·1	1 „ 10·06
Not affected by acid vapours.				
*Bark of a tree, elm, at Walton	6·0	1·6	7·6	1 to 0·26
Walton elms	9·0	20·4	29·4	1 „ 2·27
Healthy wood, sheltered from acid vapours	1·8	4·0	5·8	1 „ 2·2
Rusholme. Old thorn	0·3	..	..	..
„ New thorn	0·3	2·4	2·7	1 „ 8·00
Average	2·8	8·9	12·6	1 „ 3·72

* Not included in the average.

It is intensely difficult to get any approximate idea of the effect of gaseous emanations upon human life and health, so variable are the manifold conditions of life. On the one hand, air with acid fumes in it cannot be as good as the simple air prepared by nature; but, on the other hand, the exhalations are doubtless useful in neutralizing the evils arising from overcrowding, deficient drainage, and all the concomitants of a rude population and social state. The general freedom of chemical districts from zymotic and epidemic diseases is tolerably well established. Perhaps the best information yet collected on the subject has been that rendered by an inquiry set on foot by the Belgium Government in 1855.

The following table gives the death-rate in various districts for five years, and five years after the introduction of chemical works :—

	Before the Establishment of Chemical Works.		After the Establishment of Chemical Works.	
	Population.	Deaths.	Population.	Deaths.
Risle—				
St. Marc	1,866	46	2,057	40
Verdrin	6,805	150	7,417	116
Champion	4,037	105	4,330	77
Rhione	2,851	64	3,529	50
	15,559	365	17,333	313
	1 to 42, or 2·37 per cent.		1 to 55, or 1·82 per cent.	
Floreffe—				
Floreffe	10,895	142	11,833	182
Maloune	11,188	205	11,536	178
Floriffoux	2,334	37	2,435	52
Soye	3,377	45	3,835	51
Fraviere	2,479	35	2,746	26
	30,313	464	32,405	489
	1 to 56, or 1·53 per cent.		1 to 66–67, or 1·508 per cent.	
Moustier—				
Moustier	2,596	55	2,564	57
Momimont	956	15	1,030	20
Ham-sur-Lambre	4,015	70	4,228	63
	7,567	140	7,822	140
	1 to 53–54, or 1·85 per cent.		1 to 55–56, or 1·79 per cent.	
Auvelais—				
Auvelais	8,600	144	9,090	164
Jemeppe	5,059	75	5,234	99
Tamine	4,692	77	4,921	82
	18,351	296	19,245	345
	1 to 61–62, or 1·61 per cent.		1 to 55–56, of 1·79 per cent.	
Total	74,923	1,343	81,181	1,387
	1 to 56–57, or 1·79 per cent.		1 to 58–59, or 1·708 per cent.	

The effects of acid fumes upon the soils in the neighbourhood of chemical works would form an interesting and useful subject of examination. As a commencement the following tables are worthy of attention :—

Specimens of Soil (February, 1874).	The Water of the Soil, parts per 100,000.			Parts per 100,000 of the Dry Soil.		
	Hydrochloric Acid.	Sulphuric Acid.	Acidity calculated as SO_3.	Hydrochloric Acid	Sulphuric Acid.	Acidity calculated as SO_3.
St. Helen's: ½ mile west of, near Pilkington's old glass works. No trees; some grass and crops	9·57	12·50	18·14	2·74	3·79	5·49
,, 1 mile west of	22·03	24·30	72·86	4·42	4·90	14·61
,, ,, ...	12·53	12·96	22·29	3·33	3·30	5·92
,, 1¾ miles west of	5·00	8·12	4·45	2·28	3·72	2·04

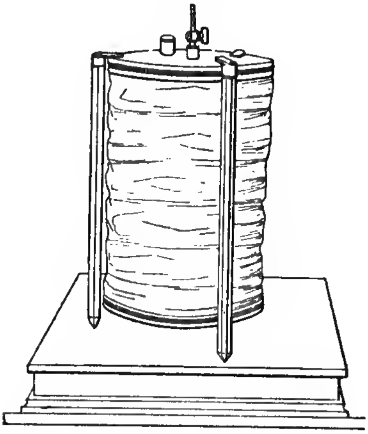
Specimens of Soil (February, 1874).	The Water of the Soil, parts per 100,000.			Parts per 100,000 of the Dry Soil.		
	Hydrochloric Acid.	Sulphuric Acid.	Acidity calculated as SO_3.	Hydrochloric Acid.	Sulphuric Acid.	Acidity calculated as SO_3.
St. Helen's: 2 miles west of, near Eccleston. Healthy vegetation	12·56	14·00	33·91	3·28	3·65	8·85
„ 2½ miles west of, within three fields of Knowsley Park	9·20	10·20	25·74	2·30	2·55	6·44
„ Between Marsh and Hibbert's works at Parr and St. Helen's, 1 mile east of St. Helen's. Poisoned land; no trees or grass	18·05	18·88	54·16	4·97	5·20	14·92
„ ¼ mile east of, near Kurtz's works. No trees or good grass. Poor corn was grown here three years ago	15·20	22·87	16·24	3·18	4·80	3·39
„ ¼ mile south of St. Helen's Junction. Fair grass; trees gone	4·66	0·62	8·94	1·59	0·21	3·04
„ At St. Helen's Junction. Grass very coarse	8·57	24·28	13·61	2·27	6·45	3·54
Near Bold Heath. Good grass	31·10	51·34	13·86	4·85	8·08	2·16
Bold Park Gates, a mile (?) from St. Helen's Junction	7·69	11·43	58·83	2·36	3·57	18·37
Widnes: Grass all gone, partly trodden by feet	4·92	11·14	16·38	1·59	3·60	5·30
„ ½ mile from. Trees bad	16·52	62·38	25·71	4·60	17·39	7·16
„ A mile from. Some grass; trees gone much farther off	12·54	2·04	15·58	3·94	0·63	4·91
Near Widnes. Fair looking grass	13·63	8·57	45·71	3·00	2·01	10·71
Penketh, east of Widnes. Good grass	8·57	11·00	0	2·62	3·60	0
Fiddler's Ferry	5·72	5·26	7·54	2·61	2·36	3·40

Specimens of Soil (February, 1874).	Parts per 100,000 of Soil as found Moist.			
	Hydrochloric Acid.	Sulphuric Acid.	Acidity calculated as SO_3.	Water.
St. Helen's: ½ mile west of, near Pilkington's old glass works	2·10	2·90	4·21	23·3
„ 1 mile west of	3·68	4·08	12·17	16·7
„ 1¾ „	1·57	2·55	1·40	31·4
„ 2 miles west of, near Eccleston. Healthy vegetation	2·60	2·90	7·02	20·7
„ 2½ miles west of	1·84	2·04	5·15	20·0
„ Between Marsh and Hibbert's works	3·90	4·08	11·70	21·6
„ ¼ mile east of, near Kurtz's works ..	2·63	3·97	2·81	17·3
„ ¼ mile south of St. Helen's Junction	1·20	0·16	2·30	24·4
„ At St. Helen's Junction	1·80	5·10	2·80	20·9
Near Bold Heath	4·20	6·99	1·87	13·5
Bold Park Gates	1·80	2·72	14·00	23·8
Widnes	1·20	2·72	4·00	24·4
„ ½ mile from	3·60	13·60	5·60	21·8
„ 1 „	3·00	0·48	3·74	23·9
Near Widnes. Fair grass	2·40	1·63	8·69	18·9
Penketh. Good grass	2·10	2·72	0	24·5
Fiddler's Ferry	1·80	1·63	2·34	31·0

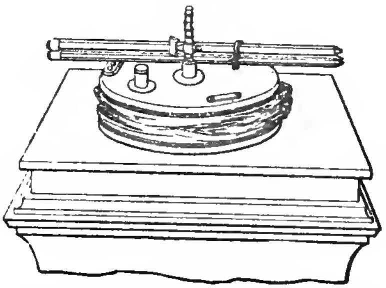
The importance of these questions, of the effect of noxious exhalations upon health and vegetation, and the necessity for grappling with them, is being keenly appreciated by all thoughtful manufacturers of hydrochloric and other acids, and makes the future of the trade increasingly difficult and uncertain. It is beyond all question that the condensing apparatus at present in operation is, either from inherent defects of construction or the action of wear and tear, altogether inadequate to the work required. It is also an unfortunate coincidence that the long-slumbering necessity for stricter legislation and supervision has come to the front just when the means of the manufacturers have been seriously impaired by a long season of depressed trade, and the cost of renovated, or improved, plant would be a burden almost too great to bear. In dealing with the subject there arises, moreover, at the outset the difficulty, or rather the impossibility, of fixing a legislative limit of condensation which shall satisfy all the interests represented. The present standard of one-fifth of a grain of hydrochloric acid per cubic foot seems to be as low as can be possibly maintained, and yet this amount of escape, owing to the pungency and potency of the gas, is sufficient to cause serious inconvenience and complaint.

For the purpose of testing the exit gases under the 95 per cent. standard it is of course necessary to draw a sample from the flue or pipe as the gases leave the pan or roaster, and compare it with a sample drawn in a similar way from the flue or pipe entering the chimney. To ascertain the amount of hydrochloric acid gas per cubic foot of air issuing from the chimney it is necessary to draw only one sample.

127.

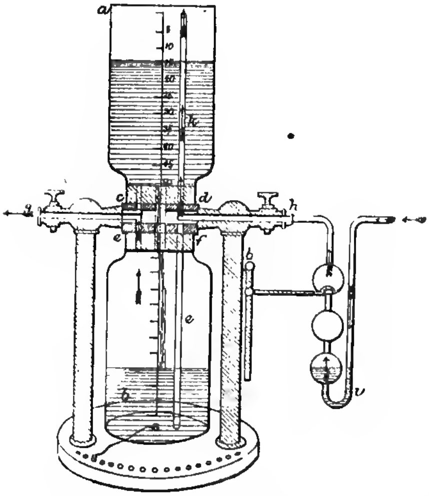


128.

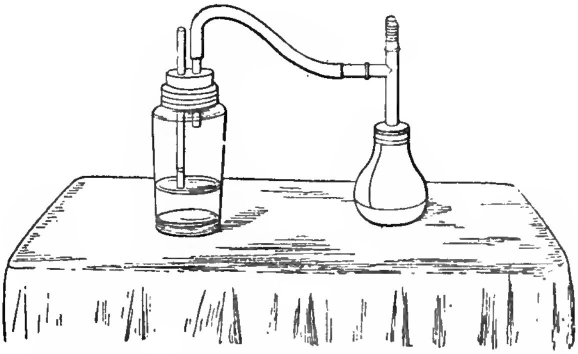


The gases are taken from the flues by means of an aspirator of known capacity, whereby a certain volume is drawn through water, or some suitable solution, and afterwards analysed, volumetrically or gravimetrically. The tube connected with the aspirator is inserted through a hole bored in the earthenware or brick flue leading from the pan or roaster, some clay being carefully placed round the pipe to prevent an influx of air into the opening. A very common aspirator for isolated trials consists of a vessel of japanned tin, about 20 in. long and 5 in diameter, the outflow pipe of caoutchouc being nearly as long as the aspirator itself, so as to make the suction more powerful. A small rectangular box fixed to the side conveniently holds the bottles of solution through which the gases are drawn.

129.



130.



Other apparatus are shown in Figs. 127 to 129. Figs. 127 and 128 represent a flexible aspirator, very convenient on account of its portability. It consists of a bag of cylindrical form, stretched out with hoops at intervals. There is a wide opening through which the air can be rapidly passed, so as to empty the vessel, in which case it collapses and takes the form shown in Fig. 128. By attaching a weight to the bottom sufficient drawing power is secured, and may be easily regulated. The objection to this aspirator is its liability to be damaged.

The swivel aspirator of Mr. Dancer, and other inventors, is shown in Fig. 129. It consists of two jars *a* and *b*, placed mouth to mouth, and mounted on an axis *g h*. The upper jar is filled with water, which, when the taps are open, flows down in *b* and allows the entry of the gases through *h*. On their way from the flue to the jar *a* these gases pass through whatever solution may be employed, as shown at *i*. As the water flows into the jar *b*, the air goes out by *c*. As soon as *a* is emptied it is turned round upon the axis and the full jar *b* takes its place. The vessels are carefully graduated into parts of a cubic foot.

A very simple form of aspirator—or, rather, pump—is shown in Fig. 130. It consists of a small bottle containing the necessary solvent, and to it is attached a caoutchouc bulb of known capacity. By pressing the latter a certain volume of air is passed into the bottle, and may be washed by shaking, and tested as required. Chiefly useful for qualitative trials, this finger pump may be also employed for rough quantitative testing, by ascertaining the amount of air or gas passed at each pressure of the bulb, and bearing in mind the sensitiveness of the silver solution—i. e. the amount of muriatic gas which will produce a cloudiness. A bulb of 2 oz. may be taken as equal to 50 centimètres. Of course a certain amount of air will be left unexhausted at each stroke, but this quantity will be almost constant, and for the bulb in question may be taken as 6¾ centimètres. The following table may be useful:—

A cloudiness produced in 50 cubic centimètres (nearly 2 ounces of a weak solution of nitrate of silver) with—

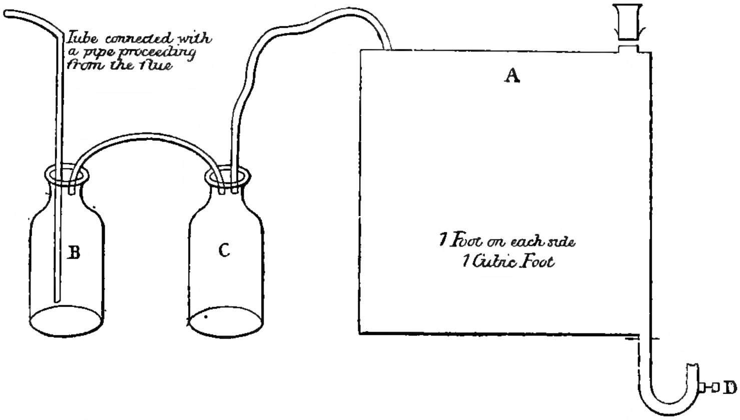
	Showing per cent. of Muriatic Acid in the Air.	Produces a Precipitate in
1 stroke of finger-pump	0·062	50 cub. cent. of air.
2 strokes of finger-pump	0·031	100 „ „
3 „ „	0·0206	150 „ „
4 „ „	0·0155	200 „ „
5 „ „	0·0124	250 „ „
6 „ ,	0·0100	300 „ „
7 „ „	0·0088	350 „ „
8 „ „	0·0077	400 „ „
9 „ „	0·0069	450 „ „
10 „ „	0·0062	500 „ „
20 „ „	0·0031	1000 „ „

and so on.

The amount of solution through which it is necessary to draw the gases to insure the arresting of the hydrochloric acid depends, of course, upon the rapidity of the operation and power of suction. Ordinarily two bottles are sufficient, but three or four may be used. Besides the usual silver solution, an alkaline solution, ammonia, or simple distilled water, may be used. It must be remembered, however, that there are present in all flues and exits other gases than hydrochloric—notably carbonic and sulphurous acids.

The first aspirator used for estimating the escape of hydrochloric acid is shown in Fig. 131, and was constructed by Mr. Gossage. The bottles B and C were filled with water and strong liquid ammonia respectively, the latter being coloured with litmus solution, to indicate the point of saturation. Interesting details concerning the early methods of testing for hydrochloric acid are to be found in the first annual report of the alkali inspector published in 1865. The minimetric system of testing therein set forth may be advantageously used for rough and approximate results, but is of little use for fine work.

131.



In testing under the 95 per cent. standard, only an average of many trials can give anything like a fair result, owing to the disturbance and constant irregularities caused by accidents of working. Thus if samples be drawn shortly after the pan (or roaster) has been charged, the result will appear abnormally good, owing to the rush of gas that comes off. On the other hand, if the trial is made when the furnaces are empty—the charge just drawn—a very slight escape from the condenser outlet will produce a bad percentage escape. It is not necessary to measure actually the quantity of gas entering the condensers; the amount may be calculated from the quantity of salt charged, and, for ordinary purposes, the result will be sufficiently near that obtained by test. An experiment made with a view to establish this gave the following results:—The charge of salt was 7 cwt, per hour, the gases from the pan and roaster joined before entering the condenser, and the draught in the flue by syphon gauge was 0·25 inches of water, equal to 10·49 ft. per second. The number of feet passing per second, 10·49, multiplied by 3600, the number of seconds per hour, gave 37,864 as the number of feet passing along the flue during the charge. The flue was 2 ft. square; the number of feet per hour, therefore, multiplied by 4 gave 151,456 as the total number of cubic feet passing during that time. Now 7 cwt. of salt, deducting 10 per cent. for moisture and impurities, contains 3,082,100 grains of muriatic acid gas, which divided by 151·456, the number of cubic feet passing during the time of its decomposition, gave 20·35 as the number of grains of acid contained in each cubic foot of the inlet gas. The amount by actual testing of the flue was as follows:—

	Inlet Gas per Cubic Foot.	Exit Gas per Cubic Foot.
5 minutes after charging	9·60	0·72
15 „ „	67·20	0·18
25 „ „ .. .	10·80	0·18
35 „ „	7·20	0·06
45 „ „ ..	7·20	0·06
55 „ „ .. .	7·20	0·06
Mean	18·20	0·21

This number, 18·20, it will be noted, agreed very closely with the 20·35 obtained by calculation. Taking the same amount passing at the exit for the two calculations the percentage is nearly the same:—

	Inlet Gas per Cubic Foot.	Exit Gas per Cubic Foot.	Percentage Escaping.
By experiment	18·20	0·21	1·15
By calculation	20·35	0·21	1·03

The slight difference is sufficiently accounted for by the amount of gas escaping from the doors, &c., or the acid left in the sulphate of soda.

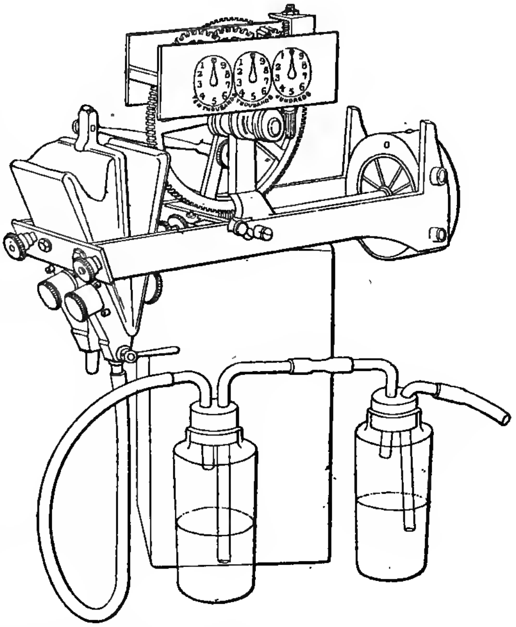
To obviate the necessity for taking multitudinous samples, and to ascertain the average result for any given time, independently of the many accidents of working, which militate against the truthfulness of isolated tests, it has been proposed to adopt some continually-working and self-acting method. Some forms of apparatus are given in Figs. 132 to 136. Mr. Fletcher's single and compound fan aspirators are shown in Figs. 132 to 134, Fig. 134 giving the mechanical part of the compound aspirator, and Fig. 133 the same apparatus in its box with its bottles and tubes. Referring to Fig. 132, at the extreme right is shown the fan; in the middle, the spindle for moving the large toothed wheel; behind, the connecting rod for driving the bellows pump. In front are the two bottles which contain the solution through which the gas is to be passed. The apparatus was designed with a view to making the chimney draught drive, or draw, the gases through a solution of nitrate of silver, and it was found that a fan of 2 in. diameter was sufficient for the purpose.

The objection to the single fan aspirator was that a sudden ebullition of gas might in a few minutes precipitate all the silver, and although only its average amount might be left in the bottle, still the record for any given period would be lost. Mr. Fletcher, therefore, devised the compound self-acting apparatus shown in Figs. 133 and 134, which registers the occurrences of several days, dividing the time into periods of any desired length, which may be from one to six hours. The description may be given in his own words:—

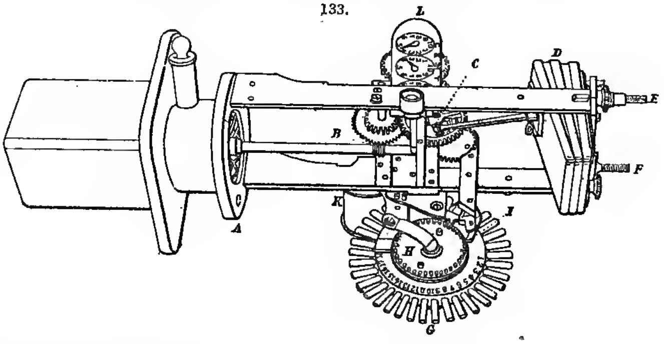
"This apparatus is readily portable, and can be placed in connection with any flue or chimney; it requires only that a hole 2 in. in diameter should be made in the brickwork. Through this aperture sufficient air passes into the flue to cause a small fan 1½ in. or 2 in. diameter to revolve rapidly, "The fan is so placed immediately in front of the hole that it is moved by the air from outside as it rushes into the flue. On the spindle which carries the fan is an endless screw, this working into a toothed wheel gives motion to a small bellows pump of vulcanised rubber by means of a crank and connecting rod.

"The pump draws a constant stream of air from the flue or chimney through a bottle containing solution of soda, nitrate of silver, or other absorbent of the acid vapour which may be in it. The gas continues to pass in bubbles through the liquid in this bottle for a period of from three to six hours; this time can be lengthened or diminished at pleasure by an easy adjustment of the apparatus, and at the end of that period the connection between the bellows and the first bottle is broken, and a connection established with bottle No. 2. The gas from the flue now passes through the solution in this bottle, during another period of the same length, when it is diverted and made to bubble up through that in bottle No. 3, and so on through any number in succession. In the instrument that has been made there are 36 four-ounce square bottles, occupying a space of 1 ft. square and 4 in. high. If each of these bottles come into action at intervals of six hours, the whole will last nine days, and then an examination of their contents would show the nature of the gas that had been passing in the flue during any six hours of that time. Attached to the apparatus is a counting dial similar to that of a gas meter; this counts the inflations of the bellows, and so indicates the number of cubic feet of gas that has been drawn through the bottles. The instrument may be adjusted to any speed, that of 1 cubic ft. per hour is found convenient. The speed will not, however, be constant, as the draught in the flue may vary with the number of furnaces at work, the direction of the wind, the height of the barometer, &c.; and, as it may be necessary to know the time at which any one bottle was in action, a photographic timekeeper has been contrived, at once much simpler and more certain in its action than a common clock in such an atmosphere. A ribbon of photographic paper enclosed in a dark box is made to unroll from one reel on to another at a slow rate, and in so doing to pass a narrow slit through which daylight is admitted. The paper passes at the rate of ½ in. per hour, and becomes darkened as it passes the opening. When the paper ribbon is afterwards removed it presents a series of alternate dark and light spaces, each about 6 in. long, shading off one into the other. The centre line of the dark space will have passed the slit at noon, the centre line of the light space at midnight, and the intermediate points at intervening times, so that the paper may be marked out and divided into spaces corresponding to days

132.



133.

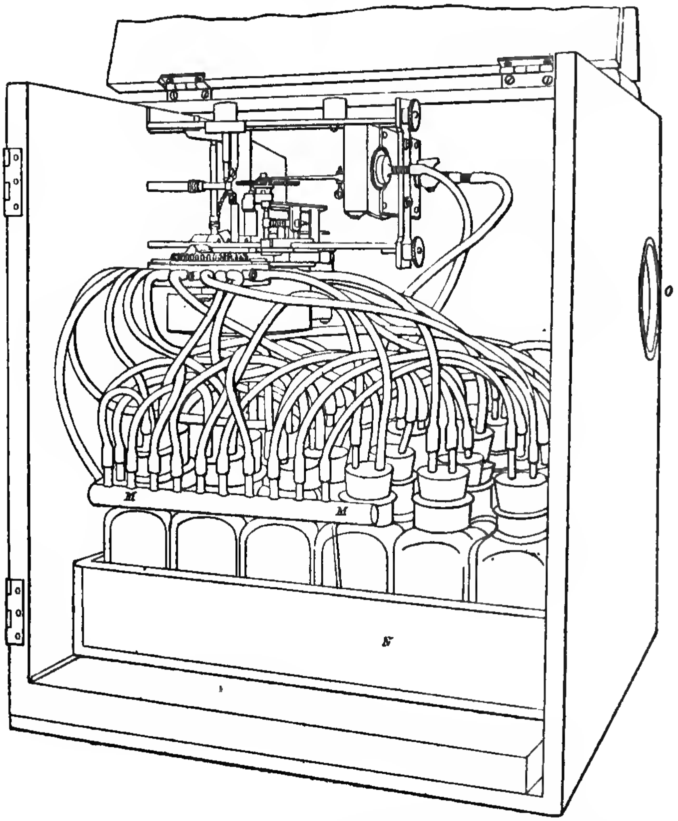


and hours. A mark is also imprinted on the paper at each revolution of the wheel, which determines the connection of the successive bottles; the position of these marks on the paper, now divided out into hours, gives the times at which the corresponding bottles were in operation. The successive connections of the bellows with the several bottles are made and broken by the sudden blow of a spring lever on one of thirty-six pins projecting from the barrel cf what may be called a 36-way cock. Caoutchouc tubes proceeding from each of the thirty-six bottles are attached to nozzles which radiate from a strong brass ring, whose inner surface is ground truly conical, and exactly fits a conical plug. In this plug there is only one channel, and this is always in connection with the bellows; as this plug revolves, this passage comes in connection with each of the thirty-six nozzles in succession, and thus each bottle in succession is put in connection with the bellows and with the flue.

"There are some minor details in the apparatus which it is unnecessary to describe. The whole is enclosed in a box measuring 1 ft. each way and which can be locked up.

"The chief point attained is the getting an aspirator which is constant in its operation and depends on no motive power other than the draught of the chimney itself."

134.



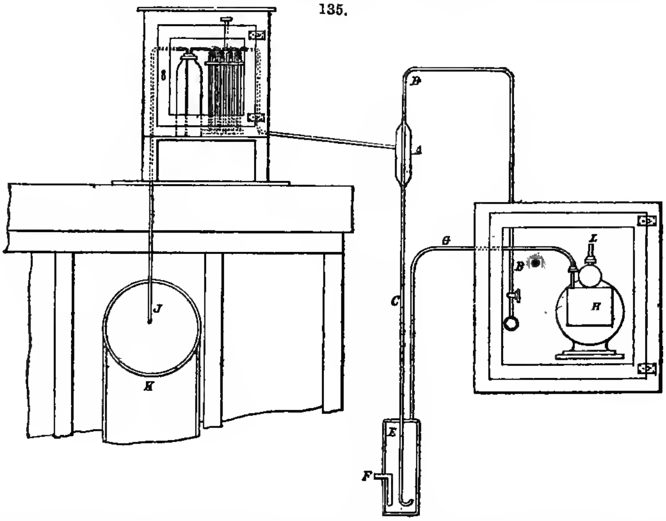
In Fig. 133 A is the fan, 2 in. in diameter; B the endless screw; C the crank to work the bellows; D the bellows pump; E the inlet tube; F the outlet tube; G the ring carrying thirty-six nozzles; H the centre plug carrying thirty-six pins; I the end of spring lever which moves H; K box containing the ribbon of photographic paper; L the counting dials. In Fig. 134, showing the apparatus in its box, M is the main tube of brass, partly encircling the bottles and attached to each; it is in connection with the chimney, and through it the gas passes to each bottle in its turn; N is a tray in which the bottles can be removed; O a lense to throw light on the small opening in the box containing the photographic paper; P the chimney or flue to which the aspirator is attached.

This ingenious apparatus has been but little used. The difficulty of keeping it in the necessarily perfect order will be understood by any practical manufacturer.

In Fig. 135 is shown Mr. Mactear's self-registering apparatus, which has been in use at the

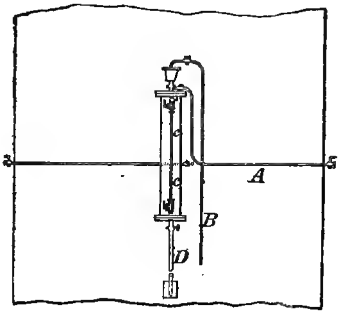
St. Rollex Works for a considerable time and given satisfactory results. A is a Bunsen's vacuum pump; B water pipe to ditto; C discharge pipe from ditto; D pipe to absorbing apparatus; E trap to collect gases passing through the pump; F overflow pipe for water from pump; G pipe for conveying gases to meter; H ordinary wet gas meter; I absorbing tubes; J pipe into flue; K flue;

135.

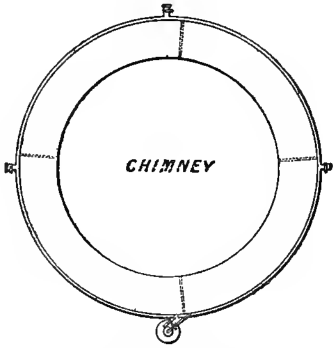


L escape pipe from meter. Fig. 136 gives another very simple form of aspirator. A is the gas pipe from chimney; B the inlet water pipe; C a gauge glass; D the waste water pipe. Fig. 137 shows this aspirator fixed to the chimney.

136.



137.

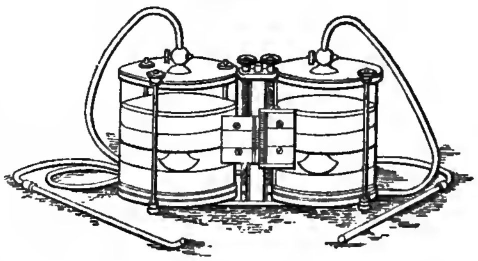


The speed at which gases are driven along the flue has been referred to as an important factor in the calculation of percentage escapes. Many methods for ascertaining this have been from time to time devised, but that perfected by Mr. Fletcher, and utilized for the purposes of inspection under the Alkali Acts will only be considered. The principle upon which the method is based is the well-known fact that the passage of a current of air across the open end of a straight tube brings about a partial vacuum, by virtue of which, if the tube is partly filled with water, the liquid will ascend to a degree depending upon the velocity of the current and completeness of the vacuum. Mr. Fletcher's own words will best describe the history and final construction of his instrument, a drawing of which is given in Fig. 138. "If a straight tube is inserted through a hole in the brickwork of a chimney or flue, so that the current of air in the flue passes across its open end, a partial vacuum will be formed in it, greater or less in proportion to the velocity of the current.

"A tube in such a position will, however, communicate a suction arising from that of the chimney itself, besides that suction produced by the current of air passing across its open end, and for the present purpose these two must be distinguished.

"To effect this *two* tubes should be inserted in the chimney, one of them having a straight and the other a bent end, the bend to be turned so as to meet the current of air; both tubes are open. In each of these tubes will be experienced the partial vacuum due to the suction of the chimney itself. In the straight tube, however, this will be increased by the suction caused by the passage of the current of air across its open end, while in the case of the bent tube this will be diminished by the pressure caused by the current of air blowing into it. The difference therefore between the suction in the two tubes will be due to the action of the current of air in the chimney, and it remains only to measure this difference in order to measure the velocity of the current itself.

138.



"To effect this let these tubes be connected with a U tube containing water, one with each limb; then the water will be raised up in one limb to a degree corresponding with the difference of suction, so that the difference of level of the water in the U tube, being a measure of the difference of suction in the tubes, becomes a measure of the velocity of the current of air in the chimney. By this arrangement the suction power of the chimney itself is eliminated, for it operates equally on each limb of the U tube, while the difference of pressure experienced will be due only to the different action of the current of air in the flue on the tube with the straight end and the one with the bent end.

"It remains then to register accurately this difference of level of the water in the U tube, and to construct a formula connecting it with the speed of the current of air in the flue, so that by measuring the one the other may be measured also.

"Experiment showed that for high speeds of air the measurement of the difference of this water level was easy, but that for speeds below 5 ft. per second the amount became too minute and uncertain for practical use.

"Many plans were then devised for constructing a pressure gauge which should be more delicate than the ordinary U tube.

"Efforts were first made to modify the U tube so that its range might be increased and its indications magnified. This might be done by drawing out its lower bend horizontally and increasing the size of the vertical portions till it assumed the form of two vertical cylinders, connected by a long horizontal tube. If now a pressure were exerted which would cause a depression of the water in one limb, the motion so caused in the narrow column of water in the horizontal tube would be so much greater, as its sectional area was smaller, than that of the vertical tubes. It was found, however, that in proportion as a greater range in the scale of the instrument was thus obtained, a greater amount of friction must also be encountered, and that thus the advantage of the one was neutralized by the evil of the other.

"It is necessary to see this clearly in order to arrive at the conclusion that *all* methods of increasing the actual motion of the fluids or of magnifying it by any mechanical arrangement of levers or otherwise must be open to the same objection. This proposition seems clear now, in the light shed by a long series of failures encountered in the attempt to act contrary to it, but it was not clear before.

"Before describing the instrument ultimately adopted for measuring the delicate variations of pressure arising in the problem in hand, it may be well to describe one which, although it was rejected along with all those which actually increase the range through which the pressure operates, has yet so much to recommend it on account of simplicity and compactness that it may be useful elsewhere. The arrangement is, I think, new.

"A piece of barometer tubing, 3 ft. long, was bent into the form, of an elongated S, and the centre portion from C to D filled with mercury; the ends A and B are open. If the bore of tube is uniform the mercury may be placed in any position in the tube and still rest in equilibrium, for whether C and D be raised or depressed they will always be level, and the opposing columns therefore balance each other. But if, instead of the bore of the bent tube being uniform throughout, that of the limb A be slightly greater than the bore of the limb B, so that a quantity of mercury which would occupy 10 in. in the former occupies only 9 in. in the latter; then if pressure be applied at B so as to depress the end of the column at D 10 in., C will fall only 9 in., and it will require a pressure equivalent to that of 1 in. of mercury to maintain it in that position; when that pressure is removed the mercury will regain its equilibrium, but the ends of the columns must return to the former positions at C and D in order to be on a level again. In other words, a pressure equivalent to 1 in. of mercury would be represented by a motion of 10 in. in the limb B, or the indications of the simple U tube would in this instrument be magnified ten times. This proportion of increase may be made greater at will by rightly adjusting the internal diameters of the tubes A and B; the more nearly they approach uniformity in bore, the greater is the distance the mercury will travel for any given pressure.

"This and other contrivances failed for the reasons already stated, that when the range through which the limited power had to act was increased, the indications of the instrument ceased to be a measure of the pressure exerted, since some of it was absorbed by friction.

"The simple U tube was therefore returned to, and means adopted for accurately seeing and measuring its slightest indications. In the first place, the limbs were increased until they were no longer small tubes of about 0·4 in. internal diameter, but cylinders of 4 in. diameter; these were connected at the bottom by a small tube. Thus the power exerted by the pressure communicated through the connecting tubes, operating on the extended surface of the liquid in the cylinders, was increased a hundredfold over that operating in the smaller U tube; but the friction could only have been increased tenfold, giving therefore a tenfold increase of delicacy. In order to observe accurately the rise and fall of the liquid in the cylinders, floats were introduced, on each of which were engraved a very fine horizontal line; and to measure accurately the comparative elevation or depression of these two lines, a finely divided scale and vernier were added, working with a delicate screw adjustment. With this it is possible to measure an elevation or depression of $\frac{1}{1000}$ in., which is sufficiently accurate for the purpose in view.

"On trying now to apply the instrument so constructed, and attempting to measure very minute variations of pressure, failure still seemed imminent, for though the motion of the water in the increased limbs of the U tube could be measured to $\frac{1}{1000}$ in., the water refused to move, except under pressures exceeding that which would be indicated by so small a column; in other words, the water seemed to stick to the cylinders. It was necessary, therefore, to make experiments with various liquids in order to choose one more suitable than water. For this purpose a very thin plate of metal was suspended from the beam of a delicate balance, and the amount of power required for its immersion in, and subsequent withdrawal from, various liquids, thus measured. This resistance is due to what is often called capillary attraction and repulsion; it is shown to exist largely in water, by the fact that a needle may be made to rest on its surface without sinking. In the case of water, 20 grains were needed to overcome it; while with many other liquids a much less force sufficed, and in the case of ether $\frac{1}{100}$ grain was sufficient. Ether was, therefore, chosen as the liquid which offered the least resistance, and also on account of its low specific gravity.

"After substituting ether for water, the action of the manometer was quite satisfactory. The lines on the floats also returned exactly to their original position after any disturbance, and its indications could be relied upon to $\frac{1}{1000}$ in.

"It remained now to ascertain the value of these indications when applied to the measurement of the velocity of air. The problem to be solved is one which does not seem to have received the attention of mathematicians. It may be briefly stated thus:—The lower end of a vertical straight tube, open at both ends, dips into a liquid. To what height will the liquid be raised in the tube by the action of a current of air passing with a given velocity across its upper end?

"On consideration, it will appear probable that the height of the column is but a measure of the impact force of the air in motion. Experiment proves this to be the case. It shows that the liquid is drawn up to the same height it would have reached had the stream of air been directed against the surface of the liquid in the cistern. The problem is now exchanged for one easier of solution.

Let v = velocity of the air in ft. per second.
g = gravity = 22·18 ft. per second.
w = weight of a cubic ft. of air at 60° F. and 29·92 in. barometric pressure = 0·076107 lbs.
P = pressure in pounds per square ft. of a flat surface held at right angles to the direction of the air current.

Then $v^2 w = g \mathrm{P}$.

Let p = the height of the column of liquid driven up the tube measured in inches.
W = weight in lbs. of $\frac{1}{12}$ cub. ft. of this liquid.

Then $\mathrm{P} = p \mathrm{W}$; $v^2 w = g p \mathrm{W}$; $v = \sqrt{p \frac{g \mathrm{W}}{w}}$, where the liquid used is water W = 5·2083

$$\text{and } v = \sqrt{p} \cdot 46 \cdot 92 \text{; or } p = \frac{v^2}{2202}.$$

"In the anemometer here described, ether of the specific gravity of ·740 is employed, and the instrument is so used that the reading is double the actual column of ether supported.

$$\text{In this case } v = \sqrt{\frac{p}{2} \frac{g \mathrm{W}}{w}} = \sqrt{p} \cdot 28 \cdot 55.$$

"In order now to see what correction will be necessary when the temperature of the stream of air is different from that of 60° F.,

Let v' = velocity of air at some other temperature, say at the temperature of t degrees F.
w' = weight of a cubic foot of air at that temperature.
vol.$'$ = volume of a cubic foot of air at that temperature.

$$\text{Then } \frac{w}{w'} = \frac{\text{vol.}}{\text{vol.}} = \frac{\text{vol. at } 32^\circ \left(1 + \frac{t - 32}{491}\right)}{\text{vol. at } 32^\circ \left(1 + \frac{60 - 32}{491}\right)} = \frac{459 + t}{519}\text{; or } \frac{1}{w'} = \frac{1}{w}\,\frac{459 + t}{519}\text{;}$$

$$\text{but } v = \sqrt{\frac{p}{2}\,\frac{g\,W}{w}}\text{, or } v' = \sqrt{\frac{p}{2}\,\frac{g\,W}{w'}} = \sqrt{\frac{g\,p\,W}{2}\,\frac{1}{w}\,\frac{459 + t}{519}}$$

$$= \sqrt{p\,\frac{459 + t}{519}} \times 28\cdot55$$

"But it is generally necessary to carry the correction a step further, and to give the velocity in feet of air at 60° temperature.

$$\text{Now } v = v'\,\frac{\text{vol.}}{\text{vol.}'} = v'\,\frac{519}{457 + t} = \sqrt{\frac{g\,p\,W}{2}\,\frac{1}{w}\,\frac{459 + t}{519}} \times \frac{519}{459 + t}$$

$$= \sqrt{\frac{g\,p\,W}{2}\,\frac{1}{w}\,\frac{519}{459 + t}} = \sqrt{p\,\frac{519}{459 + t}} \times 28\cdot55.$$

Further, to correct for variations in barometric pressure,
let v'' = velocity of air at some other pressure than 29·92 inches, say at a pressure of h inches.
w'' = weight of a cubic foot of air at that pressure.
vol.$''$ = volume of a cubic foot of air at that pressure.

$$\text{Then } \frac{w}{w''} = \frac{29\cdot92}{h}\text{; or } \frac{1}{w''} = \frac{1}{w}\,\frac{29\cdot92}{h}.$$

$$\text{As above } v'' = \sqrt{\frac{p}{2}\,\frac{g\,W}{w''}} = \sqrt{\frac{p}{2}\,\frac{g\,W}{w}\,\frac{29\cdot92}{h}} = \sqrt{p\,\frac{29\cdot92}{h}}\,28\cdot55.$$

In cases where it is necessary to give the velocity in feet of air at a pressure of 29·92 inches:

$$\frac{v}{v''} = \frac{h}{29\cdot92} \qquad v = v''\,\frac{h}{29\cdot92} = \sqrt{p\,\frac{h}{29\cdot92}} \times 28\cdot55.$$

"The complete formula, embodying the formulæ of correction for variations of temperature, and also of barometric pressure, would therefore be—

$$v = \sqrt{p\,\frac{h}{29\cdot22}\cdot\frac{519}{459 + t}} \times 28\cdot55,$$

v being the velocity of air at a temperature of t degrees F., under a pressure of h inches of mercury; but the velocity is measured in feet per second of air at the normal temperature and pressure.

"When drawing a sample of air from a chimney in order to examine it, that sample is measured, by the aspirator employed, under the existing barometric pressure; we want, therefore, the velocity to be given in feet of air under the same condition. The following is the formula then to be used—

$$v = \sqrt{p\,\frac{29\cdot92}{h}\cdot\frac{519}{459 + t}} \times 28\cdot55.$$

"The number 28·55 thus obtained by calculation differs somewhat from the number obtained by the experiments which were made two years ago. These were not carried out with the accuracy that might now be attained by help of the experience which has been gained in the use of the instrument since that time; therefore I have repeated them.

"The same method was adopted as formerly. A regular current of air was established in a long flue or air channel, one end of which was in connection with a high chimney, the other end was open. The speed of this current was measured by the anemometer, and at the same time measured by noting the time a puff of smoke took in travelling from one end of the flue to the other. These experiments were made in three separate flues, and many experiments were made in each.

"The value of C is found in each case from the formula—

$$c = \sqrt{\frac{v^2}{p} \cdot \frac{29{\cdot}92}{h} \cdot \frac{459 + t}{519}} \,.$$

No. of Experiment.	Distance. Feet.	Time occupied by Smoke. Seconds.	Speed of Smoke. Feet per Second.	Pressure shown by Anemometer. Inches.	Temperature of Air in the Flue. Degrees F.	Barometer Pressure. Inches.	Value of c.
1	55	9	6·111	0·045	54	30·10	28·56
2	117	12·3	9·513	0·1055	50	30·10	28·92
3	94	13·5	6·963	0·0575	55	29·65	29·02
4	94	16·5	5·757	0·038	55	29·65	29·21
5	145	8	18·12	0·4195	44	30·30	27·38
6	145	16	9·06	0·101	44	30·30	27·90
						Average ..	28·50

"The average value of c in the experiments is 28·50, while the value arrived at by purely mathematical considerations is 28·55. This close correspondence is the more satisfactory when the difficulty of accurately measuring short intervals of time is borne in mind.

"I have, therefore, adopted the formula $v = \sqrt{p} \times 28{\cdot}55$ as correct, and calculated from it a table showing the velocities which correspond to the various readings of the anemometer. The table is annexed, also a table showing the correction to be made for variations in the temperature of the air whose speed is to be measured. The corrections to be made for small variations in barometric pressure are unimportant. When it is necessary to make the correction, recourse must be had to the formula—

$$v' = \sqrt{p\,\frac{29{\cdot}92}{h}} \times 28{\cdot}55 \qquad \text{or} \qquad v = \sqrt{p\,\frac{h}{29{\cdot}92}} \times 28{\cdot}55.$$

according to the circumstances of the case. In the former the velocity is given in feet per second of air measured under the barometric pressure existing in the air channel; in the latter it is given in feet per second of air measured under a pressure of 29·92 inches of mercury."

The following is an exact description of the instrument, with directions for its use:—"It consists first, of two tubes; secondly of a manometer. The tubes are open throughout; the end of one is plain and straight, the end of the other is bent short round at a right angle. They may be of any length, and of any size in the bore. These, by passing through a small hole made in the brickwork of the flue or chimney, are placed so that their ends are exposed to the current of air whose velocity is to be measured. The speed of a column of air moving along a circular flue or chimney is greater at the centre than at the outside. The point of average speed will be found to be removed from the outside by one-third of the radius of the flue. Thus, if the flue or chimney be 6 ft. diameter at the place where the testing hole is made, the length of the portion of each tube passed through the hole should be either 1 foot or 5 feet. The tubes are made to lie parallel to each other and at right angles to the current of air, the bent end of the one being turned to face it. Care must be taken to prevent a rush of air entering at the test hole, and making an eddy in the flue. The outer ends of the tubes are connected by flexible tubing of any convenient length with the manometer. This measures the difference of the pressures conveyed by the two tubes. The manometer may be considered as a U tube, whose limbs are expanded into cylinders of 3 in. diameter and 3 in. height.

"The connecting tube at bottom is small. The liquid used in it is ether, on account of its low specific gravity and its mobility. To assist in noting accurately the height of the ether, each column is provided with a float of hollow metal, on which is inscribed a fine line. An ivory scale, with 20 divisions to the inch, and a vernier, enable the difference of level between the two floats to be read of to one-thousandth of an inch. In using the instrument it is not necessary to fix it strictly level, if the following method is adopted.

"Attach the straight pressure tube by means of flexible tubing to one limb of the instrument, and the bent pressure tube to the other limb. Adjust the scales to their respective floats and read off. Now reverse the connections of the flexible tubing so that the pressure tube with the straight end is attached to that limb of the instrument which was before connected with the bent tube, and the one with the bent end is attached to the other limb. Again adjust the scales to their respective floats and read off. Subtract the lesser reading from the greater, and the difference will be what is called in the annexed table the 'manometer reading'; it is twice the height of the column of ether which was supported by the difference of pressure conveyed through the two tubes whose ends are in the current of air. If the current of air has been produced by increase of pressure, as by the blast from a fan, or by diminution of pressure, as by the action of a chimney, the order of the observation is the same. In both cases the amount of the lesser reading is deducted from that of the greater, and the difference is the figure sought. It is p in the formula $v = \sqrt{p} \cdot 28{\cdot}55$. On consulting the annexed table the corresponding speed of the air will be found.

"Thus, if the first reading is 1·039, and the second reading, after reversing the connections of the flexible tubing, is 0·861, the difference will be 0·178. The speed will be found on referring to the table to be 12·05 ft. per second. This is, however, only true if the temperature of the air is 60° F. Should it in this case be 520°, the table of corrections for temperature gives the number 0·7280. This multiplied by 12·05 is 8·772, the true speed.

Table to Show the Speed of Currents of Air, as indicated by the Ether Anemometer.

$$v = \sqrt{p} \times 28{\cdot}55.$$

Temperature 60° F. Barometer 29·92 inches.

Manometer Reading: Inches.	Speed of Air: Feet per Second.	Manometer Reading: Inches.	Speed of Air: Feet per Second.	Manometer Reading: Inches.	Speed of Air: Feet per Second.	Manometer Reading: Inches.	Speed of Air: Feet per Second.
0·001	0·903	0·055	6·695	0·118	9·808	0·226	13·57
0·002	1·277	0·056	6·756	0·120	9·891	0·228	13·63
0·003	1·564	0·057	6·816	0·122	9·972	0·230	13·70
0·004	1·806	0·058	6·876	0·124	10·053	0·232	13·76
0·005	2·019	0·059	6·935	0·126	10·13	0·234	13·82
0·006	2·212	0·060	6·993	0·128	10·21	0·236	13·88
0·007	2·389	0·061	7·051	0·130	10·29	0·238	13·94
0·008	2·554	0·062	7·109	0·132	10·37	0·240	13·99
0·009	2·709	0·063	7·166	0·134	10·45	0·242	14·05
0·010	2·855	0·064	7·223	0·136	10·53	0·244	14·11
0·011	2·994	0·065	7·279	0·138	10·60	0·246	14·17
0·012	3·127	0·066	7·335	0·140	10·68	0·248	14·23
0·013	3·255	0·067	7·390	0·142	10·76	0·250	14·28
0·014	3·378	0·068	7·445	0·144	10·83	0·252	14·34
0·015	3·497	0·069	7·500	0·146	10·91	0·254	14·40
0·016	3·612	0·070	7·554	0·148	10·98	0·256	14·45
0·017	3·723	0·071	7·608	0·150	11·06	0·258	14·50
0·018	3·830	0·072	7·661	0·152	11·13	0·260	14·56
0·019	3·935	0·073	7·713	0·154	11·20	0·262	14·62
0·020	4·038	0·074	7·766	0·156	11·77	0·264	14·68
0·021	4·137	0·075	7·819	0·158	11·34	0·266	14·74
0·022	4·235	0·076	7·871	0·160	11·42	0·268	14·79
0·023	4·330	0·077	7·922	0·162	11·49	0·270	14·84
0·024	4·423	0·078	7·974	0·164	11·56	0·272	14·90
0·025	4·514	0·079	8·025	0·166	11·63	0·274	14·96
0·026	4·604	0·080	8·075	0·168	11·70	0·276	15·01
0·027	4·691	0·081	8·125	0·170	11·27	0·278	15·06
0·028	4·777	0·082	8·175	0·172	11·84	0·280	15·11
0·029	4·862	0·083	8·225	0·174	11·91	0·282	15·17
0·030	4·945	0·084	8·275	0·176	11·98	0·284	15·23
0·031	5·027	0·085	8·324	0·178	12·05	0·286	15·28
0·032	5·107	0·086	8·373	0·180	12·11	0·288	15·33
0·033	5·187	0·087	8·421	0·182	12·18	0·290	15·38
0·034	5·265	0·088	8·469	0·184	12·25	0·292	15·44
0·035	5·342	0·089	8·517	0·186	12·31	0·294	15·49
0·036	5·418	0·090	8·565	0·188	12·38	0·296	15·54
0·037	5·492	0·091	8·613	0·190	12·45	0·298	15·59
0·038	5·565	0·092	8·660	0·192	12·51	0·300	15·64
0·039	5·638	0·093	8·707	0·194	12·57	0·302	15·70
0·040	5·710	0·094	8·754	0·196	12·64	0·304	15·75
0·041	5·781	0·095	8·800	0·198	12·71	0·306	15·80
0·042	5·851	0·096	8·846	0·200	12·77	0·308	15·85
0·043	5·921	0·097	8·892	0·202	12·83	0·310	15·90
0·044	5·989	0·098	8·938	0·204	12·90	0·312	15·95
0·045	6·056	0·099	8·983	0·206	12·96	0·314	16·00
0·046	6·123	0·100	9·028	0·208	13·02	0·316	16·05
0·047	6·189	0·102	9·118	0·210	13·08	0·318	16·10
0·048	6·255	0·104	9·207	0·212	13·15	0·320	16·15
0·049	6·320	0·106	9·295	0·214	13·21	0·322	16·20
0·050	6·384	0·108	9·383	0·216	13·27	0·324	16·25
0·051	6·448	0·110	9·469	0·218	13·33	0·326	16·30
0·052	6·510	0·112	9·554	0·220	13·39	0·328	16·35
0·053	6·572	0·114	9·639	0·222	13·45	0·330	16·40
0·054	6·634	0·116	9·724	0·224	13·51	0·332	16·45

Table to show the Speed of Currents of Air—*continued.*

Manometer Reading: Inches.	Speed of Air: Feet per Second.	Manometer Reading: Inches.	Speed of Air: Feet per Second.	Manometer Reading: Inches.	Speed of Air: Feet per Second.	Manometer Reading: Inches.	Speed of Air: Feet per Second.
0·334	16·50	0·392	17·88	0·450	19·15	0·530	20·78
0·336	16·55	0·394	17·93	0·452	19·20	0·540	20·98
0·338	16·60	0·396	17·98	0·454	19·24	0·550	21·17
0·340	16·65	0·398	18·02	0·456	19·28	0·560	21·37
0·342	16·70	0·400	18·06	0·458	19·32	0·570	21·56
0·344	16·75	0·402	18·11	0·460	19·36	0·580	21·75
0·346	16·80	0·404	18·16	0·462	19·41	0·590	21·94
0·348	16·85	0·406	18·20	0·464	19·45	0·600	22·12
0·350	16·89	0·408	18·24	0·466	19·49	0·610	22·30
0·352	16·94	0·410	18·28	0·468	19·53	0·620	22·48
0·354	16·99	0·412	18·33	0·470	19·57	0·630	22·66
0·356	17·04	0·414	18·38	0·472	19·62	0·640	22·84
0·358	17·09	0·416	18·42	0·474	19·66	0·650	23·02
0·360	17·13	0·418	18·46	0·476	19·70	0·660	23·20
0·362	17·18	0·420	18·50	0·478	19·74	0·670	23·38
0·364	17·23	0·422	18·55	0·480	19·78	0·680	23·55
0·366	17·28	0·424	18·60	0·482	19·82	0·690	23·72
0·368	17·33	0·426	18·64	0·484	19·86	0·700	23·89
0·370	17·37	0·428	18·68	0·486	19·90	0·750	24·73
0·372	17·42	0·430	18·72	0·488	19·94	0·800	25·54
0·374	17·47	0·432	18·77	0·490	19·98	0·850	26·32
0·376	17·52	0·434	18·82	0·492	20·02	0·900	27·08
0·378	17·56	0·436	18·86	0·494	20·06	0·950	27·83
0·380	17·60	0·438	18·90	0·496	20·10	1·000	28·55
0·382	17·65	0·440	18·94	0·498	20·14	1·250	31·93
0·384	17·70	0·442	18·99	0·500	20·18	1·500	34·97
0·386	17·75	0·444	19·03	0·510	20·38	1·750	37·77
0·388	17·79	0·446	19·07	0·520	20·58	2·000	40·37
0·390	17·83	0·448	19·11				

Table of the Values of $\sqrt{\frac{519}{459 + t}}$ for Values of t from 0 to 1000; or Corrections for Temperature.

t Degrees F.	$\sqrt{\frac{519}{459 + t}}$	t Degrees F.	$\sqrt{\frac{519}{459 + t}}$	t Degrees F.	$\sqrt{\frac{519}{459 + t}}$	t Degrees F.	$\sqrt{\frac{519}{459 + t}}$
0	1·0634	135	0·9348	270	0·8438	405	0·7741
5	1·0577	140	0·9309	275	0·8409	410	0·7729
10	1·0520	145	0·9270	280	0·8380	415	0·7707
15	1·0464	150	0·9232	285	0·8352	420	0·7685
20	1·0409	155	0·9194	290	0·8324	425	0·7663
25	1·0355	160	0·9156	295	0·8296	430	0·7641
30	1·0302	165	0·9119	300	0·8269	435	0·7619
35	1·0250	170	0·9083	305	0·8242	440	0·7598
40	1·0198	175	0·9047	310	0·8215	445	0·7577
45	1·0148	180	0·9012	315	0·8189	450	0·7556
50	1·0098	185	0·8977	320	0·8163	455	0·7535
55	1·0049	190	0·8943	325	0·8137	460	0·7514
60	1·0000	195	0·8909	330	0·8111	465	0·7494
65	0·9952	200	0·8875	335	0·8085	470	0·7474
70	0·9905	205	0·8841	340	0·8060	475	0·7454
75	0·9858	210	0·8808	345	0·8035	480	0·7434
80	0·9812	215	0·8775	350	0·8010	485	0·7414
85	0·9767	220	0·8743	355	0·7985	490	0·7394
90	0·9723	225	0·8711	360	0·7960	495	0·7375
95	0·9679	230	0·8680	365	0·7936	500	0·7356
100	0·9636	235	0·8649	370	0·7912	505	0·7337
105	0·9593	240	0·8618	375	0 7888	510	0·7318
110	0·9551	245	0·8587	380	0·7865	515	0·7299
115	0·9509	250	0·8557	385	0·7842	520	0·7280
120	0·9468	255	0·8527	390	0·7819	525	0·7261
125	0·9428	260	0·8497	395	0·7786	530	0·7243
130	0·9388	265	0·8467	400	0·7763	535	0·7225

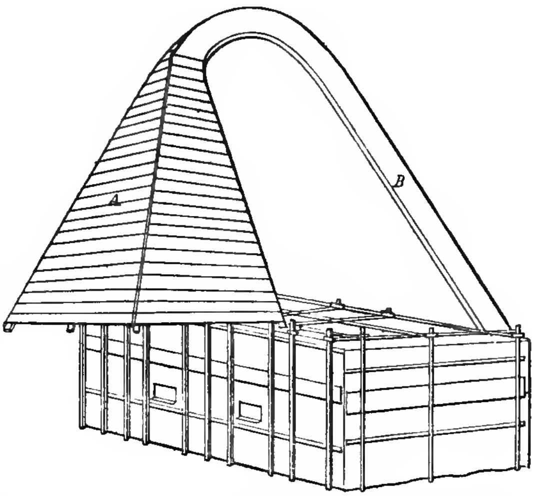
TABLE OF THE VALUES OF $\sqrt{\frac{519}{459 + t}}$ FOR VALUES OF t FROM 0 TO 1000—*continued.*

t Degrees F.	$\sqrt{\frac{519}{459 + t}}$	t Degrees F.	$\sqrt{\frac{519}{459 + t}}$	t Degrees F.	$\sqrt{\frac{519}{456 + t}}$	t Degrees F.	$\sqrt{\frac{519}{459 + t}}$
540	0·7207	660	0·6811	775	0·6485	890	0·6203
545	0·7189	665	0·6796	780	0·6472	895	0·6192
550	0·7171	670	0·6781	785	0·6459	900	0·6181
555	0·7153	675	0·6766	790	0·6446	905	0·6169
560	0·7137	680	0·6751	795	0·6433	910	0·6158
565	0·7119	685	0·6736	800	0·6420	915	0·6147
570	0·7102	690	0·6721	805	0·6407	920	0·6136
575	0·7085	695	0·6706	810	0·6395	925	0·6125
580	0·7068	700	0·6691	815	0·6382	930	0·6114
585	0·7051	705	0·6676	820	0·6369	935	0·6103
590	0·7034	710	0·6662	825	0·6357	940	0·6092
595	0·7017	715	0·6648	830	0·6345	945	0·6081
600	0·7000	720	0·6634	835	0·6333	950	0·6070
605	0·6983	725	0·6620	840	0·6321	955	0·6059
610	0·6967	730	0·6606	845	0·6309	960	0·6048
615	0·6951	735	0·6592	850	0·6297	965	0·6037
620	0·6935	740	0·6578	855	0·6285	970	0·6026
625	0·6919	745	0·6565	860	0·6273	975	0·6015
630	0·6903	750	0·6552	865	0·6261	980	0·6004
635	0·6887	755	0·6538	870	0·6249	985	0·5994
640	0·6871	760	0·6524	875	0·6237	990	0·5984
645	0·6856	765	0·6511	880	0·6225	995	0·5974
650	0·6841	770	0·6498	885	0·6214	1000	0·5964
655	0·6826						

For further information respecting the speed of air in flues, and experiments upon the subject, the reader is referred to the Report of the Chief Inspector under the Alkali Acts for the year 1874.

It has been proposed to estimate the loss, or escape, of hydrochloric acid gas by measuring the amount of liquid acid yielded by the known decomposition of salt, receiving the produce in an arrangement of suitably constructed stone cisterns. As a useful guide to the manufacturer, this system is to be recommended; but it will be readily apparent that it possesses little virtue from an inspector's point of view. The varying composition of the salt and sulphate, the multitudinous small escapes of gas, the difficulties of a perfect gauging of the acid, and the constant supervision required in order to get anything like accurate results, militate against the success of the plan.

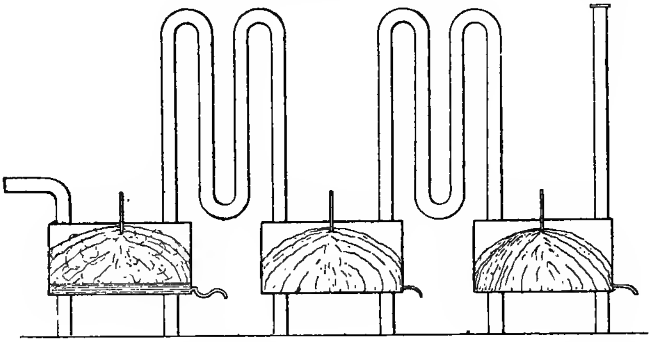
139.



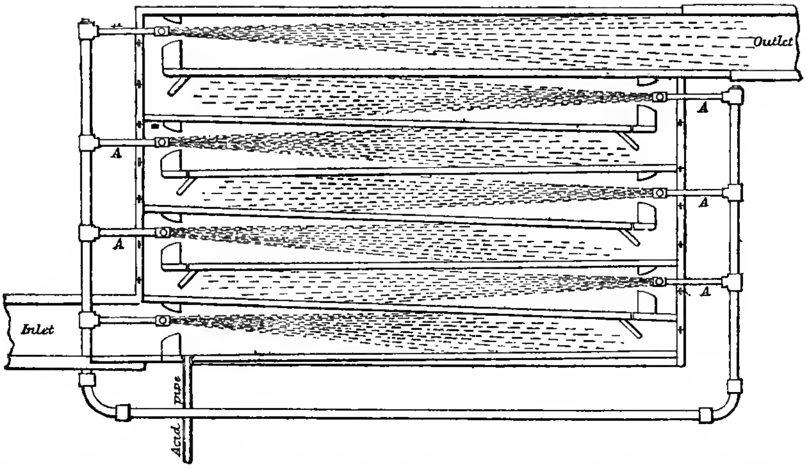
A difficulty which remains to be faced is the question of dealing with what is known as "ground gas," i.e. the free hydrochloric gas which escapes from the doors of the furnace and pan, from the charge of freshly-drawn sulphate, and from any imperfect joints. This ground gas is often accountable for the white cloud which envelopes the decomposing department of a chemical works upon a damp day, and to it is due a considerable amount of the damage done to surrounding vegetation. It seems strange that so little attention has yet been paid to this potent agent of evil. A very useful apparatus is shewn in Fig. 139. A hood, A, formed of wood or any other suitable material, is fixed over the doors of the furnace, and the gas, as it escapes from the door, or freshly-drawn charge, is drawn away to the chimney by the flue B. No chemical works ought to be without some such arrangement as this. The hood shown in the drawing is 14 ft. by 7 ft., and 18 ft. high.

Since the attention of manufacturers has been aroused to the necessity for a more perfect condensation, various new methods have been proposed. Proceeding upon the lines of the old "spray" condenser, shown in Fig. 140, Mr. J. Mather has proposed to pass the gas through a preliminary series of troughs, as shown in Fig. 141, in longitudinal section. Compressed and cooled air is driven in through the pipes A, which has the effect of raising the weak acid or water into a fine spray. Another plan of cooling and condensing the gas is given in Figs. 142 and 143. In Fig. 142 a plan is given, in Fig. 143 a cross section, showing the timber supports. The gas pipes are passed through a cistern of constantly-renewable cold water. It has been found that 24 ft. lower the temperature of the gas 64° (116 F.), or about 2·75° per foot. Occasionally an immense number of cooling pipes are employed. An apparatus of this description erected at the Runcorn Alkali Works for the Hargreaves decomposing process, is shown in Fig. 144. This process consists in the decomposition of common salt by means of the sulphurous acid direct from the sulphur, or pyrites, burners, and all the heat of combustion and combination must pass through the condensing apparatus. Two

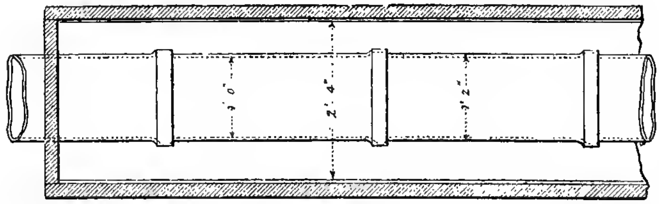
140.



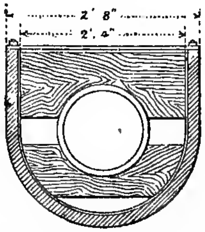
141.



142.



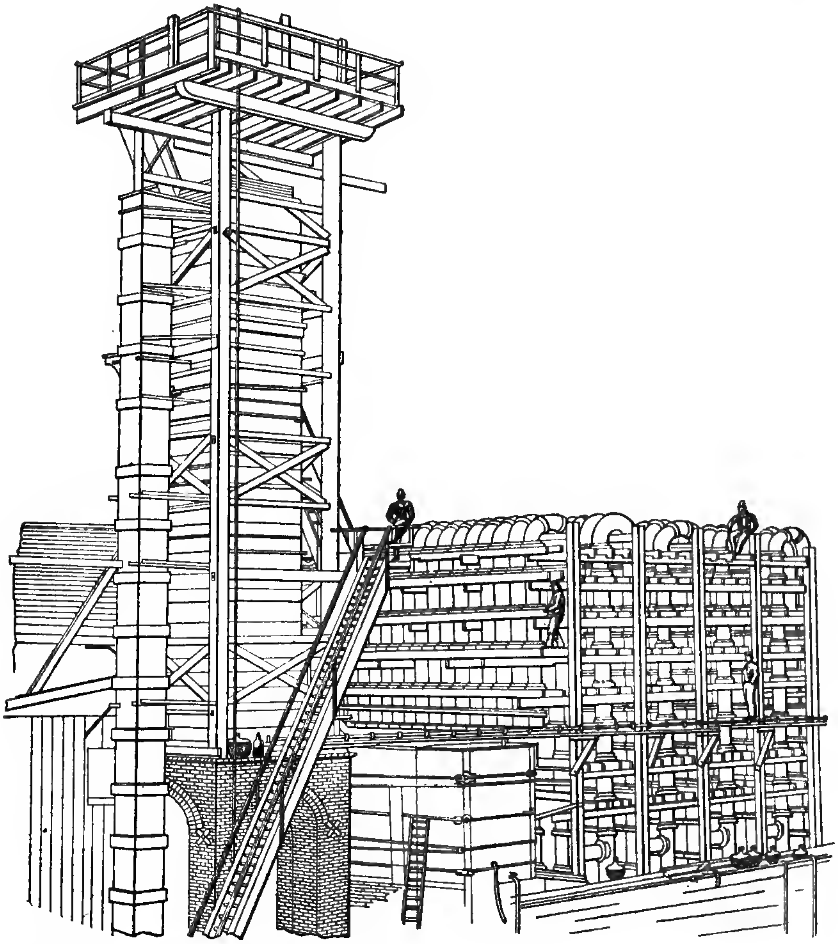
143.



stone cisterns are connected by 18 sets of pipes, each set going up and down five times. Finally, the gases go through the standing tower.

The form of condenser, or wash tower, shown in Fig. 145, though cheap, is not to be recommended, on account of leakage from the joints, and the liability of the pipes to crack. Its construction will be readily understood from the drawing. Pipes of porous earthenware, thoroughly boiled in pitch, are built up with socket joints, well stemmed with some suitable material. The whole is supported by a timber framework, and loosely packed with coke, after the manner already described.

144.



The legislation of other countries upon noxious exhalations and chemical industries presents entirely different features from our own. The French laws are based upon an imperial edict, dated from Fontainebleau, 15th October, 1810, which, after referring to the complaints preferred against chemical works on account of "unwholesome or inconvenient exhalations," decrees that "after the publication of the present enactment, the manufactures which give out an unwholesome or unpleasant odour will not be allowed to be established without the authority of the administration. These establishments will be divided into three classes. The first class will comprehend those which ought to be distant from all private dwellings. The second, the manufactures and workshops which it is not necessary to separate rigorously from dwellings, but which, nevertheless, ought not to be allowed before ascertaining correctly that the operations will be carried on in such a manner as not to cause damage or inconvenience to the neighbourhood. In the third class will be placed those establishments which may remain without inconvenience before habitations, but ought to be submitted to the surveillance of the police.

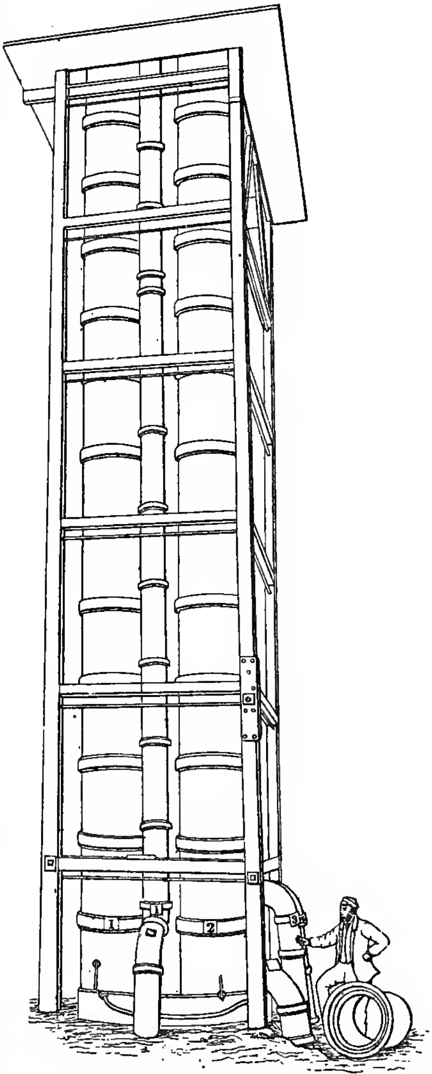
A list is appended of the manufactures and establishments giving rise to noxious exhalations which could not thereafter be commenced without the consent of the Administration. This list, issued last in 1867, in a revised form, relegated to the first class the manufactures of arsenic, hydrochloric, picric, stearic, sulphuric, and nitric acids, and the manufactures of starch, matches, explosive powders, arseniate of potash, fireworks, pearl ashes, glue, cyanide of potassium, manures, tars, fats, and various oils, together with the sulphates of ammonia, copper, soda, &c., &c. The second class comprised various modified processes of the manufactures recited in the first class, where special means were taken to prevent the emission of noxious vapours, together with the manufactures of pyroligneous acid, chlorine and the chlorides, coke, iron, murexide, animal charcoal, porcelain, sal-ammoniac, &c., &c. The third class included further, and still more carefully conducted, processes of the foregoing chemical industries, together with the manufactures of alcohol, ammonia, steel, albumen, artificial fuels, bricks, tinplates, coal gas, gelatine, litharge, paper and paper pulp, copperas, &c., &c.

In Paris the authority is vested in the hands of the Prefect of Police and the Conseil d'Hygiène, which latter consists of scientific and official men of high standing. Within the last few years, also, inspectors have been appointed in some few of the departments—Paris, Lille, Bordeaux, &c. —who are under the prefect. These inspectors are closely allied to our alkali inspectors, it being their duty to visit periodically, and report upon, the various manufactures of their districts. The Conseil d'Hygiène holds weekly meetings, and considers, not only questions relating to chemical works, but all other circumstances and conditions affecting health, including sewage, drainage, scavenging, &c. It seems to be the desire of the French Government to foster all manufactures, and they are therefore treated with great leniency. About 300 establishments existed before the decree of 1810, and, of the 2000 or 2500 set on foot since, probably by far the greater number exist *without authorization*. In some respects, at least, it is France that is the "land of the free!"

The Belgian legislation divides industrial works into three classes. For the establishment of the first, and most dangerous, class, the permission of the king is required. For the second, the permission of the permanent deputation of the provinces; and for the third, that of the administration of the communes.

Besides the decrees, there are many explanatory circulars from the Minister of the Interior to the governors of the provinces, entering into minute details.

145.



There is an inspector appointed by Government, a man of high position, as professor, but he is rather the consulting chemist to the Governmemt. He does not visit the chemical works except when complaints are made. To some extent excise officers are made to act as inspectors at alkali works, and whilst they keep the keys of the storehouse for salt, on which substance duty is paid, they make observations on the state of the atmosphere within the works; but they are not expected, nor are they fitted, to make experiments.

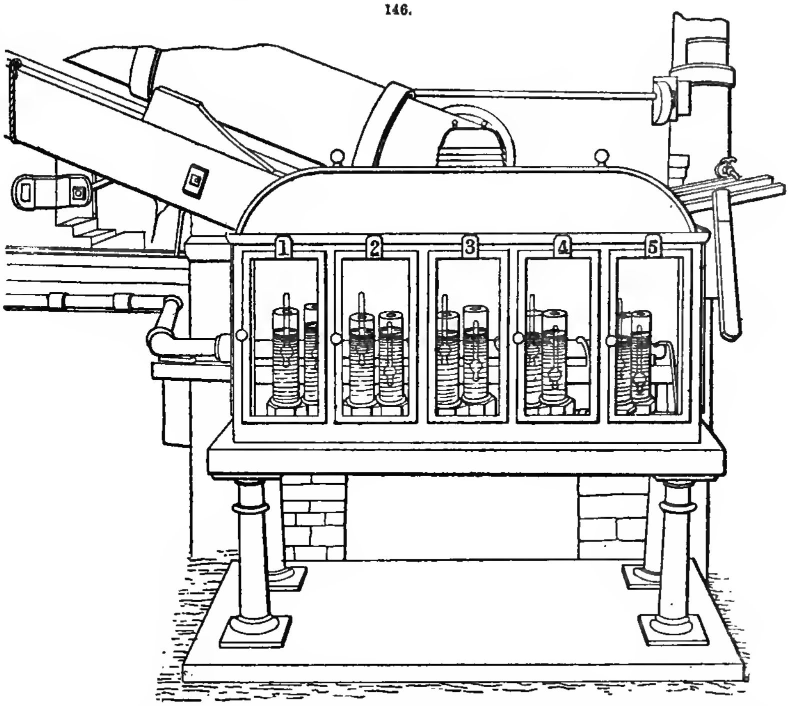
In Prussia no law similar to our Alkali Acts exist. An enactment, dated July 1st, 1861, provides certain conditions for the concession of sites and the using of streams. When it is proposed to erect works an application has to be made to the police authorities, who thereupon require the inhabitants of the given district to state their objections—if any. The question of opposition being settled, a provisional license is granted, which has subsequently to be confirmed by the Minister of Commerce. All questions of damage caused by annoyance, or pollution of rivers and streams, must be settled in the courts of law.

In testing hydrochloric acid, the usual rough method employed is to observe how far a Twaddell's hydrometer sinks in the liquid. In doing this, special note must be taken of the temperature of the acid. It may be laid down as a general rule that the reading varies 1° for every 20° of heat, in cooling from 140° F. down to 60° F. This applies to the ordinary acid of 20° to 30° Tw. With regard to the estimation by measurement which has been alluded to, the following change of volume at various degrees of heat should be noted :—

1 cub. ft.	of liquid acid	at 62° F. becomes	1·0019	cub. ft.	of liquid acid at	70°	F.
,,	,,	,,	1·0043	,,	,,	80	,,
,,	,,	,,	1·0066	,,	,,	90	,,
,,	,,	,,	1·0089	,,	,,	100	,,
,,	,,	,,	1·0113	,,	,,	110	,,
,,	,,	,,	1·0137	,,	,,	120	,,
,,	,,	,,	1·0161	,,	,,	130	,,
,,	,,	,,	1·0184	,,	,,	140	,,
,,	,,	,,	1·0208	,,	,,	150	,,
,,	,,	,,	1·0231	,,	,,	160	,,
,,	,,	,,	1·0255	,,	,,	170	,,
,,	,,	,,	1·0279	,,	,,	180	,,
,,	,,	,,	1·0302	,,	,,	190	,,
,,	,,	,,	1·0326	,,	,,	200	,,

By dividing the fractional part of the real specific gravity by 5, the specific gravity by Twaddell's hydrometer may be readily ascertained, and also the percentage of real acid, which two are pretty nearly the same. Thus, taking an acid of 1·10 real sp. gr., 20—i. e. 100 divided by 5—will be the specific gravity by Twaddell, and very nearly the percentage of real acid. This process of calculation *reversed* is perhaps more useful.

146.



With a view to remedy the evil arising from the irregularity of the strength of ordinary tower acid, affecting the testing by Twaddell's hydrometer, Mr. Kane, of Dublin, has constructed the ingenious apparatus shown in Fig. 146, of which the following is Mr. Kane's description :—

"The exit pipe from the top of the first condenser, for the convenience of connection, descends vertically into a junction pipe at the level of the condenser's bottom, and from the side of this junction another short range of similar pipes conducts the waste gas to the wash tower. This junction stands upon a stone, cut to receive it, and the mere contact of the waste gas with the sides of the exit pipe suffices to condense enough acidulated water to form a small constantly running lute in the bottom of the junction. By observing the specific gravity of this acidulated water one has, to a certain extent, a test as to whether the condensation in the first condenser is reasonably good or not. For, although a Twaddell hydrometer should only indicate one degree of specific gravity in this acidulated water, there may be some small escape of gas in the exit pipe. Yet it is a negative test for the condensation, inasmuch as the escape of gas from the first condenser must he greater in proportion if the acidulated water be of a high degree of specific gravity.

"It is difficult to compel the hydrochloric acid maker to sample this water in the ordinary way, and we therefore determined to collect it in such a manner that it should thrust itself on his observation.

"With the junction pipe already alluded to, which supports the vertical range of exit pipes from the first condenser, we connected a very small range of glass tubing, through which all the liquid formed in the exit piping and falling into the junction should necessarily flow. This glass tubing brings the acidulated water to the front of the condensers, and discharges it into a circular glass vessel, about 14 in. high and 2½ in. diameter, having an exit tube at the bottom, which is connected with another glass tube arising outside the vessel to about two-thirds its height, and discharging into an earthenware pipe connected with the stock cisterns for hydrochloric acid. By this arrangement there is always enough liquid in the vessel to float a Twaddell hydrometer, and, as the liquid constantly flows from the first condenser exit pipe through the glass vessel, and thence away to the stock cisterns, the acid maker can at any moment of the day, by merely looking at the floating hydrometer, tell whether or not the condensation in the first condenser is comparatively near perfection. Similarly we connected a range of glass tubing to the bottom of the first condenser, and through it a stream of strong acid constantly runs, the strength of which, varying as the strength of the acid in that condenser constantly varies, is indicated also by a floating hydrometer. If, therefore, a high degree of specific gravity be indicated by the hydrometer in the acid from the first condenser, and also in the acid in the adjoining glass from the exit pipe, it proves that enough water has not been supplied to the first condenser, or that for some other reason the gas has not been properly condensed, and that there is a quantity of gas going to the wash tower which should have heen utilized in the first condenser. If too much water has been supplied to the first condenser the acid maker notices the precise moment when the specific gravity of the run begins to decrease, and he can more quickly remedy his mistake. If the acid from the first condenser be of a high degree of specific gravity, at the same time that the acidulated water from the exit pipe is of a very low degree of specific gravity, it proves to the acid maker as far as an unscientific test can do, that his first condenser is working satisfactorily."

The specific gravity of hydrochloric acid is only a safe guide to its commercial value when the sample is pure. Ordinarily the presence of foreign bodies or positive adulterations disturbs this method of testing by artificially increasing the strength. The proportion of real acid is more safely ascertained by neutralization, with a test liquor of ammonia or carbonate of soda, or by saturation with carbonate of calcium. To effect the latter a given quantity of the acid is taken—say 100 grains—and diluted with twice its weight of water, in any suitable vessel. A weighed lump of white marble, in known excess of the acidity of the liquid, is added, and left in the acid until all effervescence has ceased. The marble is then taken out, washed, dried, and weighed again. The loss in weight indicates the quantity dissolved. Now, by the known equivalents, 37 grains of pure hydrochloric acid can saturate 50 of carbonate of calcium. If then the quantity taken —100 grains—has dissolved, say, 45 grains of the marble, the sample contains 33·3 grains per cent. of real hydrochloric acid or 84 per cent. of acid at 1·20 sp. gr., and should show itself 1·17 sp. gr.

The usual contaminations of hydrochloric acid are sulphurous and sulphuric acids and perchloride of iron; also, in a less degree arsenious and nitric acids, and free chlorine. The water used for condensing purposes adds its own impurities in the shape of the salts existing therein. These contaminations are chiefly due to the articles used in the manufacture of sulphuric acid and sulphate of soda, and to the action of the acids and salts upon the plant employed. On the continent, the admixture of coal-dust with the common salt—in order to avoid a salt tax—gives rise to an especial amount of sulphurous and sulphuric acids. To detect perchloride of iron, the acid may be super-saturated with ammonia, whereby a flocculent brown precipitate will slowly form; or, to the super-saturated solution sulphide of ammonia may he added, which will precipitate the iron as black sulphide. The latter is the better test, unless the presence of considerable amount of the iron salt is known.

The presence of sulphurous and sulphuric acids may be detected by precipitation with chloride of barium. The sulphate of barium thrown down indicates the existence of sulphuric acid. Freed from this by filtration, the filtrate may be treated with nitric acid to oxidize the sulphurous acid, and precipitated again with the barium salt.

Arsenious acid may be detected by the well-known Marsh's apparatus, for description of which the reader is referred to any book of chemical analysis.

The presence of free chlorine is readily detected by its odour, if present in any considerable quantity, or by the decolorization of a few drops of added sulphate of indigo solution. If nitric acid is present, a portion of gold leaf immersed in the sample will be dissolved.

Hydrochloric acid may be freed from sulphurous and sulphuric acids by careful distillation, the sulphurous acid being first transformed into sulphuric by the addition of a small quantity of powdered binoxide of manganese. The hydrochloric acid passes over and leaves the sulphuric acid in the retort. By redistillation the perchloride of iron may be similarly eliminated. Arsenious and arsenic acids may be removed by distillation with a small quantity of sulphide of barium, or by digestion with copper filings, and distilling the decanted acid.

The commercial value of hydrochloric acid varies from 10*s.* to 6*l.* per ton, according to the quality of the sample and distance from the source of supply. The tower acid is made in such enormous quantities, that, as a rule, no profitable price can be got for it, and, unless the manufacturer can utilize it in some other process, it is often run off into the river or sea. When prepared for sale it is collected in glass carboys, set in baskets of wicker work, or hoop iron.

The magnitude and growth of the trade may be appreciated from the facts that in 1862, the amount of salt consumed in the United Kingdom alone was 254,000 tons, and at the present time the consumption has reached the enormous total of 650,000 tons per annum.

Before bringing the article to a close, a few words should be devoted to one or two new processes for the manufacture of sulphate of soda, in so far as they trench upon the subject in hand —the production of hydrochloric acid. The processes themselves will be considered at a later date. Messrs. Jones and Walsh claim that by their patent furnace they effect not only a saving of wages, and improved quality of salt-cake, but a more perfect condensation of hydrochloric acid. The first two objects are certainly accomplished, but the condensation is not so good as by the old process, inasmuch as the pan has to be worked with a very strong draught. It has already been pointed out that rapidity of draught is a potent enemy of condensation.

Messrs. Cammack and Walker's furnace consists of a revolving cylinder, the salt and sulphuric acid being supplied constantly by mechanism. The same objection applies to this as to the furnace of Messrs. Jones and Walsh, in point of condensation. Both plants are, moreover, exceedingly liable to get out of order. Mr. Deacon's plan of a raised furnace has not yet been worked out. The same may be said of Mr. Mease's revolving pan, with fixed agitators, or ploughs. The mind of the manufacturer of to day is, above all things, set upon minimising hand labour, and in this respect the new processes doubtless effect a great deal. But so far as the production of hydrochloric acid is concerned, no device has in any way superseded the old method of divided condensation between pan and roaster with the ordinary stone or brick towers.

A detailed description of the salts of hydrochloric acid will be given under the heads of their respective bases.

J. L.

ACID, HYDROFLUORIC. (Fr., *Acide fluorique;* Ger., *Spathsäure*). Formula, HF; specific gravity, 1·06.

This acid, discovered by Scheele in 1771, is produced by the action of sulphuric acid upon metallic fluorides. For the preparation of the pure acid in the liquid state, powdered dry fluorspar is placed in a leaden or platinum retort, having a bent leaden tube fixed to the mouth. This tube is V-shaped, and the bottom of it is immersed in a freezing mixture. Strong sulphuric acid is introduced into the retort, and the contents are mixed and gently heated. Hydrofluoric acid gas is given off in the form of a colourless vapour, which passes into the bent tube, where it is condensed to a liquid.

If the dry gas be required, it may be prepared by igniting the double fluoride of hydrogen and potassium, which decomposes into fluoride of potash and hydrofluoric acid.

Hydrofluoric acid is used chiefly for etching upon glass. This property is due to the extreme affinity of the acid for silica, which it attacks energetically. The glass being covered with a thin coating of etching-wax, lines are traced in the wax with a fine-pointed instrument. On exposure to the gas the lines traced in the wax are etched, the rest of the glass being unacted on. The graduation of glass instruments is performed by this method. Hydrofluoric acid is used also in the laboratory for the decomposition of silicates in mineral analysis.

Fluorspar.—The mineral used for the preparation of hydrofluoric acid has a beautiful crystalline structure; it exists abundantly in England, especially in Derbyshire, where it is known as "Blue John." It is also found in Cumberland, Northumberland, Durham, Yorkshire, and Cornwall. It crystallizes usually in cubes. It is sometimes found perfectly colourless, but it generally exhibits beautiful shades of blue, green, yellow, and red. These tints disappear when the mineral is heated to redness, at which temperature it gleams with a beautiful, many-coloured, phosphorescent light. If heated considerably higher, it loses its power of phosphorescence, becoming at the same time quite colourless.

At Castleton, in Derbyshire, fluorspar is made into vases and various other ornamental articles. The colour is sometimes so intense that the articles cannot be wrought thin enough to show it, in which case the stone is heated in an oven till nearly red-hot, when the deep blue is changed into a pale amethystine hue. Fluorspar is used also by lead-smelters as a flux.

NITRIC ACID.—(Fr., *Acide nitrique or azotique*; Ger., *Salpetersaüre*), sometimes, in a diluted form, called aquafortis (eau forte, scheidewasser). Constituents, hydrogen, nitrogen, and oxygen. Formula, HNO_3.

Nitric acid may be viewed as a compound of one equivalent of the anhydrous acid with one equivalent of water. When pure it is a transparent colourless liquid of 1·52 sp. gr., giving off, in moist air, white fumes with a well-known sour taste and pungent odour. The commercial acid is usually more or less coloured, owing to the presence of certain lower oxides of nitrogen. Its mixture with water develops heat, a definite acid liquid of 1·42 sp. gr. being formed, containing 60 per cent. of the anhydrous acid. At 86° nitric acid boils and undergoes partial decomposition into water, oxygen and peroxide of nitrogen. After about three-fourths of the liquid has distilled over, the residue loses all colour, and contains 95·8 per cent. of real acid. Beyond this the boiling point rises continually, a strong acid coming over, and a weaker being left behind. When this residue attains a percentage of only 68 HNO_3, it is found to boil unaltered at a temperature of 120°, under the ordinary pressure of the atmosphere. Whatever may be the strength of the acid experimented upon this final constant liquid is always obtained. This is shown in the following table which gives the results of a series of experiments by Roscoe. Column I. gives the volume of acid employed; column II. the percentage quantity of real acid in the liquid before distillation; column III. the volume of liquid remaining in the retort; column IV. the percentage of real nitric acid contained in the residual liquid after distillation:—

No.	I.	II.	III.	IV.
	c.c.		c.c.	
I	20	70·2	5	68·1
2	20	68·3	5	68·0
3	20	68·3	5	67·9
4	20	66·9	5	68·0
5	20	66·2	5	68·0
6	20	62·2	5	68·0

If the pressure under which the operation is conducted be varied, a new, but always finally fixed, acid is obtained, with a constant boiling point. Thus under a pressure of 1·22 m. of mercury a 68·6 per cent. acid distils over unchanged, whilst under a pressure of 0·070 m. an acid with a constant composition of 66·7 per cent. comes over at a temperature of from 65° to 70°. When aqueous nitric acid is subjected to a current of dry air, a stronger or weaker acid is volatilized, according to the strength or temperature, until a residual liquid is obtained which volatilizes unchanged. Thus at a temperature of 100° the residual acid shows a composition of 66·2 per cent.; at a temperature of 60° 64·5 per cent., while at 15° the residue has a fixed composition of 64 per cent. real acid. In all these respects aqueous nitric acid resembles hydrochloric acid. For further details relating to these matters the reader is referred to the paper published by Dr. Roscoe in the 'Chem. Soc. Qu. J.,' vol. xiii. 150.

I. Kolbe ('An. Ch. Phys.' [4] X. 136) has published a new table of the exact specific gravity of nitric acid of various strengths:—

p	Density.		Contraction.	*p*	Density.		Contraction.
	At 0°.	At 15°.			At 0°.	At 15°.	
100·00	1·559	1·530	0·0000	89·56	1·521	1·494	0·0315
99·84	1·559	1·530	0·0004	88·00	1·514	1·488	0·0354
99·72	1·558	1·530	0·0010	87·45	1·513	1·486	0·0369
99·52	1·557	1·529	0·0014	86·17	1·507	1·482	0·0404
97·89	1·551	1·523	0·0065	85·00	1·503	1·478	0·0433
97·00	1·548	1·520	0·0090	84·00	1·499	1·474	0·0459
96·00	1·544	1·516	0·0120	83·00	1·495	1·470	0·0485
95·27	1·542	1·514	0·0142	82·00	1·492	1·467	0·0508
94·00	1·537	1·509	0·0182	80·96	1·488	1·463	0·0531
93·01	1·533	1·506	0·0208	80·00	1·484	1·460	0·0556
92·00	1·529	1·503	0·0242	79·00	1·481	1·456	0·0580
91·00	1·526	1·499	0·0272	77·66	1·476	1·451	0·0610
90·00	1·522	1·495	0·0301	76·00	1·469	1·445	0·0643

p	Density.		Contraction.	p	Density.		Contraction.
	At 0°.	At 15°.			At 0°	At 15°.	
75·00	1·465	1·442	0·0666	47·18	1·315	1·298	0·0850
74·01	1·462	1·438	0·0688	46·64	1·312	1·295	0·0848
73·00	1·457	1·435	0·0708	45·00	1·300	1·281	0·0835
72·39	1·455	1·432	0·0722	43·53	1·291	1·274	0·0820
71·24	1·450	1·429	0·0740	42·00	1·280	1·264	0·0808
69·96	1·444	1·423	0·0760	41·00	1·274	1·257	0·0796
69·20	1·441	1·419	0·0771	40·00	1·267	1·251	0·0786
68·00	1·435	1·414	0·0784	39·00	1·260	1·244	0·0755
67·00	1·430	1·410	0 0796	37·95	1·253	1·237	0·0762
66·00	1·425	1·405	0·0806	36·00	1·240	1·225	0·0740
65·07	1·420	1·400	0·0818	35·00	1·234	1·218	0·0729
64·00	1·415	1·395	0·0830	33·86	1·226	1·211	0·0718
63·59	1·413	1·393	0·0833	32·00	1·214	1·198	0 0692
62·00	1·404	1·386	0·0846	31·00	1·207	1·192	0·0678
61·21	1·400	1·381	0·0850	30·00	1·200	1·185	0·0661
60·00	1·393	1·374	0·0854	29·00	1·194	1·179	0·0650
59·59	1·391	1·372	0·0855	28·00	1·187	1·172	0·0635
58·88	1·387	1·368	0·0861	27·00	1·180	1·166	0·0616
58·00	1·382	1·363	0·0864	25·71	1·171	1·157	0·0593
57·00	1·376	1·358	0·0868	23·00	1·153	1·138	0·0520
56·10	1·371	1·353	0·0870	20·00	1·132	1·120	0·0483
55·00	1·365	1·346	0·0874	17·47	1·115	1·105	0·0422
54·00	1·359	1·341	0·0875	15·00	1·099	1·089	0·0366
53·81	1·358	1·339	0·0875	13 00	1·085	1·077	0·0316
53·00	1·353	1·335	0·0875	11·41	1·075	1·067	0·0296
52·33	1·349	1·331	0·0875	7·20	1·050	1·045	0·0206
50·99	1·341	1·323	0·0872	4·00	1·026	1·022	0·0112
49·97	1·334	1·317	0·0867	2·00	1·013	1·010	0·0055
49·00	1·328	1·312	0·0862	0·00	1·000	0·909	0·0000
48·00	1·321	1·304	0·0856				

The percentage, *p*, of HNO_3 was determined by adding a known weight of pure carbonate of lime in excess, and weighing the portion which remained undissolved. These figures differ considerably from, but are probably more correct than, those determined and published by Dr. Ure in his Dictionary. Dr. Ure's table is as follows:—

Specific Gravity.	Liquid Acid in 100.	Dry Acid in 100.	Specific Gravity.	Liquid Acid in 100.	Dry Acid in 100.	Specific Gravity.	Liquid Acid in 100.	Dry Acid in 100.
1·5000	100	79·700	1·4107	73	58·181	1·2705	46	36·662
1·4980	99	78·903	1·4065	72	57·384	1·2644	45	35·865
1·4960	98	78·106	1·4023	71	56·587	1·2583	44	35·068
1·4940	97	77·309	1·3978	70	55·790	1·2523	43	34·271
1·4910	96	76·512	1·3945	69	54·993	1·2462	42	33·474
1·4880	95	75·715	1·3882	68	54·196	1·2402	41	32·677
1·4850	94	74·918	1·3833	67	53·399	1·2341	40	31·880
1·4820	93	74·121	1·3783	66	52·602	1·2277	39	31·083
1·4790	92	73·324	1·3732	65	51·805	1·2212	38	30·286
1·4760	91	72·527	1·3681	64	51·068	1·2148	37	29·489
1·4730	90	71·730	1·3630	63	50·211	1·2084	36	28·692
1·4700	89	70·933	1·3579	62	49·414	1·2019	35	27·895
1·4670	88	70·136	1·3529	61	48·617	1·1958	34	27·098
1·4640	87	69·339	1·3477	60	47·820	1·1895	33	26·301
1·4600	86	68·542	1·3427	59	47·023	1·1833	32	25·504
1·4570	85	67·745	1·3376	58	46·226	1·1770	31	24·707
1·4530	84	66·948	1·3323	57	45·429	1·1709	30	23·900
1·4500	83	66·155	1·3270	56	44·632	1·1648	29	23·113
1·4460	82	65·354	1·3216	55	43·835	1·1587	28	22·316
1·4424	81	64·557	1·3163	54	43·038	1·1526	27	21·519
1·4385	80	63·760	1·3110	53	42·241	1·1465	26	20·722
1·4346	79	62·963	1·3056	52	41·444	1·1403	25	19·925
1·4306	78	62·166	1·3001	51	40·647	1·1345	24	19·128
1·4269	77	61·369	1·2947	50	39·850	1·1286	23	18·331
1·4228	76	60·572	1·2827	49	39·053	1·1227	22	17·534
1·4189	75	59·775	1·2826	48	38·256	1·1168	21	16·737
1·4147	74	58·978	1·2765	47	37·459	1·1109	20	15·940

Specific Gravity.	Liquid Acid in 100.	Dry Acid in 100.	Specific Gravity.	Liquid Acid in 100.	Dry Acid in 100.	Specific Gravity.	Liquid Acid in 100.	Dry Acid in 100.
1·1051	19	15·143	1·0651	12	9·564	1·0320	6	4·782
1·0993	18	14·346	1·0595	11	8·767	1·0267	5	3·985
1·0935	17	13·549	1·0540	10	7·970	1·0212	4	3·188
1·0878	16	12·752	1·0485	9	7·173	1·0159	3	2·391
1·0821	15	11·955	1·0430	8	6·376	1·0106	2	1·594
1·0764	14	11·158	1·0375	7	5·579	1·0053	1	0·797
1·0708	13	10·361						

Nitric acid is a strong oxidizing agent, attacking nearly all the metals, the non-metallic substances and organic bodies. The final products of the combustion of the last-named substances are, usually, acetic, formic, and oxalic acids, with various intermediate and resulting compounds. Most of the metals are converted into nitrates, while the non-metallic bodies—e. g. phosphorus, arsenic, sulphur, carbon, silicon—are dissolved into their respective acids. Gold, platinum, and titanium resist the solvent. The potency, and resulting action of, nitric acid depend to a great extent upon its strength and the temperature at which the operation is conducted. When a strong acid is used, as a rule, nitric oxide is evolved; when a weaker solvent, a lower oxide of nitrogen. Charcoal digested with a strong acid, at a temperature below 0°, liberates oxygen, with the evolution of nitric peroxide. Occasionally nitrogen is set free. Many of the proto-salts—e. g. arsenites—are converted by the action of nitric acid into per-salts. It stains many animal substances a deep yellowish brown colour. The pure liquid is much less potent than when it contains nitrous acid or nitric oxide, forming the well known, red, fuming liquid.

Nitric anhydride, discovered by Deville in the year 1849, forms transparent, colourless crystals taking the shape of prisms with six faces. Mixed with water these crystals dissolve, with evolution of heat, and form the ordinary aqueous acid. The formula of the anhydride is N_2O_5, boiling point 45° to 50°. This substance is of small value outside of the laboratory.

Nitric acid seems to have been known from very early times. As far back as the seventh century Geber, in his 'De Inventione Veritatis,' says: "Sume libram unam de vitrioli de cypro et libram salis petræ et unam quartam aluminis Iameni, extrahe aquam cum rubendine alembici." From this it appears that nitric acid was obtained by distillation from a mixture of saltpetre, alum, and sulphate of copper. According to Herapath, the Egyptians were acquainted with this substance, using a marking fluid containing nitrate of silver for its base. This opinion was founded upon a microscopical examination of the hieroglyphics discovered upon the wrappings of a mummy, and seems to be a fair inference from all appearances. The name of aquafortis was bestowed by the alchemists, who made use of the acid in various ways, especially in the separation of gold and silver. The term "aqua fortis" was not, however, as is often supposed, confined to nitric acid. In the writings of the thirteenth century directions are given for preparing it from saltpetre and sulphate of iron. The present method of preparation—the distillation of saltpetre, or nitre, with sulphuric acid—was probably first employed by Glauber, and for a considerable period the product was known as "spiritus nitri fumans Glauberi." In 1776 Lavoisier demonstrated that one constituent, at least, was oxygen, but little more was accomplished until Priestley and Cavendish experimented upon the substance. The former, passing a series of electric sparks through air enclosed between two columns of litmus solution, observed that a red colour was produced, and that a contraction of the air volume took place. Cavendish used lime water and caustic potash in place of the litmus solution, and arrived at the belief that the reaction in question was caused by the production of an acid. He afterwards passed a series of electric sparks through a mixture of oxygen and nitrogen over caustic potash, and found that nitrate of potassium was produced. In the 'Phil. Trans.' for 1784, f. 119, Cavendish reports thus upon his experiment: "The phlogisticated air (nitrogen) was enabled by means of the electric spark to unite to, or form a chemical combination with, the dephlogisticated air (oxygen), and was thereby reduced to nitrous acid which united with the soap lees (caustic potash), and formed a solution of nitre; for in these experiments these two airs actually disappeared, and nitric acid was formed in their room." In later times the constituents, proportions, and properties of this body have been further investigated and determined by Davy, Gay-Lassac, and others.

Nitric acid does not exist free in the mineral and vegetable kingdoms, but is found largely in both, combined with various bases—soda, lime, potash, and magnesia. If the old experiment of Cavendish, with oxygen and nitrogen, be performed with the addition of a little hydrogen gas, the action is much more marked, and a small quantity of nitrate of ammonia is formed. Hence, probably, the existence of this salt, in the rain water of thunderstorms. M. Bobierre in his report upon some researches into the chemical composition of rain water collected at different altitudes, says, "I evaporated in an oil bath 372 litres of rain water having carbonate of soda present, and determined month by month the amount of nitrogen in the fixed organic matter, the nitric acid, and the chlorine; then by fractional distillation, by Boussingault's method, I determined the amount of ammoniacal nitrogen.

"Suspended matter was separated by filtration and examined by a microscope. I extract from my Memoir some of the principal figures, which show the nature of the results (at 47 metres height and down below):—

GRAMMES OF AMMONIA, NITRIC ACID, AND CHLORIDE OF SODIUM IN A CUBIC METRE OF RAIN WATER COLLECTED AT NANTES IN 1863.

Month.	Ammonia.		Nitric Acid.		Chloride of Sodium (commou salt).	
	154 ft. high.	Below.	154 ft. high.	Below.	154 ft. high.	Below.
January	5·225	6·398	5·790	3·200	14·10	8·40
February	4·610	5·900	"	"	15·10	10·00
March	1·880	8·620	7·115	5·980	16·10	11·90
April	1·840	6·680	2·309	1·813	7·30	9·20
May	0·747	4·642	3·501	1·998	5·00	9·40
June	2·222	3·970	13·218	10·237	15·00	17·40
July	0·272	2·700	"	"	"	"
August	0·257	2·112	15·520	16·000	14·80	19·30
September	1·432	5·512	9·999	5·720	11·20	14·80
October	1·688	4·289	4·989	3·198	12·00	9·00
November	0·593	4·480	6·278	5·574	22·80	26·10
December	3·178	15·665	4·890	3·100	21·60	16·30
Mean	1·997	5·939	7·360	5·682	14·09	13·80

The atmosphere in the neighbourhood of works where the manufacture of sulphuric acid is carried on is often largely contaminated by nitric acid and other oxides of nitrogen, though the introduction of denitrating apparatus has done much to lessen the evil. The following table gives the results of divers experiments.

NITRIC ACID IN EXITS OF VITRIOL CHAMBERS IN ALKALI AND OTHER WORKS.

Grains of Nitric Acid per Cubic Foot.	Remarks.	Solution in which the Gases were Dissolved.	Grains of Nitric Acid per Cubic Foot.	Remarks.	Solution in which the Gases were Dissolved.
0·3009	.. ..	Potass. bichrom.	0·0594	Contains free SO_2	Potass. bichrom.
0·0753	Oil of vitriol culvert	" "	0·0141	.. ..	" "
0·0842	.. ..	" "	0·0680	.. ..	" "
0·1112	.. ..	" "	0·0157	Exit from covered vitriol pan ..	" "
0·0487	.. ..	" "	0·0166	.. ..	" "
0·0293	.. ..	" "	0·0910	.. ..	" "
0·0711	Smell of oxides of nitrogen	" "	0·0380	.. ..	" "
0·0823	.. ..	" "	0·0337	.. ..	" "
0·0307	.. ..	" "	0·0512	.. ..	" "
0·0770	.. ..	" "	0·0312	.. ..	" "
0·0226	.. ..	" "	0·0193	.. ..	" "
0·0659	.. ..	" "	0·0124	.. ..	" "
0·0486	Chamber flue ..	" "	0·0401	.. ..	" "
0·0381	" ..	Water.	0·0238	.. ..	" "
0·2577	Contains free SO_2	Potass. bichrom.	0·0431	.. ..	" "
0·0451	" ..	" "	0·0217	.. ..	" "

NITRIC ACID IN CHIMNEYS OF ALKALI WORKS.

Grains of Nitric Acid per Cubic Foot.	Remarks.	Solution in which the Gases were Dissolved.	Grains of Nitric Acid per Cubic Foot.	Remarks.	Solution in which the Gases were Dissolved.
0·0011	Contains free SO_2	Potass. dichrom.	0	.. ..	Potass. dichrom.
0·0074	.. ..	" "	0·0044	.. ..	" "
0	.. ..	..	0	.. ..	" "
0	. ..	Potsss. dichrom.	0	.. ..	" "
0·0055	.. ..	" "	0·0044	.. ..	" "
0·0055	.. ..	" "	0·0036	.. ..	" "
0·0067	.. ..	" "	0·0133	.. ..	" "
0·0022	.. ..	" "	0	.. ..	" "

NITRIC ACID IN CHIMNEYS OF ALKALI WORKS—*continued.*

Grains of Nitric Acid per Cubic Foot.	Remarks.	Solution in which the Gases were Dissolved.	Grains of Nitric Acid per Cubic Foot.	Remarks.	Solution in which the Gases were Dissolved.
0·0486	.. ..	Water.	0·0343	.. ..	Potass. dichrom.
0·0044	.. ..	Potass. dichrom.	0·0022	.. ..	” ”
0·0067	.. ..	” ”	0·0086	Main flue	” ”
0	.. ..	” ”	0	”	Water.
0·0156	.. ..	” ”	0	” at entrance to chimney . ..	Pot. dichromate.
0·0122	Flues from six vitriol chambers pass into the chimney	” ”	0·0044	At foot of chimney	” ”
0·0600	.. ..	” ”	0·0080	From retort room	” ”
			0·0044	Smoke flue	..

The action of the nitric acid present in the air of chemical works is of course to oxidize the sulphurous acid. From what has been said respecting the other oxides of nitrogen it may he readily supposed that they have greater potency than the acid itself. This seems to be borne out by the following results of experiments—the sulphurous acid in some cases appearing almost to be preserved by the nitric acid:—

I.

Number of Hours before the SO_2 was determined.	Milligrammes.			Cubic Cents. Water in which the Acids met.	Grains.			
	HNO_3.	SO_2.	SO_3.		HNO_3.	SO_2	SO_3.	Water in which the Acids met.
	17·93	8·35	added to each 10·41	200	0·2767	0·1289	added to each 0·1606	3086
19		0				0		
43		0				0		
	17·93	16·70	”	200	0·2767	0·2579	0·1606	3086
19		7·07				0·1092		
43		0				0		
	17·93	33·40	”	200	0·2767	0·5158	0·1606	3086
19		23·59				0·3641		
43		14·29				0·2206		
	35·86	1·42	”	200	0·5534	0·0219	0·1606	3086
5		0·78				0·0210		
	35·86	1·67		150	0·5534	0·0258		2315
19		0				0		
43		0				0		
	35·86	14·23	104·10	200	0·5534	0·2197	1·6063	3086
45		0·39				0·0060		
	35·86	16·70	10·41	226	0·5534	0·2579	0·1606	3487
19		4·44				0·0685		
43		0				0		
	358·6	8·35	”	200	5·5339	0·1289	0·1606	3086
19		3·93				0·0607		
45		3·93				0·0607		

II.

Number of Hours before the SO_2 was determined.	Milligrammes.		Cubic Cents. Water.	Grains.		
	HNO_3.	SO_2.		HNO_3.	SO_2.	Water.
	3·58	3·47	90	0·0553	0·0535	1389
17		0			0	
	35·86	3·47	90	0·5534	0·0535	1389
17		0			0	
	358·6	3·30	80	5·5339	0·0509	1234
17		1·92			0·0297	
	358·6	4·40	90	5·5339	0·0679	1389
17		2·83			0·0437	
	Without HNO_3	3·30	80	Without HNO_3	0·0509	1234
17		0			0	
	Do.	3·47	90	Do.	0·0679	
17		0			0	

III.

Number of Hours before the SO_2 was determined.	Milligrammes.		Cubic Cents. Water.	Grains.		
	HNO_3.	SO_2.		HNO_3.	SO_2.	Water.
	3·58	11·01	100	0·5553	0·1699	1543
2		10·61			0·1638	
22		5·90			0·0910	
	35·86	11·01	101	0·5533	0·1699	1558
2		9·93			0·1532	
22		8·14			0·1256	
	358·6	11·01	110	5·5339	0·1699	1697
2		9·08			0·1401	
22		8·00			0·1235	
	896·5	11·01	125	13·8347	0·1699	1929
2		9·83			0·1517	
22		8·35			0·1289	
168		3·94			0·0609	
	1793·0	11·01	150	27·6695	0·1699	2315
2		8·94			0·1456	
22		8·84			0·1365	
168		6·78			0·1047	
	Without HNO_3	11·01		Without HNO_3	0·1699	
2		10·61			0·1638	
22		2·75			0·0424	

ACTION OF OXIDES OF NITROGEN ON SULPHUROUS ACID.

The gas prepared by acting on copper with HNO_3 was passed into water, and a known amount of SO_2 was then added.

Hours standing before the SO_2 was determined.	Milligrammes.		Cubic Cents. Water in which the Gases were dissolved.	Grains.			REMARKS after standing.
	Oxides of N calculated as HNO_3.	SO_2.		Oxides of N calculated as HNO_3.	SO_2.	Water in which the Gases were dissolved.	
	1·66	11·79	225	0·0257	0·1820	3472	
4		2·21			0·0341		No smell, but decolorized iodide of starch.
23		2·21			0·0341		Do. do.
	4·26	5·89	115	0·0658	0·0910	1775	
4		2·26			0·0349		Do. do.
23		0			0		No smell, and does not decolorize iodide of starch.
	4·84	23·58	192	0·0747	0·3640	2963	
4		15·10			0·2330		
23		11·33			0·1748		Smell of SO_2.
	47·65	5·89	110	0·7354	0·0910	1697	
4		0			0		
23		0			0		Smell of oxides of N.
	97·79	11·79	68	1·5092	0·1820	1037	
4		0			0		
23		0			0		Do. do.
		11·79	169	Without oxides of N.	0·1820	2623	
4	Without oxides of N.	6·68			0·1031		
23		0			0		

The process of nitrification that has been referred to, the production first of nitric acid and then of a nitrate, is an important agency in nature, especially in warm climates, and where there is an unfailing supply of decaying organic matter. From this cause proceed the artificial nitre beds of the Continent, and the various deposits of nitrates of soda, potash, and lime occurring in South America, India, Persia, Ceylon, &c. Concerning this more will be said in treating of the respective bases. The formation of the salt in all these cases probably proceeds from the same natural cause.

The deposits are found far from human habitations, and always upon porous rocks, or light earths, where the air can circulate freely, and where a considerable amount of moisture can be held suspended. Upon hard rocks no deposit is found, and rarely in sheltered places, unless there is considerable humidity. Nitrate of lime may often be observed upon old walls, forming a distinct efflorescence. Lavoisier found nitrate of potash, mixed with nitrate of lime, upon specimens of chalk from Roche Guyon and Mousseaux. These salts have been obtained in considerable quantities from the floors of old stables and cowsheds; indeed, in some places, and at certain times, the collection has become quite a trade. It is, moreover, a noteworthy fact that the nitrate-bearing earths and rocks perpetually renew the formation when it is removed, so long as the necessary base is present. The deposits never penetrate far below the surface. Rain and dew dissolve the salts, the solutions rise by capillary attraction, and, evaporated by the action of the sun and air, form an efflorescence on the surface. The process of nitrification goes on most vigorously when animal or vegetable matter in a state of putrefaction is present. Oxidation of the ammonia, or nitrogenized organic substances, then proceeds rapidly, especially when the temperature is higher than 20°. Nitrate of lime is artificially prepared on the Continent by mixing cinders, or any porous material, with decaying animal and vegetable matters. The masses are moistened from time to time with urine, turned over occasionally to expose every portion to the action of the air, and after the lapse of a couple of years, subjected to lixiviation to obtain the lime salt.

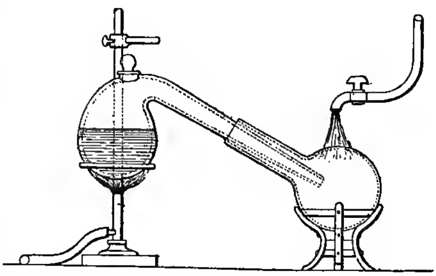
Nitric acid assumes a very important place in the arts and manufactures. Perhaps, with the exceptions of sulphuric and hydrochloric acids, it enters more largely into every-day commercial life than any other acid. It is chiefly esteemed for its solvent and oxidizing powers, and in these ways forms a most important agent in analysis, dissolving and oxidizing metals, and so separating them from the few which resist its action—e. g., silver from gold—peroxidizing antimony, tin, manganese, iron, &c., and, generally, separating soluble and insoluble precipitates. Nitric acid forms a valuable test for organic bodies; is employed in etching upon copper, steel, and stone; is used as a solvent in the preparation of certain mordants, and imparts to others their potency by its oxidizing influence. In medicine it forms a tonic, and is also extensively used as a powerful caustic. It enters into the manufacture of nitro-benzine and many similar organic preparations, nitro-glycerine and gun-cottons. Finally, it forms a series of valuable salts termed nitrates, of which more will be said hereafter.

The methods of preparation are various, but, as a rule, exceedingly simple. The experiments of Cavendish, by which, passing a series of electric sparks through air, he first demonstrated the composition of the acid, have already been referred to. When nitrogen is mixed with twelve times its bulk of hydrogen, and burnt in oxygen, a small quantity of nitric acid, together with nitrate of ammonia, is found in the resulting water. By the decomposition of the oxides of nitrogen—as by electrolyzation, and by the action of water upon nitrous oxide, and nitric anhydride—considerable quantities of the acid may be produced. Other and more feasible methods that have been proposed, are the following;—By heating chloride of manganese with nitre,

$$5\,Mn\,Cl + 5\,Na\,NO_3 = 3\,Mn\,O\,Mn_2\,O + 5\,Na\,Cl + 5\,NO_2 + O.$$

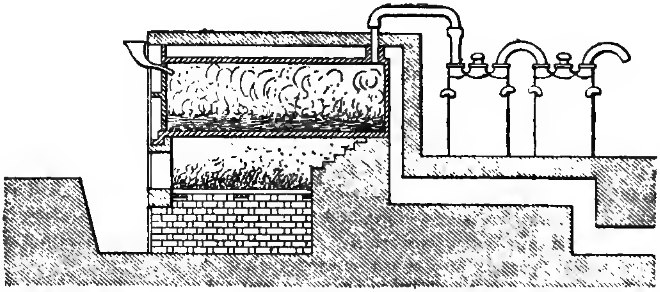
The mixture of nitric peroxide and free oxygen then brought together in presence of water, is converted into nitric acid. By the action of the sulphates of manganese, zinc, magnesium, calcium, &c., upon nitre, similar results are obtained. When a strong solution of nitrate of barium is decomposed by equivalent quantity of oil of vitriol, sulphate of barium is precipitated, and a weak nitric acid of sp. gr. 1·08, may be decanted off and concentrated by boiling. All these processes, however, belong, as yet at least, only to the region of the experimental chemist. The huge bulk of the nitric acid of commerce is obtained by heating nitrate of soda, or nitrate of potash, with sulphuric acid. Upon a small scale this operation may be performed with the apparatus shown in Fig. 147. Into a stoppered glass retort equal weights of nitre and sulphuric acid are placed, and a gradually increasing heat applied from a Bunsen's burner. A bisulphate of soda, or potash, is formed in the retort, and nitric acid distils over and is collected in a flask or suitable receiver, kept cooled with water. When this operation is carefully conducted, a very pure acid of 1·50 sp. gr. may be obtained, in weight equal to two thirds of the nitre employed. It is advisable to take equal quantities of acid and nitre, rather than the equivalent proportions, because in the latter case a much greater heat is required to set free all the nitric acid, and the neutral sulphate left behind sets into a hard mass, difficult to remove and in danger of cracking the vessel. By raising the temperature at which distillation is effected, a portion of the nitric acid undergoes decomposition.

147.

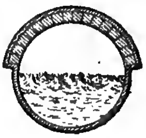


Upon a large scale the decomposition of nitre by sulphuric acid is carried on in the various retorts shown in Figs. 148 to 154. Iron vessels for the distillation were first employed by the French manufacturers, but their use has gradually spread until only a comparatively small amount of nitric acid is made in glass retorts. Perhaps the best form of retort is the cast-iron cylinder shown in Fig. 148. This is almost exactly similar to the retort used for the manufacture of hydrochloric acid, and already described. Each retort may have its separate fireplace, or they may be set in pairs. The shape and substance are alike in both cases, a good size being 6 ft. long, by 2 ft. 6 in. or 3 ft. diameter, with plates 1½ to 2 in. thick. The end over the fire is removable—sometimes both ends, to facilitate cleaning out—and through it the charge of nitrate of soda, or potassium, is introduced. The door is then securely luted on, and the necessary amount of sulphuric acid introduced through the funnel shown in the drawing. When the charging is completed this funnel is withdrawn, the hole stopped up with a plutedlug, and the fire gently set away. When the operation is completed, the cylinder is allowed to cool down, the door opened, and the mass of sulphate, or bisulphate, of soda raked out. The nitric acid disengaged passes off through earthenware pipes, luted into the top or further end of the retort, into a row of Woulfe's bottles, or other suitable condensers. A cylinder of the description here given will work off 12 to 15 tons of nitre per week. It is better to take the acid off through the top of the retort to hinder any possible carrying over of the contents when the disengagement of gas is active. When a cylinder is cracked it may be repaired by bolting a piece of sheet iron, with red lead, on the *inside*, and countersinking the bolts; but it is very questionable if such attempts are advisable. The most profitable plan is to renew the cylinder as speedily as possible, and realize the old metal. In order to protect the metal

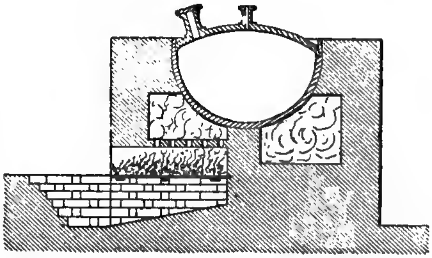
148.



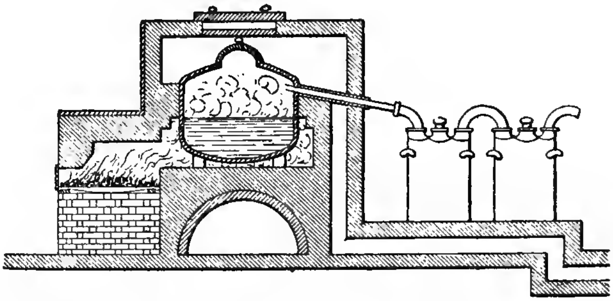
149.



150.



151.



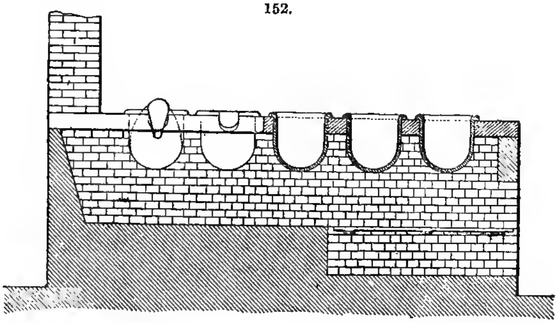
from being eaten away by the nitric acid vapours, a retort of the description shown in Fig. 149 is occasionally used, the upper half being lined with fire-bricks. Or the cylinder may be turned round from time to time. If, however, the heat is carefully managed, and no acid allowed to condense on the plate, a cylinder will rarely fail by the mere action of the acid.

Another form of cast-iron retort, used in Germany, is given in Fig. 150, and is especially adapted to the manufacture of a strong acid. The charge consists of 700 kilos of sulphuric acid of a sp. gr. of 1·84, and 600 kilos of nitrate of soda. A somewhat similar retort, closely resembling the acetate of lime pot shown in Fig. 35, is in use in England. The cover is usually formed of segments of stoneware, or fireclay "quarls," bound together with iron. The difficulty of cleaning out the residual cake, and the continual breaking of the covers, are objectionable features.

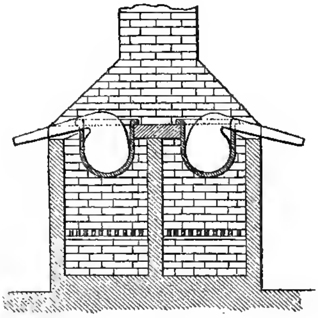
A French furnace is shown in Fig. 151, and consists of a deep cast-iron boiler or kettle, about 1½ yard in diameter, and 3 ft. deep. The advantage of this retort and method of setting is that the flames and heat envelop the whole of the vessel, and so, by keeping up a uniform temperature, preserve the metal. A double lid is employed—one of metal, fitting the kettle, and an upper one of earthenware, stone, or bricks, bound together, and luted into the brickwork setting of the furnace. It is well to line the iron tube which conveys the gases to the condensers with a glass or earthenware tube, allowing this lining to project two or three inches into the retort.

The use of nitrate of soda has now almost entirely superseded that of nitrate of potash on acount of its cheapness. The former also contains, weight for weight, a greater amount of nitric acid—about 60 per cent. as against 53 per cent. The process is the same whichever salt is used. Much diversity of practice exists with regard to the proportions of nitre and sulphuric acid. These may vary from the exact equivalents up to a large excess of acid. If the theoretical quantities are used, the operation takes longer and requires a greater heat. First the acid acts upon a portion of the nitre, disengaging nitric acid and forming an acid sulphate of soda. Then this acid salt acts upon the remainder of the nitre, again liberating nitric acid and leaving, finally, a neutral sulphate. This residue forms an exceedingly compact mass which it is difficult to remove from the cylinder. Moreover the high temperature required decomposes a portion of the nitric acid, giving rise to peroxide of nitrogen, and oxygen, the former of which dissolves in the strong acid and imparts a red colour to it. This last disadvantage is more apparent when nitrate of potash is used. Nitrate of soda, even when only equivalent proportions are used, yields up its nitric acid at a lower temperature, and the small portion that is decomposed only slightly colours the product, which may be

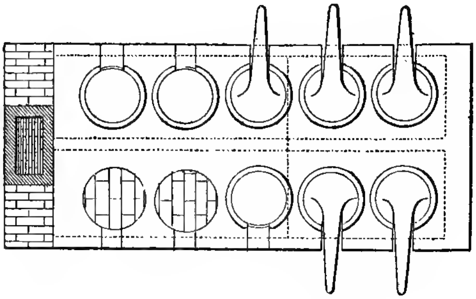
152.



153.



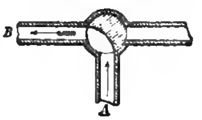
154.



afterwards purified by dilution with water and the application of a gentle heat. Usually the manufacturer uses a large excess of acid, proceeding entirely by rule of thumb—an excess of acid even beyond equal weights. By this means he saves fuel, gets a better product, and by forming an acid, and always fused, sulphate in the retort, greatly facilitates the cleaning out operation.

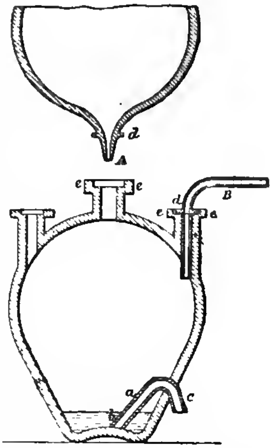
Many descriptions of glass retorts are still used. The apparatus shown in Figs. 152 to 154 is to be recommended, the construction of which will be readily understood. With this setting the retorts can be removed at will. To prevent any portion being carried over into the receivers, the charge of nitre should be very carefully put into the retorts—shaken well down. Glass retorts are used when nitrate of potash is employed, and when a carefully made acid is required. At the commencement of the operation red fumes are formed by the decomposition of a portion of the nitric acid, and the acid that first comes over, impregnated with these fumes of peroxide, should be collected separately. Gradually the coloration subsides, though rarely entirely absent. When the red fumes reappear it is a sign that the operation is completed, and distillation should be promptly stopped.

155.



156.

157.



Passing now to the condensation of the product, the apparatus usually employed consists of an arrangement of Woulfe's bottles. These may be set as shown in Fig. 88 when treating of the condensation of hydrochloric acid. The acid that collects in the first bottle is usually very impure, in the last too weak for sale, especially when running water is employed to assist condensation. A good plan is to keep only a very small quantity of water in the Woulfe's bottles, and connect the range with a low tower packed with coke, down which a stream of water is conducted. The weak acid may be added to the stronger, pure product of the middle bottles. The strength required depends, of course, upon the destination of the acid, and varies from 1·3 to 1·5—or 100° Tw. All the acid as it first condenses is coloured by the peroxide of nitrogen, as described. For decolorization it is placed in bottles, similar to those used for condensing, set over a furnace, or a sand-bath. A gentle heat—not more than 85°—is applied from below until all evolution of red vapours ceases. Or, to obtain a thoroughly pure acid, the rough product may be distilled carefully in glass retorts. Peroxide of nitrogen and chlorine first come over and are separated, then a pure nitric acid is collected in a receiver, distillation being checked when a small residue is left in the retort. This residuum contains all the iodic and sulphuric acids and whatever sulphate of soda may have collected. The iodine which helps to colour commercial nitric acid, comes from the original nitre.

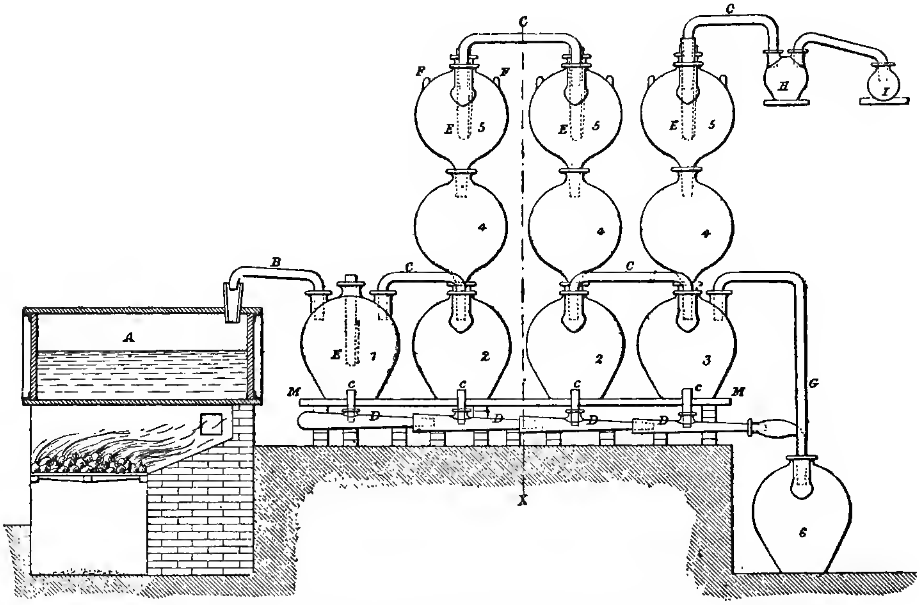
An ingenious tap arrangement has been designed by M. Chevé to obviate the necessity for discharging the colour from nitric acid in the manner described. It is shown in Figs. 155 and 156, and will be best understood from the section given in the latter drawing. The products of distillation enter at A. The first portions contain the colouring gases, and the tap being turned as shown in Fig. 156, are conducted to a range of Woulfe's bottles for condensation in the usual way. After a time, when the gas is beginning to lose its colour, the tap is turned so as to close up B, and the acid fumes are conducted along C to a separate range of bottles, which thus yield an almost colourless product. Towards the close of the distillation, if the red fumes reappear, the current can be readily passed through B again into the bottles containing the first-collected and impure acid.

The range of bottles is occasionally warmed by the waste heat from the retorts in order to prevent their fracture by the first, hot, acid which comes over, the fire being diverted into a second flue as soon as the operation has well begun. It is very questionable, however, if this refinement is either necessary or advisable.

The condensing apparatus of M. D. Plisson, shown in Figs. 157 to 163, possesses some advantages over the usual Woulfe's bottle arrangement. Fig. 157 gives a vertical section passing through the siphon nozzle of a bottle. *a* is a small stoneware pipe fixed to the bottom of the vessel, with a small opening at *b* to admit a certain portion of the contents of the bottle. This pipe rises above the level of the liquid and issues through the side of the condenser at *c*. Into the neck of this bottle the tubular end A of an upper vessel is inserted, while another communication pipe B forms a connection with the next bottle placed alongside. A shoulder *d* fits into the dished neck at *e*, and is carefully luted. Figs. 158 to 163 give various views of the condensing apparatus fitted together. Fig. 158 is a side view, Fig. 159 an end view of a portion to the right of the line

X, Figs. 160 to 163 different plans of Fig. 158. A, Fig. 158, represents the retort into which the nitre and sulphuric acid are introduced. The evolved gases pass off through B into the bottle marked 1: here a portion condenses, the remainder passing on through C into bottle No. 2, and so on in the direction of the arrows. The gas condensed in the bottles 4 and 5 falls down into the lowest range 1, 2, and 3, fitted with siphon nozzles, through which the condensed liquid flows into the main D, and finally into the receiver marked 6. F F, Figs. 160 and 161, are the handles.

158.



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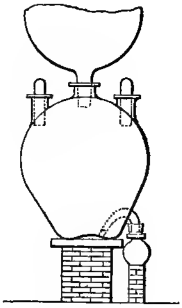

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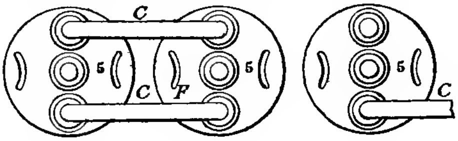
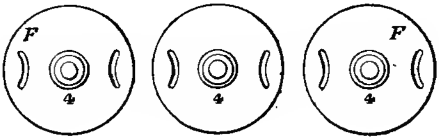
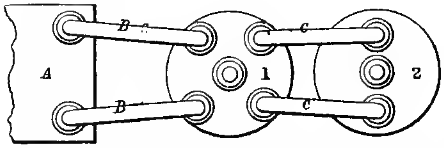




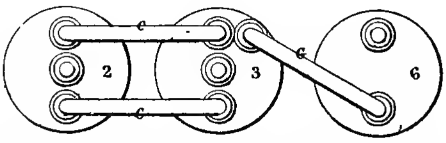
161.

The pipe G takes the vapours that may be evolved in bottle 6 and conveys them back into the condensers to be liquefied. H and I are auxiliary bottles to catch whatever gas may be uncondensed in the main range.

162.



163.



The cost of a ton of good commercial acid is about 23*l*. 10*s*., allowing 25*s*. for the nitre cake which is removed from the retort, broken up, and sold to the manufacturers of sulphate of soda for mixture with the charge of common salt. The operation consumes about 1 ton of coal to a ton of nitric acid, labour figures for 40s. per ton, packages for 25s., and wear and tear for 10s. The selling price varies from 2d. to 3½d. per lb., according to quality. This crude sulphate—"or nitre cake"—is usually of about the following composition:—

Sulphate of soda	75·90
Free sulphuric acid	16·61
Water	6·01
Insoluble	1·29
	100·00

This sample would be esteemed by the alkali manufacturer on account of the large amount of free acid contained.

Anhydrous nitric acid—nitric anhydride—is obtained by decomposing nitrate of silver with chlorine gas. Both should be perfectly dry, and the operation should be slowly performed. The following equation represents the decomposition:—

$$\underset{\text{Nitrate of silver.}}{2\,AgNO_3} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Chloride of silver.}}{2\,AgCl} + \underset{\text{Oxygen.}}{O} + \underset{\text{Nitric anhydride.}}{N_2O_5}$$

The silver salt, in well dried crystals, is placed in a U-tube, which is immersed in a bath of water with a supernatant layer of oil, and heated by means of a spirit lamp placed below. The chlorine gas is admitted from any suitable gas-holder, and dried by being passed through tubes containing chloride of calcium, and pumice-stone moistened with sulphuric acid. With the tube containing the silver salt is connected another tube, immersed in a freezing mixture, at the bottom of which is a small receiver to separate a small quantity of volatile nitrous anhydride which is produced during the operation. When the apparatus is fitted together the nitrate of silver is heated to about 175°, and a stream of chlorine gas passed over it at the rate of about 60 cubic in. in twenty-four hours. After the crystals of nitrate have been thoroughly dried the temperature should be gradually lowered to about 70°. The chlorine then decomposes the salt, freeing nitric acid and oxygen, and forming chloride of silver. The oxygen finally passes off, and the nitric anhydride condenses in the cooled receiver. Some little difficulty in this process arises from the fact that the acid acts upon the caoutchouc joinings. The U-tubes, however, cannot well be in one piece, or absolutely joined together, as is sometimes recommended, by melting the ends, as it is necessary to separate the parts in order to remove the condensed nitrous compound.

A method that has been proposed for the production of the red, fuming, nitric acid is the following:—100 parts of nitrate of potash are roughly ground with 4 parts of starch, the mixture introduced into a retort, and 100 parts of oil of vitriol of 1·85 sp. gr. added. The mouth of the retort leads into a piece of glass tubing three or four feet long, and from thence the products of distillation pass into an ordinary cooled receiver. A very slight degree of heat is sufficient to complete the operation, the proportions named yielding about 60 parts of a deep red, fuming, acid.

The chief impurities in nitric acid are sulphuric and hydrochloric acids, and chloride of iron. Occasionally, too, with a view to increase the strength artificially, nitrate of potash is dissolved in it. The last-named substance can be readily detected by evaporating the acid, when the nitrate, if present, will be left behind. To discover the presence of sulphuric acid, a small quantity of the sample may be evaporated in a platinum dish to about one-eighth its bulk, diluted with water, and a solution of nitrate of barium added. If sulphuric acid be present a white precipitate of sulphate of barium is produced, insoluble in water, acids, and ammonia. Dilution with water is necessary to dissolve any precipitate of nitrate of barium and nitrate of silver which might form and pass for sulphate of barium.

The presence of chlorine, hydrochloric acid, or the chlorides, is detected by diluting the sample with three or four times its bulk of water, and adding a solution of nitrate of silver. The formation of a white curdy precipitate, soluble in excess of ammonia, but reappearing again upon the addition of an excess of acid, shows the presence of one or more of the impurities in question. For laboratory or special purposes a pure acid may be obtained by adding a sufficient amount of nitrate of silver, decanting or filtering the liquid from whatever precipitate may be formed, and distilling it in a glass retort with a glass receiver.

The following constitute tests for nitric acid:—(1) Copper wire or turnings reduce the acid to nitric oxide, which forms bright yellowish-red fumes in the vessel. (2) Sulphuric acid decomposes all nitrates, freeing nitric acid, which may be recognized by a purple discoloration of starch paper moistened with iodide of potassium. (3) Strong sulphuric acid is added to a solution of a nitrate, and the mixture allowed to cool: upon the addition of a solution of ferrous sulphate, or chloride, the iron liquid turns a deep brown from the formation of a compound of nitric oxide and the ferrous salt. (4) A minute quantity of nitric acid added to water coloured by solution of sulphate of indigo, upon boiling bleaches the liquid, by the oxidation of the indigo. (5) Hydrochloric acid added to nitric acid confers upon it the power of dissolving gold leaf.

The ordinary rough estimation of nitric acid is made by the hydrometer. A more exact estimation may be made by careful neutralization with carbonate of barium, filtering, evaporating to dryness, and weighing the dry nitrate of barium produced. The equivalent proportions readily give the original amount of acid. Many other methods are employed, for a detailed description of which the reader is referred to any good work upon chemical analysis. Among the best may be named neutralization and volumetric determination; the oxidation of a ferrous into a ferric salt; the reducing action of mercury or copper at a red heat; conversion into ammonia, &c., &c.

It has already been said that nitric acid forms a series of well-defined salts termed nitrates. These are for the most part crystalline, and soluble in water. They melt readily, and decompose at a high temperature. Heated with combustible substances, a more or less violent deflagration ensues. The nitrates of lime, soda, potash, and ammonia occur largely in nature, and are formed whenever nitrogenized organic matters are acted upon by the air in contact with a base. The more important members of this series of salts are the nitrates just named, together with those of alumina, barium, cobalt, copper, iron, lead, magnesium, mercury, nickel, silver, strontium, tin, and zinc. A detailed description of the nitrates will be given under the heads of their respective bases.

J. L.

OXALIC ACID. (Fr., *Acide oxalique;* Ger., *Sauerkleesäure*). Formula, $C_2H_2O_4$.

Oxalic acid exists in the crystallized form in transparent, quadrangular prisms. The crystals are soluble in nine times their weight of cold water, but require only their own weight of boiling water; they are also soluble in alcohol. In cold sulphuric and hydrochloric acid, they may be dissolved without undergoing decomposition. When heated suddenly to a temperature of 100°, the crystals melt in their own water of crystallization; but if the process be conducted gradually and gently, they fall into an opaque white powder, losing 28·5 per cent. of water. The residue remaining, $C_2H_2O_4$, cannot be deprived of its lost equivalent of water by heating, but it may be replaced by some metallic oxides. If these dried crystals be placed in a retort, and heated by means of an oil bath of 150° to 160°, they slowly sublime unchanged, and may be condensed in the form of white needles. This sublimation commences at about 100°, and if the heat be allowed to exceed 160°, the crystallized acid will be decomposed.

If the crystallized acid be heated quickly, without having previously undergone dessication, it dissolves in its water of crystallization, and at 155° resolves, with apparent ebullition, into a mixture composed of carbonic anhydride, carbonic oxide, formic acid, and water. Thus:—

$$C_2H_2O_4, 2H_2O = CO_2 + 2H_2O + HCHO_2 \text{ (Formic acid)},$$

the carbonic oxide being derived from the formic acid, which yields on decomposition by heat carbonic oxide and water, $HCHO_2$ becoming CO and H_2O. Heated in contact with powdered charcoal, explosion accompanies its decomposition.

Bromine and chlorine decompose this acid, as do also iodic, nitric, phosphoric, and sulphuric acids on the application of heat. When heated with concentrated sulphuric acid (O.V.), or with phosphoric anhydride, it splits up into equal volumes of carbonic oxide and anhydride. Berthelot has proved that oxalic acid may easily be converted into formic acid by dissolving the former in glycerine and heating to about 150°, when formic acid slowly passes over, and carbonic anhydride escapes; but on raising the temperature some 26° carbonic oxide is obtained.

This acid reduces chromic acid, as well as the peroxides of cobalt, lead, manganese, and nickel, with formation of carbonic acid and water. It precipitates metallic gold from an aqueous solution of the chloride, carbonic acid being evolved. The aqueous solution of the acid has an intensely sour taste, and even 1 part in 2000 of water still reddens litmus. If swallowed, it acts as a powerful poison, producing death in a very few hours; but effective antidotes exist in chalk or magnesia suspended in water.

During a series of investigations into the physiological action of light upon minute organisms, Dr. Downes and Mr. Blunt have observed that a decinormal solution of oxalic acid was entirely destroyed when freely exposed to the influences of sunlight for a lengthened time, while a similar solution placed under similar conditions, except that the tube containing it was encased in opaque material, remained altogether unchanged. It was found at the end of two months (when the solution was examined again) that the destruction of the acid had been so complete that it ceased to redden litmus paper, and yielded no precipitate with chloride of lime, while the reaction produced with permanganate of potash was so slight as to be barely recognizable. Mr. D. N. Hartley noticed the same phenomena when using a solution of oxalic acid for the analysis of air by Pettenkofer's method, but it struck him that some solutions were more proof against destruction than others. He believes that the oxalic acid made by oxidizing sugar with nitric acid is more stable in solution than that obtained by recrystallizing the commercial article. Also, the mycelium of a fungus was found by him in every instance where decomposition had taken place in the liquid, and hence he has attributed the change to the action of a fungus. On the other hand, Dr. Downes and Mr. Blunt found no trace of such mycelium in any case, the liquid being always quite clear, and they would not have suspected its development in strong sunlight. Schœsing and Müntz consider the change due to the action of an organized ferment, and Warrington adds that *darkness* is apparently essential to the process, which may be explained probably by the fact that light is inimical to the development of such organisms. In order to preserve the volumetric solution, Mr. Hartley prepares it with water containing from 10 to 25 per cent. of alcohol, which he finds efficacious for four months at least. Oxalic acid is widely diffused in a natural state, and in the vegetable kingdom especially it is more widely distributed than perhaps any other organic acid. Commonly, it is found combined with lime, and in this form it constitutes the chief solid part of many lichens, especially the *Parmelia* and *Variolaria*. In one species of *Parmelia*, gathered on the Persian and Georgian sands after a period of drought, has been found as much as 66 per cent. of oxalate of lime, and towards the end of its growth the cells of the plant contain the excess of this salt, which is there deposited in a crystalline form. It occurs thus in *Ficus Bengalensis*, *Tradescantia discolor*, *Iris florentina*, *Fritillaria Meleagris*, and others. As an oxalate of potash, it is found in *oxalis acetosella* (wood sorrel), from which plant the acid derives its name, and in *Rumex acetosa* (common sorrel), both of which plants have been used in the manufacture of the acid; and also in *oxalis corniculata*, *Rumex acetosella*, *Spinacia oleracea*, *Herba belladonnæ*, and in the various parts of several other plants. *Salsola kali* and *S. soda*, besides several species of *Salicornia*, contain the acid as a salt of soda, while in the pods of the chick pea it exists in an uncombined state.

This acid is also distributed throughout the animal kingdom, being found in the mucous membrane of the impregnated *uterus*, in blood, as a characteristic constituent of the *mulberry calculus*, frequently in urine, and in the mucus of the gall-bladder of man, the ox, the dog, and the pike, as well as in the *liquor allantoïdis* of the cow and in the secretions of the caterpillar. In guano, too, it is found in combination with ammonia.

Even in the mineral kingdom this acid is not unknown; three varieties of oxalate of lime have been named respectively Whewellite, Thierschite, and Conistonite. Thierschite was discovered by Liebig as a grey, warty incrustation on the marble of the Athenian Parthenon, and is considered to have been formed by the action of some plant on the marble. Grey found the conistonite to consist of

Oxalic acid	28·02
Lime	21·05
Magnesia and soda	0·82
Water	49·15
	99·04

Rarely, the acid occurs as a ferrous salt in lignite beds, especially at Koloseruk, in Bohemia, which, analysed by Rammelsberg, shows:—

Oxalic acid	42·40
Protoxide of iron	41·13
Water	16·47
	100·00

Manufacture. 1. *From Plants.*—The extraction of oxalic acid from vegetable growths originated in Germany, and was carried on in Swabia. Only two plants appear to have been used—the wood sorrel, containing, according to Savary, 0·255 per cent. of binoxalate of potash, and the first to be employed, and the common sorrel, yielding by Bannach's analysis 0·764 per cent. of the salt. The large percentage contained in the latter plant led to its being cultivated for the express purpose of producing the binoxalate of potash, the plant being sown in March and reaped in June. The leaves were reduced to a pulpy condition in large mortars made of wood, when it was transferred to other vessels, and there treated with water. Allowed to stand for five or six days, the liquid was removed, and the solid residue was pressed and again treated with water. All the solutions thus obtained were mixed together and run into wooden cisterns for purification, having been carefully filtered from the undissolved mass. A small quantity of pure white clay, added while the liquor was kept constantly stirred, effected its purification and clarification, after the liquid had been allowed to stand for twenty-four hours, that the sediment might completely fall to the bottom. The clear liquid was decanted into copper pans, and then evaporated till a pellicle or thin saline film commenced to appear on the surface, when it was run into coolers made of glazed stoneware, and then permitted to crystallize. A crop of crystals of binoxalate of potash was thus procured, and these were again dissolved and re-crystallized in order to remove all possible traces of colouring matters from the salt.

2. *From Guano.*—Though the extraction of oxalic acid from guano is not now in practical opera-

tion in this country, under certain conditions and in certain localities it may be profitably conducted; and we shall therefore notice the main features of the process.

It is essential to divide guano into two classes in their relation to this manufacture—(1) those in which the products of avine urine are intact and in a perfect state; and (2) those in which chemical changes have produced various substances not originally present in the urine of birds, the latter being by far the more common. The class to which any sample of guano belongs may be easily ascertained by treating it with cold water, when the solution formed will give an acid reaction (like fresh urine) if it be of the former kind, but an alkaline reaction if it be referable to the latter species.

The treatment to which the former kind of guano is subjected is as follows. The mineral must first be reduced to a fine powder, and then be steeped and well washed in cold water, to remove the soluble urine salts, consisting essentially of sulphates and muriates of soda and potash and super-phosphates of calcium. These can be recovered by boiling the solution to dryness, and possess valuable manuring qualities. The insoluble matters remaining after the treatment with cold water must be digested in a strong solution of carbonate of potash or soda, in the cold, in order to remove from the guano all colouring matters that it may contain. The next step is to separate the uric acid from the urate of ammonia and bone earth which form the now remaining residuum. This may be effected in several ways. By treating the compound with dilute sulphuric acid, the uric acid will be liberated, and brought into a condition that will enable it to be acted upon by peroxide of lead, care being taken that the sulphuric acid present shall always be a little in excess of the proportion actually required to neutralize the ammonia. A second, and perhaps better method consists in boiling the compound in a dilute solution of soda or sodic carbonate, whereby a solution of urate of sodium is obtained, about 32 lb. of soda being required for every 168 lb. of uric acid present. This operation entails the evolution of large quantities of ammonia, which may be collected and economized by conducting the process in a still of sufficiently large dimensions to accommodate the frothing of the ammonia. The water used in separating the urate of soda from the residual earthy matters must be as hot as possible, on account of the slight solubility of the salt in cold water, and the residue should be carefully washed free of urate of soda by boiling water. The strong solutions of urate of soda must be again treated with carbonate of soda in the same quantity as before, and then evaporated until a deposit commences to form. Left to cool, it forms a crystalline mass, from which the liquid must be pressed and drained, and the solid residue be washed with cold water. This plan enables a pale, lemon-coloured oxalate of soda to be produced even from dark-coloured guanos of the second species. Occasionally, however, the guano is so deeply coloured that the sodic urate thus obtained does not yield a sufficiently colourless oxalic acid, in which case the salt should be once more boiled in a strong solution of sodic carbonate, thus dissolving the colouring matter, and the little urate taken up by the carbonate need not be lost, as the carbonate used in decolorising one crop may be employed to dissolve the uric acid out of a fresh sample of guano. The urate of soda is now to be added to boiling sulphuric or hydrochloric acid, the acid being in such excess as to ensure the complete separation of the soda, and the ebullition to be continued for 15 to 20 minutes.

The uric acid derived from this process is carefully washed with cold water to remove all adhering acid—a point essential to success—and is then boiled with pure plumbic peroxide. This salt is generally more expensive than the similar salt of manganese, but it works a rapid change on the acid while the effects of peroxide of manganese are very slowly manifested. When plumbic peroxide is used the boiling is conducted as follows. A measured quantity of uric acid is placed in a cylindrical vessel made of iron, open at the top, of such dimensions as to be able to hold two gallons of water for every 1lb. of the acid and adapted to boiling by steam. To this water is added, or a clear saturated solution of lime water, and as soon as this is boiling briskly the dark puce-coloured lead salt is applied in gradual portions as long as the boiling liquor decolorises it, but great care must be exercised that no excess of plumbic peroxide be introduced, and that it be in a state of impalpable powder and absolutely free from acid and chlorine. In the case of pure materials, 240 lb. of the lead salt will be whitened by 168 lb. of the acid, so that when the quantity of lead added approximates to the maximum quantity that can be bleached by the acid, future portions should be inserted with great caution, and any slight excess created must be counteracted by the introduction of just sufficient uric acid to attain that aim. The white powder produced is oxalate of lead.

The liquid is then drawn off for future treatment, and the powder is washed with clean water.

The cleaned powder is now put into a leaden vessel and boiled with hydrochloric acid diluted with its own weight of water; 200 lb. of acid at 1·179 sp. gr. being the correct proportion for every 240 lb. of peroxide of lead that have been converted into oxalate of lead. The liquid will now contain oxalic acid, and should be treated with dilute sulphuric acid, carefully and gradually applied, as long as a precipitate forms. The oxalic acid is obtained as a solid by evaporation and crystallization, while the insoluble precipitate, consisting of chloride of lead, is collected and washed to be reconverted into the peroxide.

The liquid that had been drawn off (in which the uric acid had been boiled with peroxide of lead) contains urea and allantoin. On evaporating this liquid by means of heat until a film commences to form on its surface, and then allowing it to cool, the major portion of the allantoin crystallizes out. What remains is obtained by further evaporation of the mother liquor, which finally forms a thick syrupy liquid, composed of urea. The allantoin is now introduced with any caustic alkali or alkaline earth solution into a vessel where it may be subjected to ebullition, when the allantoin is decomposed in oxalic acid and ammonia, the acid uniting with the alkali while the ammonia passes over and may be recovered. If potash has been the alkali used, the oxalic acid generated may be collected as oxalate of potash; or if a solution of baryta has been employed, oxalic acid may be recovered from the oxalate formed by decomposition with sulphuric acid.

The syrup of urea is useful for the manufacture of ammonia, or of compounds of cyanogen. In the former case it is boiled with milk of lime, when it decomposes into ammonia, which is caught as it passes off, and carbonic acid, which unites with the lime. With the latter object in view, it must be thoroughly desiccated in a water bath, and may then be mixed with coal tar, or the dry urea may be heated up to 120° in a retort. At this heat the urea decomposes into ammonia, which passes into a suitable receptacle, and cyanuric acid, which remains in the retort in a solid state. By adding the latter to fused potassium carbonate charged with carbonaceous matter, it forms potassium cyanide. Success can attend the process only if the precautions indicated be rigidly observed. To ensure the uric acid being free from foreign acid, it may be advisable to decompose the urate of soda by hydrochloric acid, and then to subject the uric acid to a steam heat until it is thoroughly dry.

But oxalic acid also exists in guano, in combination with lime and ammonia. The ammonia oxalate is extracted by the cold water with which the guano is first treated, and may be precipitated from it by any baric or calcic salt. It is, however, considered a better plan to treat the guano with a weak solution of calcium chloride in the cold, by which insoluble calcium oxalate is left with the other insoluble portions of the guano, and on being boiled with a dilute solution of sodium carbonate forms both urate and oxalate of soda. By allowing the whole to cool before drawing off the liquid, the greater portion of the urate of soda will be deposited, after which the solution is evaporated, the urate of soda being first deposited, and afterwards the oxalate also. The oxalate thus produced may be clarified by washing with cold carbonate of soda and allowing it to crystallize, and the pure acid may be extracted from it by precipitating with barium sulphide and using sulphuric acid as a decomposer.

In order to reconvert the sulphate or chloride of lead to peroxide for repeated use in the manufacture, the following method has been proposed. The apparatus required will consist of an ordinary chlorine still attached to a Woulfe's apparatus, composed of at least two vessels, each of sufficient capacity to hold 20 gallons of water for every pound of chloride of lead to be treated, and provided with a rouser, or arrangement for stirring up the mass. Each vessel is charged with a milk of lime carefully prepared in the proportion of 1 of lime to 40 of water, and the chloride of lead to be operated upon in the proportion of 1 of lime to 2 of chloride. The chlorine still is now charged, and the chlorine generated passes into the first Woulfe's vessel, and is quickly absorbed by the milk of lime and chloride of lead, which should be kept from forming a sediment at the bottom of the vessel by means of the stirring arrangement. The chlorine should be generated continuously until it is found to pass through the first vessel without further absorption, which indicates that the process in that vessel is completed. The contents are then removed, and their place is filled with a new charge of lime and chloride, while the chlorine gas is introduced anew, but passed first into the *second* Woulfe's vessel so that they are worked off alternately.

In this way the chloride of lead is converted into peroxide, while the milk of lime becomes a solution of chlorides of lime and chlorine. This bleaching liquor is decanted from the peroxide of lead, and treated with chloride of lead till it loses its smell of chlorine. The peroxide of lead should be repeatedly washed with boiling water till it loses all taste, and should then be boiled in a very dilute sodic solution, and again washed till tasteless, when it is in a fit condition for use, and should be kept under water to preserve its impalpable state.

Another process differs from the one we have described only in using permanganate of potash, red lead, or dilute nitric acid to produce the chemical reactions.

3. *By the Action of Nitric Acid on Vegetable Substances.*—It was proved by Bergmann that oxalic acid might be produced by treating vegetable substances with nitric acid, the best results being obtained from those which contained no nitrogen, e. g. sugar, starch, and woody fibre. Treacle and coarse sugars have been principally used on account of their low market price, about 116 lb. of oxalic acid being obtained from 1 cwt. of the former, and 140 lb. from the same quantity of the latter. The operation may be conducted in lead-lined wooden vessels or in stoneware jars. The latter are made to hold about two gallons; they are ranged in rows in water baths, and are heated by steam. The leaden tanks are generally about 8 ft. square and 3 ft. deep, and are provided with a coil of leaden pipe for conducting the steam through their contents.

Supposing the manufacture to be conducted in lead-lined tanks, the method of procedure is as follows. About 825 lb. of treacle are run into the cistern, and to this 11 lb. of sulphuric acid are first added, in order to separate out the lime contained in the treacle, when the lime (as sulphate) has settled, the purified molasses is transferred to another tank containing by preference about 15,000 lb. of mother liquors from previous operations, and 900 lb. of nitric acid at 1·200 to 1·270 sp. gr. The contents are well stirred together, and the temperature is increased to about 30° (86° F.) by passing steam through the leaden pipe-coil. This is maintained for twenty-four hours, at the expiration of which the mixture is removed to another vessel, and left for a day or so, in order that the remaining impurities may subside. To the clarified liquor is now added 66 lb. of concentrated sulphuric acid, as well as 2200 lb. of nitric acid, the latter in quantities of about 3 cwt. at a time and twelve hours apart. The temperature during the first twelve hours of this stage should be kept at about 38° (100° F.); during the second twelve hours it is increased to 43° (109° F.); during the third twelve hours it should reach 49° (120° F.), and for the remainder of the operation it may vary from 52° (125° F.) to 54° (129° F.).

About twenty-four hours later the mother liquors are decanted and the crystals drained, dissolved in clean water, and recrystallized. It is said that the use of the mother liquors is essential to procure good results.

Care must be taken that the strength of the nitric acid used shall not exceed the limit mentioned above, or the saccharine matter may be converted either into carbonic or formic acid. The proportions of the materials used will vary to some extent, according to the nature of the substances used, but when good molasses is employed the amount of nitric acid produced by the action of 320 lb. of sulphuric acid on 278 lb. of nitrate of soda, should be sufficient for the oxidation of 1 cwt. of the treacle, and should yield 100 lb. of marketable oxalic acid.

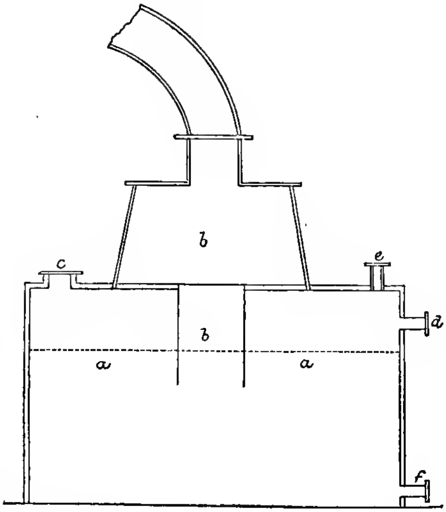
Some careful experiments by L. Thompson yielded 17½ oz. of oxalic acid from 28 oz. of raw sugar but when the mother liquors of previous operations were employed the product was increased to 30 to 32¼ oz. of the crystallized acid, accompanied by 20 to 22¼ oz. of carbonic acid.

The chief fault of this process lies in the waste of the nitrogen compounds which are disengaged by the oxidation of the saccharine matters, and for the prevention of which many plans have been tried with more or less success. From the fact that these compounds are mixed with carbonic acid, which exercises a remarkable influence in counteracting their affinity for oxygen, one of the most obvious uses to which they might be applied, viz. the manufacture of sulphuric acid, is put out of the question.

One plan of indirectly overcoming this obstacle has been undertaken by Firmin, who passes the gases up a column packed with coke, down which sulphuric acid is made to trickle. The nitro-sulphuric acid thus obtained may be injected into the sulphuric acid chambers in the form of spray, and will thus serve the same purpose as nitrate of soda or nitric acid.

Two other plans of economizing these waste gases have originated with the same inventor. In one he employs such an arrangement as is shown in Fig. 164, of which *a a* is the decomposing vessel, made of slate, or of wood lined with thick lead, and provided inside with coils of leaden pipe for conducting the steam necessary to heat the contents; *b b* is a large eductor dipping into the solution, and by means of which the gases are carried away; *c* is the hole for charging the cistern; *d* forms the connection of a pump for forcing in air oxygen or other gases; at *e* communication is made with the nitric acid tank, and *f* is a tap for emptying the decomposer of its contents.

164.



Into the decomposer are introduced 100 lb. of sugar or a proportional weight of starch or treacle, and then 600 lb. of nitric acid of 1·220 sp. gr. are added gradually during a space of twelve to fifteen hours. Steam is turned on to heat the mixture, and when the conversion into oxalic acid is complete, which point may be known by the absence of coloured fumes on the admission of air, the contents are drawn off at the top *f* into water baths for concentration, and thence are carried into suitable coolers for crystallization. Whilst the nitric acid is reacting, air is pumped in through *d*; or the gases having been collected and mixed with air, are pumped in through the saccharine liquid.

In the second process the object aimed at is the production of cyanogen compounds, for which purpose the gases are taken over a mixture of carbonaceous substances, iron and an alkali, heated to a high degree, and are passed thence through water, and after being collected are forced through a pipe connected with the faces of some retorts or tubes arranged in furnaces. Similar retorts to those used in the manufacture of coal gas may be used, but double ones are preferable, that is, two retorts connected so as to form one of about 10 to 12 ft. in length, and fixed in two furnaces; they may be of iron, and several pairs may be placed in the same oven.

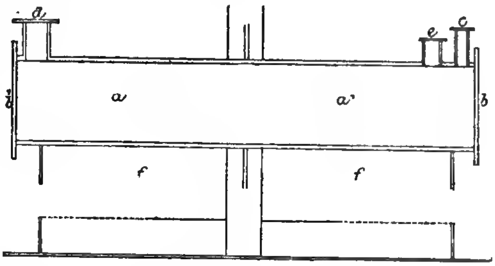
The proportions recommended are :—

Commercial potash	100 parts.
Coal dust, coke, or soot	100 „
Iron filings	30 „

or a strong solution of alkali (preferably potash) may be made, and absorbed by sawdust, and a mixture formed consisting of 30 parts of iron borings or filings and 100 parts of small coal for every 100 parts potash used.

Fig. 165 is a section of one pair of retorts; *a a′* are the retorts furnished with movable plates *b b′* *c* is the cock connecting the pipe through which the gases are forced, *d* is the exit pipe for uncondensable gases, *e* is a safety valve, and *f f* are the furnaces.

165.



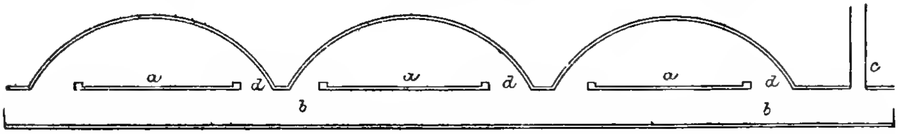
Having heated the retorts, a charge of the mixture is introduced, nearly sufficient to fill one retort, *a′*, and when it has attained a dull red heat the nitrogenous gases are passed over it with occasional stirring for about three or four hours, at the end of which time the plate *b* is removed. The half-finished charge is then forced into *a*, where it is heated to a bright red degree, a new charge is inserted into *a′*, and the same treatment continued. The charges in both retorts must be stirred occasionally, which may be done by means of an iron rake or stirrer introduced through the cover-plates. After three or four hours the plates *b b′* are removed, when the charge in *a* is drawn into a suitable vessel and covered, the charge in *a′* is transferred to *a*, and a new charge introduced. By this arrangement all the gases from the fresh charge, together with the uncombined gases from the pipe *c*, have to pass over the half-finished charge. The charge drawn from *a* having been allowed to cool, is ground and treated in the usual manner for obtaining the cyanides. Of the uncombined gases we shall speak presently.

Instead of the arrangement shown in Fig. 163, a reverberatory furnace may be used, into which is introduced such a charge as that already described, or a mixture of

100 parts	sulphate of potash.
84 „	chalk.
100 „	small coal.
30 „	iron filings or borings.

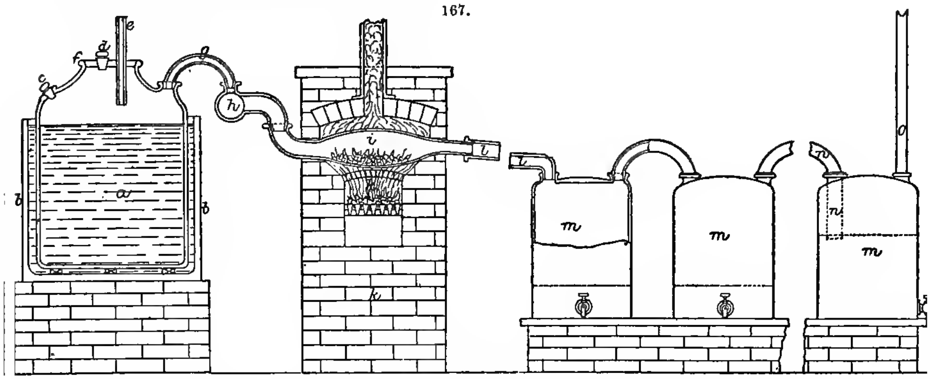
It is preferred to arrange the furnaces so as to compel the nitrogenous gases, together with the uncombined gases from the ordinary combustion of coal, to pass over the charges placed in communication with each other. Fig. 166 is an arrangement which meets this requirement; *a a a* are reverberatory furnaces, *b b* is a main flue from ordinary furnaces, *c* is the pipe through which nitrogenous gases are forced from the gas-holder into the flue; *d d d* are fires in the reverberatory furnaces. The furnaces are so provided with dampers that any one of the series may be stopped without interfering with the working of the others. Into each furnace a charge is introduced, and when it has attained a red heat the gases are passed over it, with occasional stirring, for six or eight hours, when the charge is withdrawn, and treated as before mentioned.

166.



The gases passing off from the retorts or furnaces, together with a jet of steam (if ammonia be required) are forced by means of a pump or fan through a furnace containing spongy platinum, iron, or clay burnt and broken in pieces to render it permeable, or any mixture of these substances, which are heated to about 370° (700° F.), and are conducted thence into a suitable condenser for collecting the cyanides of potash and ammoniacal salts which are formed. These may be separated in the usual manner, or may be applied to the manufacture of artificial manures, thus:—The residue of the ground charges from the retorts or furnaces, after having washed out the cyanides, consists of some cyanide of potash, iron, sulphate of iron, sulphate of lime, carbon and some undecomposed sulphate of potash. This mixture is treated with ammoniacal liquors in such quantities as to present sufficient free ammonia to decompose the sulphate of lime, or it may be mixed with bone dust, superphosphate of lime, or other salts, to form a suitable fertilizer. Fig. 167 shows the arrangement of the apparatus employed by Jullion with the object of recovering and utilizing the liberated nitrogen compounds resulting from the manufacture of oxalic acid by the action of nitric acid on vegetable substances.

167.



In the first place, instead of using the ordinary jars or open vessels for the manufacture of oxalic acid, he places the mother liquid, together with the organic substance to be acted upon, in closed or covered vessels formed of earthenware capable of containing about one hundred gallons each, having the necessary pipes and openings, as shown in the accompanying figure, where *a* is a decomposing vessel (of which there may be several if required), set in a water bath *b*, which is heated by steam or in any other convenient manner. The materials to be operated upon are supplied to the decomposing vessel through the aperture *c*, which is stoppered, and when the materials are decomposed the residuum or products are withdrawn from the vessel through the same aperture by means of a syphon. A small stoppered opening *d* is made in the ground air-tight cover *f* for the purpose of applying a thermometer to ascertain the temperature of the contents of the vessel, and *e* is a pipe for supplying the vessel with atmospheric air or oxygen. The gases evolved from the decomposition of the materials in the vessel *a* pass off through the pipe *g* to the main *h*. The pipe *e* for the supply of atmospheric air or oxygen gas is connected with a gas holder, so that a proper supply of air or gas may always be maintained in the vessel *a*, or it may be drawn in by an exhausting apparatus, arranged suitably for the purpose. The main *h* is connected with a vessel or tube *i*, filled with platinum in the state of sponge, or with asbestos, coated or covered with platinum, and the tube is kept at an elevated temperature by means of the furnace *k*. It is preferred to heat the vessel *i* to from 315° (600° F.) to 482° (900° F.). The apparatus being properly connected and arranged, and a portion of nitric acid having been added, in the usual way for making oxalic acid to the contents of the decomposing vessel *a*, heat is applied to it. As soon as decomposition of the materials commences and the gases or oxides of nitrogen begin to be liberated, there is blown or forced through the pipe *e* into the decomposing vessel, and directly upon the surface of its contents, a regular stream of oxygen gas or atmospheric air, either at common temperatures or in a heated state; by which means the oxides of nitrogen are converted into higher states of oxidation, one portion remaining in the liquor, and another portion, by condensing with aqueous vapour on the cooler parts of the vessel, being returned to the said liquor and there performing the same part as a new addition of nitric acid, and thus diminishing the quantity of nitric acid required to complete the operation; while the remainder of the gases which have escaped condensation pass off in conjunction with the excess of oxygen or atmospheric air through the exit pipe *g* into the main *h*, by which they are conducted into the tube *i*, containing the platinum or platinized asbestos, where a combination takes place with the formation of nitrous and nitric acids. The acids so produced, together with the excess of oxygen or atmospheric air, must be passed through a pipe *l* into a condensing apparatus, which should be formed of a series of vessels *m m*, of a description similar to those used in the ordinary process of manufacturing or distilling nitric acid, in which water or dilute nitric acid should be placed. The delivering or exit pipe *n* from the last of these receivers should be made to dip about an inch or an inch and a half into water or dilute nitric acid in another vessel *m*, so as to place the condensing acids under slight pressure, and the uncondensed vapours may pass off through the exit pipe *o*. Care should be taken in this process that such a quantity of atmospheric air or oxygen gas be supplied to the decomposing vessel, that a portion of oxygen shall still be mingled with the gases that pass off through the water after the conversion of the whole of the oxides of nitrogen into nitrous and nitric acids. In all cases where the oxides of nitrogen are comparatively dry, as in the early part of the process for manufacturing oxalic acid, when the heat employed for the decomposition of the materials is insufficient to raise any great amount of water in the state of vapour, it is recommended that a jet of steam should be passed, along with the mixed gases, through the tube containing the platinum or platinized asbestos, the presence of aqueous vapour greatly assisting the formation of nitric acid.

In the foregoing process for the conversion of the oxides of nitrogen into nitrous and nitric acid, any of the substances known to chemists as catalytic or contact substances may be employed, of which mention has only been made of platinum as a type of the class. Instead of the platinum and tube *i*, a closed vessel containing water may be used, which decomposes hyponitrous and nitrous acids, giving rise to nitric acid. This principle has been applied in the following ways:—The oxides of nitrogen, as evolved from the liquor in the decomposing vessel, as before mentioned, coming in contact with oxygen as already described, are converted into hyponitrous or nitrous acid, which upon being mingled with steam are decomposed into nitric acid and binoxide of nitrogen, or the introduction of steam may be obviated by using heated air or oxygen in the decomposing vessel, by which means moisture will be furnished from the liquor; the amount of evaporation thus caused will also prevent an inconvenient increase in the quantity of mother liquor. The compounds thus formed are then passed into a refrigerating vessel or apparatus, which may be either an earthenware worm surrounded by water, or a series of receivers, such as are ordinarily used for the condensation of nitric acid, and if the atmospheric air or oxygen so supplied has been in slight excess the whole of the gases, or nearly all, will be condensed as a nitric acid. It may be remarked here that by forcing in atmospheric air or oxygen gas at any other part of the apparatus, the same effect in converting the gaseous oxides of nitrogen into hyponitrous, nitrous, and nitric acids may be obtained.

The next step was to render the process continuous instead of intermittent, and this is accomplished by an apparatus of the following nature. The mother liquor is placed in a covered vessel termed a generator, in the top of which is an opening for the insertion of the mother liquor and the withdrawal of the product upon completion of the process, and which may be rendered air-tight by a well-fitting lid. At another opening in the top of the generator a thermometer is fixed, to show the temperature of the contents of the generator during the operation. Two funnel pipes, with elongated stems, pass through the top of the generator, and reaching nearly to its bottom, serve to convey proportionally and by degrees the materials to be decomposed or acted on from feeding vessels which are furnished with stopcocks so as to enable the operator to regulate the supply according to the length of time over which it may be wished to extend the operation. Steam or hot water circulates through a pipe for the purpose of heating the liquor in the generator. There is an opening in the top, to which an eduction pipe is adapted to convey away the gases generated during the operation to a receiver, which pipe dips below the surface of the fluid in the receiver, and the receiver is filled up to an overflow pipe at the commencement, while any excess escapes into a reservoir, and so maintains the same amount of pressure throughout the process. A pipe attached to a chlorine generator admits a current of chlorine gas, which pipe also dips below the surface of the fluid. Connecting arms convey the gases or vapours to a series of condensers, and overflow pipes convey away the condensed fluid from the condensers through a pipe with the necessary openings to allow the overflow pipes to descend to the bottom of the main; there is a waste pipe or cock situated 2 in. from the bottom of the main, which discharges its contents into a collecting pan. A pipe passes from the last condenser into the exterior atmosphere, to carry off the waste gases. The whole of the above-described apparatus having been properly arranged and a quantity of mother liquor placed in the generator, and nitric acid and syrup in the usual proportion to such quantity of mother liquor placed separately in the feeding vessels, heat is to be applied, and the temperature of the liquor raised as quickly as possible to 82° (180° F.) to 91° (200° F.). Streams of nitric acid and syrup are then caused to flow by turning the stopcocks through the funnel pipes into the liquor in such quantity that the delivery of the whole shall occupy about eighteen hours, at the expiration of which time the process will be completed. The gas or gases arising from the decomposition of the materials so supplied will pass off through the eduction pipe into the receiver, where a stream of chlorine is to be introduced from the chlorine generator through the pipe, sufficient to convert the whole of the oxides of nitrogen into nitric acid. A portion of the water in the receiver will be decomposed, its hydrogen combining with the oxide of nitrogen to form nitric acid, while its hydrogen will combine with the chlorine to form hydrochloric acid; these mixed vapours passing onward into the condensing vessels will there be condensed. The whole of the nitric acid and syrup having been run in, and the liberation of the gases or oxides of nitrogen having ceased, the liquor is drawn off from the generator by means of a syphon, and placed in a convenient vessel to crystallize. Although we have described in the above process the application of a temperature of from 82° to 91° as being that which is preferred, still if it be thought desirable the liquor may be heated even to the point of ebullition without detriment to the success of the process.

As regards the second part of the invention, which relates to the manufacture of salts, it consists, first, in manufacturing nitrates by means of the oxides of nitrogen and oxygen gas, or atmospheric air, in conjunction with basic substances, the oxides of nitrogen, however procured, being mixed with atmospheric air or oxygen gas, and made to pass through a chamber or other apparatus containing a metal or metallic oxide, or any alkali or alkaline earth, the presence of which basic substances induces a simultaneous combination of the oxide with oxygen, and the base thus employed forms a nitrate; for example, lime in the state of quicklime, hydrate, or carbonate is placed in a chamber on trays, or in an apparatus similar to the "dry lime purifier" used in gasworks (or a series of them), and a current of the mixed gases passed slowly through them; and when the gas that is given off from the last vessel is found to contain nitrous acid, the contents, which will be nitrate of lime, should be withdrawn and the vessel replenished. We would here remark that care should be taken to ensure the presence of a sufficient quantity of atmospheric air or oxygen in the vessels, so as to cause the entire conversion of the oxides of nitrogen to the highest degree of oxygenation, and their consequent combination with the basic substance as nitrate. The following mode of ascertaining this has been found sufficient for the purpose, namely, the absence of any of the oxides of nitrogen, together with the presence of free oxygen in the gas that issues from the last vessel, shows that sufficient oxygen has been furnished; on the contrary, should red fumes make their appearance upon allowing a portion of the gases to escape into the atmosphere, and which gases were previously colourless, it is a proof that there has been a deficiency of oxygen, and consequently more atmospheric air or oxygen gas must be passed into the apparatus. When a metal is employed, in the place of lime as above-mentioned, it is preferable to reduce it previously to small particles by granulation, or otherwise, so as to expose a larger surface to the action of the mixed gases.

Among other plans proposed we may mention Ecarnot's, in which the gases are mixed with steam and with air from a blast, and the whole then passed over the surface of pumice stone. M'Dougall & Rawson have patented the method of withdrawing the waste gases by an air pump through a series of Woulfe's jars filled with water, and into which air is admitted, while Dale employs the liberated nitrogen vapours for the peroxidation of the protosalts of tin.

4. *Manufacture with Alkalies.*—So long ago as 1829, it was found by Liebig that a certain quantity of oxalic acid might be formed by heating neutral organic materials, such as woody fibre, starch, &c., with soda or potash in excess, and about thirty years elapsed before this discovery was applied practically to the manufacture of the acid.

M. Possoz, who was one of the first to take the matter up, made a series of experiments with various substances to test their relative yield of the acid, the result of which, as published by him, was substantially as follows. By the action of 300 parts of caustic potash on 100 parts of

		Crystallized Oxalic Acid.	
Borage	he obtained	112	parts
Clover	,,	110	,,
Hay	,,	140	,,
Horn	,,	20	,,
Lucerne	,,	110	,,
Leather	,,	6	,,
Mugwort	,,	115	,,
Nettles	,,	100	,,
Potato starch	,,	125	,,
Pure woollen rags	,,	10	,,
Pure silk rags	,,	12	,,
Sawdust	,,	70	,,
Tansy	,,	130	,,
Tobacco stems	,,	150	,,
Wheat straw	,,	100	,,
Wheaten bran	,,	150	,,
Wild chicory	,,	120	,,

When using starch, the experiment was conducted as follows. The caustic ley was concentrated up to a boiling point of 437° F., and then cooled down to 356° F., upon which the starch was gradually introduced in small quantities, the compound being maintained for about four hours at a temperature varying between 392° and 437° F. When the mixture had become white it was heated with water.

When employing other materials, the experimenter found it better to mix them with a caustic ley of 1·500 sp. gr., and then to evaporate. The woody fibre is thus dissolved; and should the compound retain a brown colour after becoming thick, it will be found that it contains a quantity of ulmic acid, but neither oxalic, acetic, nor carbonic acids. But by heating the mass to between 200° (392° F.) and 225° (437° F.), and maintaining it at that point for some four or five hours, the colour will change to yellow, and ultimately nearly to white, and the three acids named will replace the ulmic acid. The process may be finished more rapidly by increasing the temperature, but it will have the effect of reducing the production of oxalic acid.

When the potash is replaced by caustic soda a different series of reaction ensues. First, the woody fibre is dissolved and ulmic acid is formed as in the case of potash, but when the heat is augmented and maintained the acetic, formic and oxalic acids apparently decompose one another as they form, and hence it is impossible to obtain 10 per cent of the yield rendered by potash even under the most favourable conditions; and from such substances as leather, wool, and silk absolutely no oxalic acid can be derived. There is no difficulty in observing the presence of these three acids throughout the whole process, but at whatever point the operation may be checked, or however much caustic soda be used, the yield of oxalic acid is very small. It would seem as if the production of oxalic acid by the agency of soda is only momentary, probably due to the fact that the latter is much less readily melted than potash and acts more energetically. When, however, the two alkalies are mixed together in such proportions as to have the same melting point, the product of oxalic acid equals and even excels that yielded by potash alone. The action of the potash appears to be increased by the addition of a certain amount of sodium hydrate, causing a larger quantity of organic matter to be decomposed, and giving a higher produce of oxalic acid with the same weight of alkali.

The results of Possoz's experiments upon the best proportions of the alkalies may be summed up thus:—By the addition of 1 part of hydrate of soda to 3 parts of hydrate of potash, ten per cent. more starch is decomposed than when potash alone is employed, and the yield of oxalic acid is augmented in direct proportion to the amount of starch used; 1 part of soda hydrate to 2 parts of potash hydrate decomposes $\frac{1}{8}$ more starch with proportionally increased yield; the two alkalies mixed in equal proportions behave similarly to the potash hydrate alone; 2 parts of the hydrate of soda to 1 of the potash, give 10 per cent. less yield than the potash alone; while 3 parts of the soda hydrate to 1 of the potash produce 20 per cent. less oxalic acid. It is evident therefore that hydrate of soda cannot be made to replace potash, but that when mixed with the latter in certain proportions it has a decidedly beneficial influence upon the manufacture.

We believe that Messrs. Roberts, Dale & Co., who are, perhaps, the largest manufacturers of the acid in this country, adopt the following plan:—2 equivalents of potash are mixed with 3 equivalents of soda and after the alkalies have been partially causticized, the ley is concentrated up to about 1·350 sp. gr. Then 30 to 40 parts of sawdust are added for every 100 parts of real alkali in the concentrated ley. The sawdust is spread evenly and carefully over iron plates by means of an iron rake, and the ley is gradually and completely incorporated with it. When the mixing is completed the temperature is raised by means of heated flues beneath the plates, and the heating is maintained for 4 to 6 hours. The first effect of the heat is to evaporate the water contained in the mixture, and when all the moisture has been driven off, the heat is continued with constant stirring of the mass till it reaches 177° (350° F.) to 205° (400° F.), at which point it must be carefully kept while the compound is regularly agitated until the sawdust has disappeared.

The crude mass is now composed of a mixture of oxalate of soda with carbonated and caustic alkali. Owing to the slight solubility of the oxalate of soda, and the very minute state of division in which this salt exists when obtained by the usual process of concentration, the ordinary plan of separating two soluble salts by dissolving and crystallizing them is inapplicable to this compound.

When quite cold, therefore, the mixture is placed in a row of tanks such as are used in soda manufacture and submitted to the action of cold or warm water, so that the partially saturated solution from the first tank flows into the second, or that containing a salt more recently subjected to the washing process, and so on as in the manufacture of alkali. Cold water is run over the oxalate until the liquor flowing from the vessel has a sp. gr. of 1·030, when the oxalate of soda will be left in the tank in an almost pure condition. In this simple manner the potash and other foreign substances are dissolved away from the soda oxalate, and by evaporating the water from the washings the potash may be recovered from them for re-use. The oxalate of soda obtained may be employed to produce either oxalic acid or binoxalate of soda.

Possoz prefers to prepare his caustic ley by reducing alkaline sulphate to sulphide by the agency of some form of carbon, treating the solution of sulphide with black oxide of copper and concentrating the caustic alkaline liquor up to strength. The sulphide of copper produced is roasted to reform black oxide, ready for further use. When it is intended to employ the same caustic alkali repeatedly, and to avoid the formation of acetates, carbonates, formates and ulmates, it is recommended to make the caustic potash in lixivium and to concentrate it until its boiling point is about 193° (380° F.), and whilst keeping it at a temperature between 160° (320° F.) and 205° (400° F.) to add for every 100 parts genuine caustic potash, 100 parts of bran or other organic matter, mixed with 500 parts of manganate of potash which has been previously produced by melting 250 parts of genuine caustic potash with 250 parts peroxide of manganese. After the mixture is made it should be heated and stirred until the mass becomes a thick paste, easily detaching itself from the implement, care being taken that the temperature does not rise beyond 260° (500° F.).

It appears to be an advantageous plan, however, to operate each time with new alkali instead of repeatedly using the same. In this case 250 to 300 parts of genuine caustic potash, concentrated to a boiling point, of about 205° (400° F.), or into 400 to 500 parts of genuine caustic soda, concentrated to about 149° (300° F.) boiling point are introduced 100 parts of organic matter—bran, ley, straw, guano, dried meat, blood—the whole mass being subjected to a gentle heat. When it is intended to collect and recover the ammonia which is liberated, the process is best conducted in a distilling apparatus provided with an agitator and the ammoniacal vapours may be condensed in pure or acidulated water. When nearly all the ammonia has been disengaged the mass may be heated in an oven by a current of warm air, or by other suitable apparatus, great care being observed in the regulation of the heat. It has been noticed that less heat is required with pure soda than with potash, and that the heat must be well distributed among the whole mass. The best heat for soda is from 149° (300° F.) to 205° (400° F.), and for potash from 205° (400° F.) to 260° (500° F.). The heating of the mass is continued and the stirring repeated until it becomes a paste or even dry, according to the substances used.

When this point has been reached by either of the two processes the mass must be dissolved in warm water in order to obtain saturated solutions, and then left to cool and crystallize. The mother liquors are concentrated to 1·560 sp. gr. for potash, and to 1·320 sp. gr. for soda. The potash or soda oxalates, when crystallized and separated from the mother liquors, are converted either into oxalic acid, or acid oxalates, by any well-known process. The solutions of the potash and soda oxalates are heated with milk of lime, either in the cold or under the influence of heat, by which an insoluble oxalate of lime is produced, and the alkali is recovered as caustic ley for further use; while the oxalate of lime is decanted, thoroughly washed, and afterwards decomposed by sulphuric acid to eliminate the oxalic acid.

The alkaline mother liquors obtained by the second process are composed chiefly of acetates, carbonates, ulmates, and caustic alkali. When potash has been employed they are suitable for manufacturing prussiate of potash, with animal matters. If soda has been used, a certain quantity of soda acetate may be separated by crystallization, and what remains may be converted into carbonate of soda by calcination, and the ordinary treatment.

Thorn, in a foreign scientific journal, has published the results of an extensive series of experiments on the production of oxalic acid from bran, lignose, and sawdust, from which we gather the following:—

The mixtures were prepared in a round iron saucer, 2 in. deep, 5¼ in. in diameter, at the top, and 4 in. in diameter at the bottom. Into the boiling ley at 55° to 75° Tw. the sawdust is introduced, and the whole is heated over an open fire, with continual stirring. If the ley be concentrated to about 80° Tw., it is absorbed by the sawdust and the laborious agitation of the mass is dispensed with. In the course of his experiments the author noticed that the yield differed according to the thickness of the layer of materials acted upon. In consequence another series of experiments was made, in which the compound was heated in flat shallow sheet iron dishes in layers of about 0·4 in. to 0·6 in. The sawdust used was from pine wood, and contained moisture about 15 per cent. Soda alone was tried in the proportion of 2 to 4 parts of soda-hydrate to 1 part of wood. The results obtained from 50 grains of sawdust, heated with 100 parts of soda, at 200° (392° F.), 36 per cent. of oxalic acid in the wood; at 240° (464° F.), 32·2 per cent. only. But when heated in thin strata, at 200°, 34·68 per cent.; and at 240°, but 31·6 per cent. When 25 parts of sawdust were employed with 100 parts of soda, at 240°, 42·3 per cent., and in thin layers at the same temperature, 52·14 per cent. If the heat employed be higher than 200°, great care must be exercised over the process, as with a sudden rise in the temperature there is danger that the oxalic acid already formed may suffer decomposition.

According to general experience, a mixture of potash and soda gives better results than those yielded by potash alone, but as regards the proportions there is much diversity of opinion. Fleck says that at Messrs. Roberts, Dale & Co.'s works at Warrington, 1½ parts of hydrate of potash are used, with one part of soda hydrate. Another authority puts the proportions at 1 equivalent of potash to 2 of soda, which would agree approximately with 1 part of potash hydrate, with 1½ parts of soda hydrate. In Kuhnheim's establishment at Berlin, the two alkalies are employed in equal proportions.

With a mixture of 20 parts of potash with 80 parts of soda, a violent decomposition takes place, even with a temperature not exceeding 180° (356° F.). Heat was applied for 45 to 60 minutes.

Ratio of Potash to Soda.	Temperature, Degrees F.	Percentage of Oxalic Acid in Wood used.	Ratio of Potash to Soda.	Temperature, Degrees F.	Percentage of Oxalic Acid in Wood used.
20 : 80	374	19·78	50 : 50	392	25·76
„	392	21·5	„	464–473	39·04
„	464	30·04	60 : 40	392	30·57
30 : 70	374	21·38	„	464–473	42·67
„	464	38·89	80 : 20	392–428	45·59
40 : 60	374	14·00	„	464	61·32
„	392	30·35	90 : 10	464	64·24
„	464–473	43·70	100 : 0	464–473	65·51

These results then tend to prove that potash alone is better than any commixture with soda. A considerable difference was perceptible, according to whether it was heated in thick or thin layers. Again, sawdust was added to boiling ley at 80° Tw., in the proportions of 50 parts of wood to 100 of potash. All the ley was absorbed, and the mass heated on iron plates in a stratum of about 0·4 in. The heat was maintained for 1 to 1½ hours, during which the compound was frequently agitated. The results then were:—

Ratio of Potash to Soda.	Temperature, Degrees F.	Percentage of Oxalic Acid.	Ratio of Potash to Soda.	Temperature, Degrees F.	Percentage of Oxalic Acid.
0 : 100	392–428	33·14	40 : 60	464–482	80·57
10 : 90	446	58·36	60 : 40	„	80·08
20 : 80	464–482	74·76	80 : 20	473	81·24
30 : 70	„	76·77	100 : 0	464–182	81·23

When heated in thin strata, and if care be taken to prevent fusion, it is found that a mixture composed of 40 to 60, or 1 equivalent of potash to 2 of soda, is as good, practically, as potash alone.

Next, the experiment was made of passing currents of hot air over the mass, but the product was not sensibly augmented thereby. Neither was the addition of manganese found to be beneficial. Special tests proved the superior yield of soft wood over hard species. Further, an increase of the proportion of sawdust in relation to the alkali was also attempted, but there appeared to be serious practical difficulties in the way of heating the mass, and of ultimately extracting the acid from it.

After being heated, the compound is boiled in water till almost completely dissolved, and the mixed decoctions are concentrated to about 70° Tw., when the soda oxalate crystallizes out. Either filter presses or centrifugals may be used to free the crystals from the mother liquor, which may be got quite free from oxalic acid, if the fused mass has been properly boiled. The oxalate of soda thus obtained may be transformed into oxalate of lime by dissolving it in boiling water and adding milk of lime gradually, so that the latter may be slightly in excess. If the liquid be not somewhat diluted the decomposition will be slow. If a filtered sample, made acid by the addition of a little acetic acid, gives a precipitate with chloride of lime, a little more milk of lime must still be added. As soon as the decomposition is fully accomplished, the caustic ley is decanted, and the deposit is repeatedly boiled in water and filtered. A large excess of sulphuric acid is needed in the decomposition of the lime oxalate, even 3 equivalents of acid to one equivalent of the oxalate. The oxalate of lime is reduced to the consistency of thin paste by the addition of water, and then the requisite quantity of sulphuric acid at 25° to 35° Tw. is poured in, while the liquid is kept constantly in commotion. More water is then added, and the whole subjected to gentle heat for one or two hours, without relaxing the stirring. When the decomposition is finished the liquid is strained off, and the deposit of sulphate of lime frequently turned over and washed. The filtered liquid contains oxalic and sulphuric acids, and sulphate of lime. When concentrated to about 25° Tw., the latter crystallizes out when the clear liquid is drawn off, and further concentrated to about 55° Tw. When cool the oxalic acid separates itself from the mass in long crystals, which are further purified by re-crystallization. After the waste alkaline leys have been concentrated to about 75° Tw., they are mixed with sufficient sawdust to absorb them, and are calcined in thin strata on iron plates, or in a reverberatory furnace, but a portion taken out and washed with warm water shows but very little colour. The dark grey calcined mass is lixiviated with the weak ley produced when the soda oxalate is decomposed with lime. The lixivium obtained is causticized with lime, concentrated to about 80° Tw. by evaporation, and is then again ready for use.

In 1872, Dale patented a process for using woody fibre, from which nearly all the impure matters had previously been removed, leaving only the pure cellulose, instead of employing the uncleaned fibre as is commonly done, and he claims to obtain very great advantage by this plan. The method of obtaining the pure woody fibre, or cellulose, with the view of subsequently using them in the manufacture of soda and potash oxalates, that receives most favour with the patentee, consists in submitting the sawdust to the influence of an aqueous solution of caustic alkali at a high temperature, either in the open air or under pressure. By this means the impurities are removed from the sawdust, and a product is obtained, which yields, on treatment with a mixed solution of caustic soda and caustic potash, in the proportions of about two parts of the former to one of the latter, a crude soda oxalate containing a much greater percentage of oxalic acid than that prepared by the ordinary methods in use. If it be desirable to produce potash oxalate, then caustic potash alone must be used instead of the mixture of the two caustic alkalies.

It is hardly necessary to repeat that when oxalic acid is manufactured by the action of caustic alkalies on woody fibre, the renewed alkalies need to be subjected to a high temperature in a furnace, in order to render them again fit for use. The patentee finds, that before burning these recovered alkalies they are eminently suited for treating the sawdust as described above, and thus a special advantage is derived from the use of these recovered alkalies before they are calcined.

5. *From Madder.*—A natural consequence of the conversion of madder into garancine, is that the oxalate of lime present in the madder is decomposed by the sulphuric acid. The thus liberated oxalic acid is commonly lost in the wash liquors; but Pernod conducts these waters into suitably constructed tanks, where they are saturated with lime hydrate, which causes the formation of a large precipitate of oxalate of lime. This salt is collected and decomposed by the aid of sulphuric acid added carefully, and in quantity just sufficient for the perfect combination of the mineral acid with the lime. The sulphate of lime deposit is separated by filtration through flannel, and the solution of oxalic acid is evaporated in leaden pans, re-crystallized, and is then fit for the market. The quantity of acid thus obtained will vary somewhat, in accordance with the quality and kind of madder employed, and it is also worthy of remark, that the Avignon madder used by Pernod, naturally contains a large proportion of lime, a base which greatly influences the formation of acids—and especially oxalic acid—in plants generally.

6. *Other Sources.*—Many other methods of preparing oxalic acid on an industrial scale have been proposed and patented, but, owing to the cheapness of sugar, and the excellence of the new method introduced by Messrs. Roberts, Dale, and Company, it is not probable that they will ever become of commercial value. Of these, the best is, perhaps, a method patented some years ago by Jullion, of converting formic acid into oxalic acid. It has also been ascertained that when a mixture of sesquichloride of carbon and pulverized hydrate of potash—8 equivalents of the former to 1 of the latter—is heated for some days in an oil-bath of 210° (410° F.), the result is a mixture of oxalate and chloride of potassium. And also that when 1 equivalent of protochloride of carbon is heated for some time to 200° (392° F.) with at least 6 equivalents of pulverized hydrate of potash, oxalate of potash is again formed, with evolutions of hydrogen gas.

Recovery of the Acid.—When cloth that is partially impregnated with oxalic acid (or tartaric acid) is passed through the discharge vat, containing chloride of lime, with a greater or smaller excess of lime, decomposition ensues and the acids are converted into their calcium salts, and these being insoluble settle with the excess of undissolved lime at the bottom of the vat. If the slimy deposit so obtained be allowed to remain for some weeks in the working vat and be frequently stirred, it will become continually richer in the salts, and poorer in free lime, till it attains even such a percentage of the former as 65·5 per cent. of tartrate of lime and 18 per cent. of oxalate.

From this mixture the acids may be liberated by washing it, and partially diluting it with water, and then adding a previously determined quantity of sulphuric acid of 1·568 sp. gr., and after stirring and boiling, with as much more water as is equal to the weight of the original deposit, the liquid is separated from the sulphate of lime by means of a centrifugal machine. Any excess of sulphuric acid contained in the liquid is removed by boiling with barium tartrate.

This plan affords still better results when chloride of soda—*Eau de Labarraque*—is employed in the discharging vat in place of the chloride of lime. As the tartrate and oxalate remain insoluble it is only necessary that a quantity of chloride of lime solution be added from time to time, sufficient to precipitate all the tartaric and oxalic acids as lime salts, and to restore the original working strength of the vat liquor. In this case the precipitate will contain neither hydrate nor carbonate of calcium and hence a great saving will be effected in the consumption of sulphuric acid. Also another advantage is found to follow the use of the soda solution, which is that the whites are whiter and the reds are less injured than when the chloride of calcium is employed.

In 1873 Messrs. Dale, of Manchester, procured a patent for concentrating or evaporating the acid *in vacuo*. As we have seen, in the process of the manufacture, it is necessary that a mixture of sulphuric and oxalic acids shall be concentrated together, in order that it may reach a strength at which the latter acid will crystallize out of the solution; and it is of great importance that the concentration be conducted at the lowest possible temperature, in order to provide against decomposition setting in, and the loss ensuing in consequence. The operation is therefore conducted in suitable leaden vessels, preferably by means of steam, which may be conducted into the vessels by means of a series of pipes in connection with the steam chest of a boiler, while above the vessels are placed vacuum pumps, or other suitable apparatus for rapidly removing the steam produced in the vessels by the evaporation. The patent refers equally to the concentration of other solutions, but is found to be especially applicable to oxalic acid.

A simple method of obtaining dehydrated acid, HO, C_2O_3, from the ordinary crystallized acid, consists in drying the latter acid at a temperature not under 100° and not above 120°.

Reichhardt dissolves the ordinary oxalic acid in concentrated sulphuric acid, from which solution the monohydrated acid crystallizes out in course of time. The first crystals that form are of the ordinary trihydrate, then a bihydrate separates and, after a week, small rhombic octahedral crystals of C_2O_3, HO deposit. They quickly attract moisture, and must be isolated and dried with great care.

The process given by some authors for the preparation of pure oxalic acid is inaccurate. It is recommended to purify by repeated crystallization, replacing the mother liquors by distilled water, and the last crystallization will, it is said, be the most pure. In reality, however, the contrary is the case, however little alkali the acid may contain, the successive crystallizations become richer and richer in it, which may readily be understood when the less solubility of the acid oxalates is considered. Maumené dissolved a kilogramme of oxalic acid in three litres of hot distilled water. The filtered solution deposited an abundance of very white crystals. 63 grammes of these were then dissolved in a litre of water to make a standard solution of the acid. The weather was very cold and next day crystals were found to be deposited. On calcination, 3·74 grm. of these dried crystals gave a residue of 0·64 $KOCO_2$, corresponding to nearly $\frac{1}{16}$ of their weight of quadroxalate of potash, while 4·95 grm. of crystals obtained from the mother liquor of the latter, yielded 0·047 $KOCO_2$, equivalent to $\frac{1}{105}$ of the total weight, or 1 KO to 88 C_2O_3. Thus, it is evident that the first crystals are richest in alkali; and successive crystallization from pure water does not affect the purification of the acids.

Next, M. Maumené examined the yellow mother liquor from the first crystal. This, in evaporation, yielded a crop of beautiful crystals, of which 5·81 grms. gave on calcination only 0·010 of sulphate of lime, mixed with a little iron, and the residue exhibited no reaction on reddened litmus. By a crystallization from distilled water, this purification was almost complete, 2·156 of well dried crystals giving only 0·002 of non-alkaline residue.

The way to obtain pure oxalic acid then, is to dissolve the ordinary acid in sufficient water to give 10 or 20 per cent. of crystals according to the impurity of the sample. The first crystals are rejected, and the mother liquor is evaporated to furnish a fresh crop, which after two or three crystallizations will be found to be quite free from alkaline oxalate. How found similar results, when following Mohr's method, in which the directions are to leave a large quantity of the acid undissolved by lukewarm water—the author evidently being aware of the difficulties threatened —and relying upon the acid oxalates being left undissolved. How thinks that he may have dissolved these up by using water in too great quantity or of too high temperature, but despairing of the whole process, he dissolved all the crops of crystals together in nearly boiling water, with the addition of enough nitric acid to make the liquid thoroughly acid. The crystals deposited in cooling were in thick prisms, and when washed and pressed they left a very small residue. After two crystallizations of these, a crop of crystals was obtained, which when dry left only ·016 per cent. of a reddish coloured, slightly alkaline residuum, and the mother liquor of the crop preceding these gave, on evaporation, crystals approaching ·0159 per cent. of a similar residue, while from the mother liquor of both these crops evaporated together, crystals were obtained of such purity that the residue from about 30 grains could not be weighed. As M. Maumené's purest crystals contained 0·09 per cent. of residuum, it is evidently an excellent plan to render the original water strongly acid when purifying oxalic acid.

Oxalic acid forms a large number of salts, of which the following only possess any commercial importance:—

The acid, or bin-oxalate of potash, originally procured, as already described, from the wood sorrel (*oxalis acetosella*). The manufacture from this source still holds its ground in some parts of Germany and Switzerland. It crystallizes in oblique rhombic prisms, and dissolves in 14 times its amount of boiling water.

The quadroxalate is made in a similar manner to the binoxalate, but three equivalents of oxalic acid are added to the neutral compound. It crystallizes in colourless transparent prisms.

The neutral ammonia oxalate is prepared by neutralizing oxalic acid with carbonate of ammonia and crystallizing. It is used in the laboratory for the detection and determination of lime.

Oxalic acid is consumed chiefly by dyers and printers as a discharger in certain kinds of calico printing, as well as in woollen dyeing and printing, and in silk dyeing. Its cleansing properties are very great, and though it can scarcely be called a staple article of manufacture, it is undoubtedly of no small importance. For whitening leather and cleaning boot-tops it is invaluable, as well as in the bleaching of straw used in the making of bonnets, and for removing ink stains and iron moulds from linen. In cleaning copper utensils, and in many other ways, it may be used with great advantage over the more commonly employed mineral acids.

The largest manufacturers of acetic acid in this country produce about 20 tons weekly. The price has been reduced in a few years from 16*d.* to 5*d.* per lb.

A. L.

TARTARIC ACID. (FR., *acide tartarique;* GER., *weinsaüre*). Formula, $C_4H_6O_6$.

Tartaric acid is another of the organic acids that occurs frequently in a natural state, especially in the vegetable kingdom, not having been detected, we believe, in either the animal or mineral kingdoms. In a free state it occurs in the grape, pine-apple, tamarind, &c., with other acids in the mulberry, in sumach berries, in the needles of pine-trees, in sorrels and other sour-leaved plants, and in the roots of wheat, dandelion, and couch grass, as well as in the potato and so-called Iceland moss. In combination with lime, it has been met with in madder root, squills, and quassia-wood.

Commercially, it seems to be derived solely from grapes, at different stages in the manufacture of wines. The following table shows the percentage, by weight, of this acid in the various wines mentioned:—

Benicarlo	·0545	Langlade	·0510
Bergerac, White	·0448	Madeira	·0102
Bordeaux, ordinary	·0390	Muscat Rivesaltes	·0357
Bordeaux, Sauterne	·0207	Narbonne	·0606
Burgundy, Beaune	·0477	Port Wine	·0283
Burgundy, Pommard	·0525	Rhine Wine	·0480
Champagne	·0408	Roussillon	·0545
Cotes, White	·0390	St. George	·0414
Hermitage	·0364	Tavella	·0699
Lachryma Christi	·0336	Teneriffe	·0351

But if these estimations be made by means of soda, some deduction must be allowed for the tannic acid, which, in the red wines more particularly, would tend to increase the percentage. Much the larger proportion of the acid occurs, however, combined with various bases, chiefly potash, and these tartrates of potash, obtained principally during the fermentation of the wine, are the most valuable of the salts present. Being but slightly soluble in a mixture of water and alcohol they are deposited in accordance with the generation of the alcohol, both in casks and in bottles, in the former case being known as *argol* and in the latter as *crust.* The deposit occurs as a hard crystalline crust, varying in quantity with the character of the grape, its degree of ripeness and the peculiarity of the treatment it has undergone for the production of wine. A ton of grapes will yield about 1 to 2 lb. of this deposit, which varies greatly in composition. Scheurer-Kestner's analyses of argols from Alsace, Burgundy, Hungary, Spain, Switzerland and Tuscany, show that the white contain from 67·30 (Hungary) to 88·50 (Tuscany) of bitartrate of potash, and from 4·6 (Alsace) to 18·3 (Switzerland) of tartrate of lime; while the red yield from 24·20 (Spain) to 32·10 (Burgundy) of the former, and from 45·20 (Spain) to 46·25 (Burgundy) of the latter product.

The best argols come from Bordeaux, Marseilles, Montpelier, and Italy, but in quantities that do not equal the demand, and much of the tartar imported contains the tartrates of potash in minute crystalline powder, and often the biracemate replaces the bitartrate of potash, and the generally uncertain character and composition of crude tartars render tartaric acid making far less simple than it looks.

The ordinary process of manufacture adopted in this country is as follows:—A large wooden vat of some 3000 to 4000 gallons capacity, called a generator, is provided with a series of revolving horizontal stirrers. This is about half filled with water, to which 40 cwt. of crude tartars are added; then whiting or powdered chalk is carefully and gradually introduced to neutralize one equivalent of the tartaric acid of the bitartrate of potash, known by its creating no further effervescence. It may be useful to state that 100 parts of pure bitartrate of potash require rather less than 24 parts of dry chalk. During the operation steam is forced into the vessel so as to maintain a temperature of 100°, and the stirrers are kept in constant motion to prevent the tartrate of lime from settling as a hard, dense mass. The solution will contain neutral tartrate of potash, which is decomposed by the addition of sulphate of lime. Sulphate of lime is preferred generally to chloride as it costs nothing, and the sulphate of potash which it yields is more valuable than the chloride. A slight excess of gypsum is necessary beyond the theoretically required amount, as otherwise the reaction proceeds very slowly, and part of the potash tartrate is in danger of escaping decomposition.

The mass has next to be boiled, while constantly agitated, for about 2 hours, at the end of which time the second equivalent of the tartaric acid will have been deposited as tartrate of lime, while the sulphate of potash only is left in solution. Care must be taken that the contents of the the generator be allowed to become quite cool before the supernatant solution is decanted, as tartrate of lime is not absolutely insoluble, and is more soluble in hot than in cold liquids. The solution is evaporated to recover the sulphate of potash. The tartrate of lime is subjected to several washings with cold water, and is then decomposed by the addition of sulphuric acid, thus yielding free tartaric acid, and a deposit of sulphate of lime. Some of the latter is used to decompose the neutral tartrate of potash, as already described, and the remainder may be employed as a manure. The quantity of sulphuric acid required may be calculated directly from the amonnt of chalk used, and the previously ascertained percentage of lime, present as a tartrate, with crude tartars employed. The separation of the gypsum will be promoted if the sulphuric acid be allowed to be a trifle in excess, say ·2 per cent.

The whole compound is next transferred to a filtering apparatus, consisting sometimes of only a shallow reservoir with a perforated false bottom, over which is spread thick flannel, while in other works a deep vessel is employed, and the filtration is promoted by the application of pressure. The sulphate of lime deposit is washed repeatedly, and with great care to free it entirely from tartaric acid.

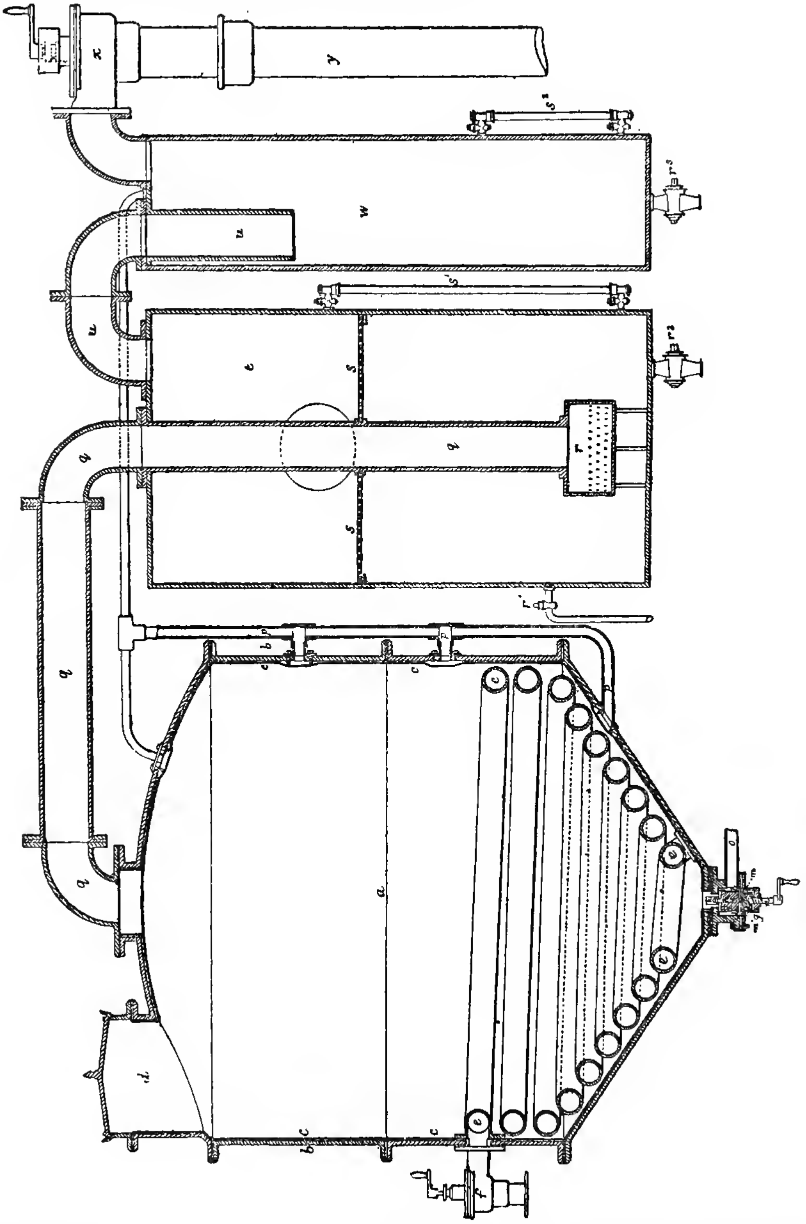
The solution of tartaric acid, and the washings of the gypsum, are evaporated together in shallow leaden pans, heated externally by water baths, or internally by coils of steam pipe. This plan, however, is accomplished by a large loss, owing to the decomposition set up by the action of any temperature exceeding 60° (140° F.) to 65° (150° F.), especially in the presence of sulphuric acid.

Pontifex, a large manufacturer of this acid, has devised a plan of concentrating the solutions *in vacuo*, thus not only reducing the temperature, but offering other great advantages in shutting out all air, decreasing the time occupied in concentration to about one-tenth of what it was by the old system, and keeping the liquid constantly in agitation. The last is a most important consideration, as when evaporating with a steam coil, there is so little motion occasioned in the liquid that a portion of it will remain in contact with the coil, whose temperature is about 105° (220° F.), for an inconveniently long time. By the modern plan, however, the temperature of the first solutions never need rise above 49° (120° F.) to 54° (130° F.), and though some difficulty was at first experienced from the disposition of the sulphate of lime to deposit itself in a flocculent form, which it was troublesome to separate, this obstacle has been overcome by careful attention.

Pontifex first separates or filters the liquors, from which tartaric and citric acids, and tartrate of potash and soda are obtained, from so much of the sulphate of lime, or baryta, &c., as is not in solution, as well as from other impurities, by pressure through textile fabrics. The liquor is then evaporated *in vacuo* nearly to concentration, and, if necessary, the concentrated liquors are allowed to deposit any sulphate of lime or baryta, or other matters that may have been previously held in solution by the weak acid-liquor, and afterwards the concentration is completed to the point of crystallization. When the crystals have formed they are remelted, and, after the liquor has been decolorized in the usual way, it is evaporated *in vacuo* and crystallized, the operation to be repeated if required, till the crystals are sufficiently pure. The melting in the various re-crystallizations is also best conducted in the vacuum pan.

The apparatus employed consists of a vessel in which the liquors are to be evaporated, and this vessel is placed within a second vessel, which is exhausted, by which means the pressure of the atmosphere is removed both from the outside and the inside of the inner vessel, and thus the most convenient metal, lead, may be used to contain the liquors. The lead may also be dressed down upon the outer vessel with some pigment, or cement, between the surface, so as to expel the air, and the joints so arranged that no air can enter between them; or glass, earthenware, or enamelled iron, or other material not affected by acids, may be used as the evaporating vessel, without the addition of another vessel to sustain the pressure. The overflow vessel contains at the bottom a quantity of chalk, milk of lime, or other alkaline or carbonated solution, through which the vapour from the vacuum pan is conducted by means of a pipe terminating in a rose. Above the surface of this alkaline or carbonated solution, a priming plate, perforated for the escape of the steam, is fixed in the overflow vessel, to prevent the solution being carried away by the overflow of steam through it. The overflow vessel is fitted with suitable taps and pipes for the supply of fresh, or discharge of spent solution. The object of employing the solution here is to collect the acetic, butyric, sulphurous, and other acids, that would otherwise pass over and injure the apparatus. The overflow vessel would also collect any tartaric acid that might accidentally boil over from the vacuum pan. The steam may be condensed by the ordinary injection condenser; but the patent condenser that bears the name of Edmund Pontifex is preferable, not only on account of its economy in air-pump power and quantity of condensing water required, but because by means of it the whole of the products of evaporation can be more conveniently collected, and the escape or loss of tartaric acid be detected.

168.



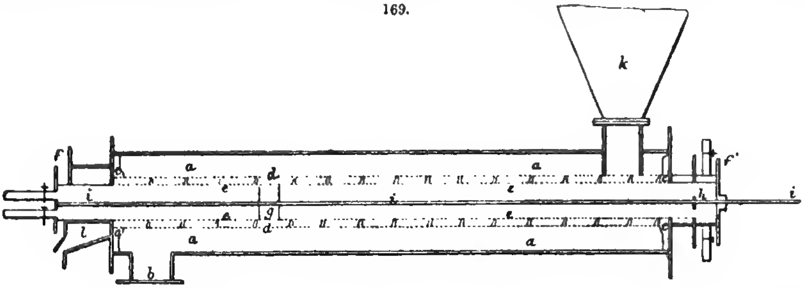
In order to prevent leakage in the valves or taps attached to the vacuum pan, caused by the action of the acid in the substance of which they are composed, the body of the tap or valve should be of cast iron lined with lead, the valve face and disc, gland of indiarubber, and the spindle must be secured from the action of the acid by a covering of lead.

Fig. 168 shows a sectional elevation of the apparatus employed; the vacuum pan *a* is formed of a cast-iron case *b*, and a leaden lining *c*; *d* is a manhole; *e* is a leaden steam coil; *f* is a valve for the admission of steam to *e*; and *g* is a valve for discharging the contents of the vacuum pan. This valve *g* is composed of a spindle *h*, carrying the leaden piece *i*, which is covered with india-rubber *k*; *l* is an india-rubber disc or diaphragm; *m* is a nut and washer, and *n* is a screw spindle, which is fitted with a handle by which the valve is worked; *o* is a pipe leading from the valve *g*; *p p* are pipes for exhausting the space between the cast-iron case *b* and the lining *c*; *q q* is the passage to the overflow receiver which contains the carbonated or alkaline solution at the bottom, through which the vapour from the vacuum pan is conducted by the pipe *q*, which terminates in the rose *r*; r^1 is a supply tap and pipe; r^2 and r^3 are draw-off taps; *s* is the perforated priming plate; and s^1, s^2 are gauge glasses; *t*, the upper part of the overflow vessel, may be called a safety vessel, and is connected by a passage *u*, with a second safety vessel *w*; *x* is a valve for cutting off communication between the pan, &c., and the condenser, and *y* is a pipe which leads to the condenser and air-pump. The valve *g* is found to be well adapted to all parts of the apparatus where such is necessary.

The first crop of crystals must always be re-dissolved and freed from the colouring matter that is always present in some degree. This is accomplished by boiling them with animal charcoal, from which the earthy phosphates and carbonates have been removed by treating it with hydrochloric acid.

Firmin has devoted much attention to the filtration and decolorization of the resultant liquids. First, the solution is separated from the earthy sulphate by passing it over an exhausted surface, provided with numerous perforations, while water, steam, or both, are forced through the sulphate, so as to insure the removal of all the acid. For this purpose a vessel fitted with a perforated cover, over which an endless cloth is made to pass, is placed in connection with an air-pump, and upon this cloth the earthy sulphate, mixed with the acid solution, is gradually placed and the vessel exhausted by means of the pump. The cloth is caused to move slowly along over the perforated cover, by means of rollers, placed at each end during its passage. A finely divided shower of water is made to fall on to the sulphate and is drawn through it by the pump, or a second method of causing the sulphate and acid to pass over an exhausted surface is shown in Fig. 169.

169.



An iron cylinder lined with lead *a* is connected by a pipe *b*, with a receiver that communicates with an air-pump and is fitted with a gauge to show how much liquor is in the receiver, and with a tap to empty it, which is of lead. Inside *a* is placed a perforated leaden or copper cylinder *d*, which is fixed at each end by the rings *c c*. Another perforated copper cylinder *e*, having a worm attached to it revolves in *d*, the ends being carried through the plates *f f'*, where they are fixed in stuffing boxes. This cylinder *e* is hollow and at the end *f*, taps are inserted for the regulated admission of air to the cylinder *e*, which air is allowed to pass as far as the division *g*, which divides the lower from the upper part of the cylinder at the end *f'*. A stationary chamber *h* is fixed, to which are attached taps communicating with a water cistern placed above, also taps for the admission of air or steam. The driving spindle *i* is brought through this chamber with a stuffing box and connected to the power with a slow motion; *k* is the hopper which may be connected with a vessel containing the salts to be operated upon, the latter being kept in a state of thick cream; and, finally, *l* is the exit valve.

In using this arrangement the sulphate and acid solutions are passed through the hopper *k*, where they fall on the screw *e*, which, revolving, carries them to the exit *l*, but in their passage water and steam are admitted at *f'*, and air at *f*. The air-pump exhausting the cylinder *a*, and the receiver causes the water and steam to pass through the sulphates during their passage through the cylinder to *g*, while the air which is admitted at *f* effectually forces the remaining liquor from the earthy sulphates, which are delivered at *l* free from the acid solution. The two perforated cylinders are about $\frac{5}{8}$ in. apart, and the screw fits so as to clear the outer cylinder, which is covered with a filtering cloth. The solution of tartaric acid is then run into a vessel lined with lead, placed near the evaporating pan. The capacity of this vessel is known and a given quantity is run into the evaporating or vacuum pan at each charge. This evaporating pan is preferably of iron, having an iron dome or cover, well painted and lined with lead. In it is an opening, closed by a movable cover to enable the workman to remove the gypsum, which will be largely deposited upon the pipes, sides, and bottom of the pan, and which, unless removed, would collect and stop the progress of evaporation. The pan is heated by means of coils of steam pipes inside and an iron jacket for steam or hot water outside; in the bottom is a pipe for discharging the contents into a suitable receiver, which pipe is closed by a top or valve. From the top of the evaporating pan a pipe is carried to a receiver of iron lined with lead, which will retain any of the liquor which may boil over. This vessel must be fitted with a gauge to show how much liquor has been passed into it, and with a tap at the bottom to draw it off. From the top of this vessel a pipe is conducted to the condenser, where the steam meets a stream of injected water, and thence to an air-pump for exhausting the vessels. The solution being sufficiently concentrated is run into the receiver, where it is kept warm, until any gypsum which may be carried from the pan with the liquor is deposited. The degree of concentration of the solution may be ascertained by examining a small quantity by means of the sampler, a copper bath containing about a pint, fitted near the bottom of the evaporating pan, having a communication with the vacuum space above and a tap for emptying it. The liquor is then drawn from the receiver into a suitable vessel, where it is kept in agitation till it granulates and cools. It is then placed upon a vessel connected with the air-pumps, having the top covered with perforated sheet lead over which is placed a cloth through which the liquor from the salt is drawn by the action of the pump into the vessel, which may be large enough to retain it, or may be connected with an air-tight receiver, or, in place of this vessel, a cylinder, similar to that described for separating the earthy sulphates from the acid solutions, may be used, admitting air and finely divided water. Or, the concentrated solutions, when granulated and cool, are placed in a centrifugal machine, in a similar manner to that in which the crystals of sugar are frequently separated from the mother liquor. The salts obtained are, if necessary, dissolved, filtered through properly prepared animal charcoal, and again subjected to evaporation, as before, and the colourless concentrated solution is either treated as before described, or drawn into leads to crystallize, as is now practised. The mother liquor from the first evaporation, consisting of sulphuric and tartaric acids, is treated with tartrate of lime to remove a portion of the sulphuric acid, and after filtration is subjected to evaporation as before.

Firmin, also a large manufacturer, has improved upon the preceding method of filtering, and forces the liquids through a layer of finely divided, insoluble matters by means of a vacuum under the filter bed, and allowing the pressure of the air to exert itself on the surface of the liquids, or pressure may be obtained by closing the filter at the top and forcing the liquid into the vessel by a pump.

170.

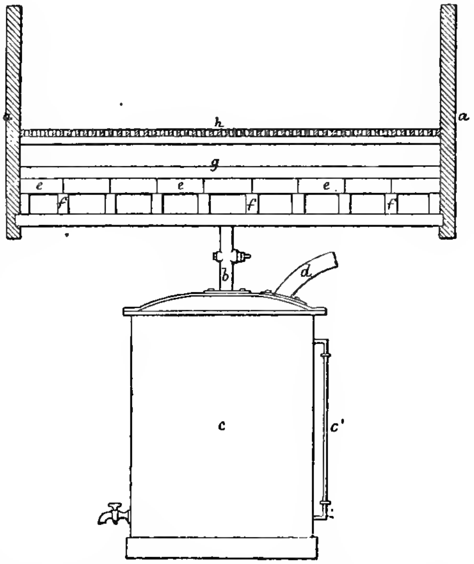
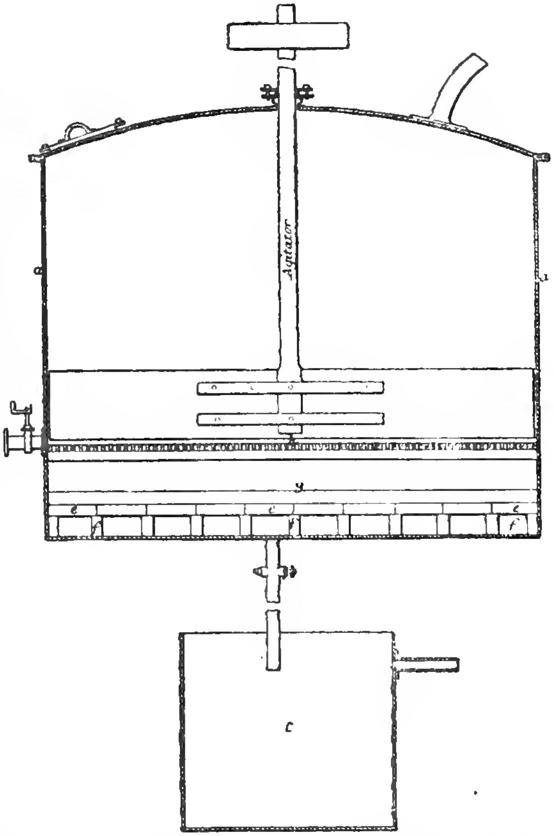


Fig. 170 is a longitudinal section of the filter. It consists of a wooden vessel *a*, from the bottom of which a pipe *b* passes to a vessel *c*, and a vacuum is maintained in this vessel by an air-pump in connection with the pipe *d*, which enters the vessel. The vessel *c* should be made of such a capacity as to contain all the liquid which it is required to filter at one time; it is fitted with a glass tube gauge c^1, to indicate the quantity of liquid in it. At a short distance above the bottom of the vessel *a*, a layer of bricks *e* is laid, supported on other bricks *f*; the joints between the bricks *e* are left open, no mortar or cement being used in laying them; on the bricks is placed a layer of pebbles *g*, over this a layer of fine sand, and on the sand a grating of wood *h*, the intervals between the bars of the grating being also filled with sand which just covers the bars. The liquid to be filtered is run into the vessel *a*, and a vacuum being formed in the vessel *c*, it speedily passes through the layer of sand. The solid matter separated may be removed by shovels from the filter, which is prepared to be again used by spreading a thin layer of fresh sand on the wooden grating, or the precipitate may, if desired, be stirred up with a small quantity of water by means of an agitator with which the vessel *a* may be furnished.

Fig. 171 shows a vertical section of a similar filter, constructed to work by artificial pressure at the top, as already mentioned, in place of by vacuum below; this filter is, as will be seen, fitted with an agitator. The filters are prepared for use by washing them first with water, then with dilute hydrochloric acid, and again with water. We would remark that although we have spoken of the use of sand to form the filter bed, other finely divided and insoluble matters may be employed, as, for example, the sulphate of baryta, which indeed, when it can be readily obtained in a suitable form, is to be preferred to sand, as it is difficult to obtain the latter free from alumina, which acts injuriously on solutions of the acids. Raw cotton fibre may also be conveniently employed when filtering concentrated solutions which might be acted on injuriously by sand.

171.



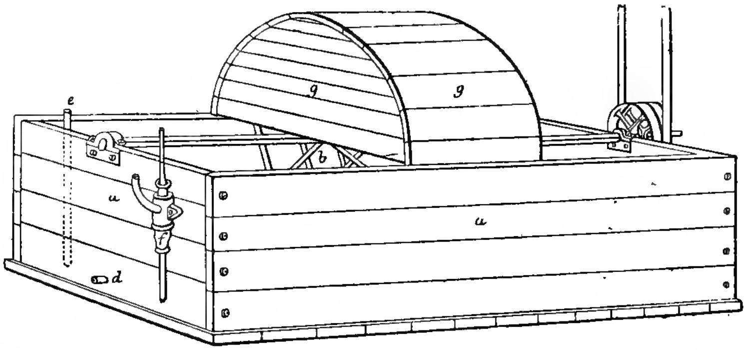
When a precipitate of tartrate or citrate of lime, or other insoluble tartrate or citrate, has been obtained by any process ordinarily practised, and which requires to be washed to free it from impurities, it is mixed with water and run into the vessel *a* of the filter. The precipitate is allowed to subside, and the supernatant water is run off, when the remaining water is made to pass through the filter, either by vacuum or pressure. By means of an agitator, it is again mixed with water and the operation is repeated, and so on till the precipitate is sufficiently purified; it is then again mixed up with a small quantity of water, and run into another vessel to be decomposed with sulphuric acid to set the tartaric or citric acid free in the usual manner. This process of decomposition produces a precipitate of sulphate of lime (if lime be the base with which the citric or tartaric acid was previously combined), and this is also separated by filtration through a filter such as already described. This filtered liquid is, by preference, evaporated and granulated by keeping it agitated while it cools.

More recently, How has proposed further improvements in the manufacture, by submitting the crude argol or tartar to preparations capable of purifying them to a greater extent than is usually done, at the same time using less water in washing, thereby saving loss in solution, and, which is most important, rendering the acid liquors produced so pure and of such a strength that great cost of evaporation and repeated crystallization may be avoided.

In treating crude argol or tartar in the preparation of tartrate of lime, or other base for the manufacture of tartaric acid, to the mixture of whiting or other base that may be used to neutralize the free acid existing in the argol or tartar, as much ferrocyanide of potassium is added as is found necessary to precipitate all the iron existing therein as prussian blue, the tartrate of potash being decomposed with a salt of lime, either sulphate, nitrate, or muriate (according to the current value of the potash salts), formed in the usual manner, and with the usual apparatus for mingling and treating the mixture. The ferrocyanide of potassium may be used to precipitate the iron from the solution at any stage of the process, and whether such solution be strong or weak. The tartrate compound being formed as before mentioned, the precipitate is first allowed to subside, and as much as possible of the clear liquid is drawn off into suitable reservoirs. Then, after well mixing up the precipitate that remains, with or without the addition of cold water as may be necessary, the whole contents of the "generator" are run into a vessel, which we now proceed to describe.

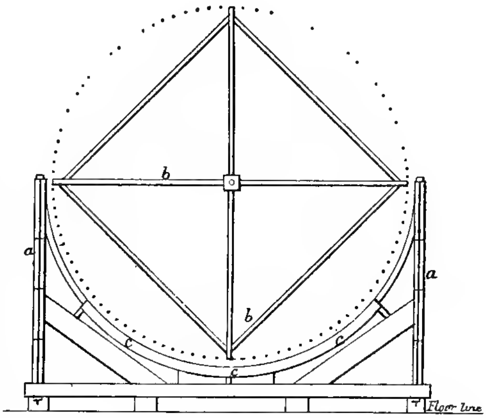
Figs. 172 and 173 show the apparatus in perspective and in sectional elevation. *a* is a wooden cistern lined with lead (called the "decomposing tank") of any convenient size, the bottom of which is slightly rounded so as to facilitate the action of the stirrers *b*, as shown in the section. The stirrers consist of splints of wood fixed into a square spindle occupying one-third more or less of the whole length, the spindle when in action being turned by a band on a pulley at the end of it, and actuated by any suitable motive power. *c* is a false bottom made of wood covered with flannel or any other filtering material; *d* is an outlet pipe for the filtered liquor, and *e* is an outlet pipe for the air contained in the chamber. *f* is a leaden pump to produce a partial vacuum when necessary, and *g* is a cover to prevent splashing from the stirrers.

172.



The mode of using the apparatus is as follows. The tartrate compound being run into the decomposing tank, the liquid becomes entirely separated by virtue of the filtering medium, to be treated as circumstances may require. Cold water is then allowed to percolate through the mass until it has removed from it all impurities, when it is fit for decomposition by means of sulphuric acid, for which purpose (the outlet being closed), as much washing from a previous operation is added to the partly dry mass as is necessary to make it semi-fluid, and also some mother liquor of a previous working in order to extract from the latter the excess of sulphuric acid which it has gained from frequent concentration, and then as much more sulphuric acid as may be required to complete the decomposition and liberate the tartaric acid, and show a slight reaction with a soluble salt of lime, the stirrers being meanwhile kept in motion. A complete admixture of the contents of the tank being thus effected, the outlet pipe is then again opened and the liquor run into a suitable reservoir, the remaining sulphate of lime or other base being washed clean with water in the ordinary way, the weaker washings being kept for future operations. The results are that the colouring matter and the iron contained in the tartar under treatment are effectually removed, and the tartrate of lime or other base is washed more completely, and thereby rendered less liable to fermentation than when washed by the ordinary means, while the solution of tartaric acid is produced in a much purer and more concentrated state, thus effecting a great saving in the expense of evaporation and recrystallization.

173.



Messrs. Dietrich and Schnitzer propose a plan for removing the inconveniences attending the separation of the tartaric salts contained in wine residues, due to the mucilaginous properties of the accompanying impurities, which is substantially as follows.

The residues are heated according to their nature and to the means employed, for a greater or less time to a temperature of about 129° (284° F.) to 170° (338° F.). This heating causes the foreign matters partly to become insoluble and partly to be transformed into a condition in which they no longer offer any difficulty in separation. The heating may be conducted in a variety of ways:—In closed or open vessels by means of an ordinary open fire, or by hot baths, or by steam either superheated or under pressure; but it is perhaps preferable to heat the residues in a dry state, when possible, and when it is not possible to render them dry, closed vessels are best, in which the heating is effected by direct steam. Hitherto, in the manufacture of tartaric acid from tartar (bitartrate of potassa), the acid alone is separated, and the potassium of the tartar remains, and can by several combinations be obtained as an accessory product, but the attempts which have often been made to obtain this potassium in a valuable form are without a fair result.

The following method of manufacture, due to Franz Dietrich, a Swiss chemist, indicates decided improvements. If tartar (bitartrate of potash) be treated by a surplus of carbonate of lime and water, these substances are decomposed, as shown by the following equation :—

(*a*) $C_4H_5KO_8$ — 188·1 bitartrate of potash = $C_4H_4CaO_6$ — 188·0 tartrate of lime.
$CaCO_3$ — 100·0 carbonate of lime $KHCO_3$ — 100·1 carbonate of potash.
288·1 288·1

But this transformation is only effected under the condition that the operation be conducted in closed vessels, and the developed carbonic acid prevented from getting out of the vessel. In consequence thereof a pressure is produced, which hastens the reaction; this latter is effected as follows: —Owing to tartar not readily dissolving in cold water, only a small quantity of the tartar dissolves, meets the carbonate of lime in suspension, and decomposes it according to the equation (*b*), namely :—

(*b*) $2C_4H_5KO_6$ — 376·2 bitartrate of potash = $C_4H_4CaO_6$ — 188·0 neutral tartrate of lime.
$CaCO_3$ — 100·0 carbonate of lime $C_4H_4K_2O_6$ — 226·2 „ „ potash.
CO_2 — 44·0 carbonic acid.
H_2O — 18·0 water.
476·2 476·2

The neutral tartrate is now dissolved; the carbonic acid prevented from escaping is also dissolved under a pressure proportionate to the size of the vessel and the quantity of the substances which have undergone the reaction. By these means carbonate of lime is dissolved with facility, and there is obtained a solution of bicarbonate of lime, which is transformed together with the neutral tartrate of potassa according to equation (*c*), namely :—

(*c*) $C_4H_4K_2O_6$ — 226·2 neutral tartrate of potash = $C_4H_4CaO_8$ — 188·0 neutral tartrate of lime.
$CaCO_3$ — 140·0 carbonate of lime $2KHCO_3$ — 200·2 bicarbonate of potash.
CO_2 — 44·0 carbonic acid.
H_2O — 18·0 water.
388·2 388·2

As soon as bicarbonate of potassa has been formed, the decomposition goes on more rapidly, as the tartar can now dissolve directly in this salt according to equation (*d*), namely :—

(*d*) $C_4H_5KO_6$ — 188·1 bitartrate of potash = $C_4H_4K_2O_6$ — 226·2 neutral tartrate of potash.
$KHCO_3$ — 100·1 bicarbonate „ CO_2 — 44·0 carbonic acid.
H_2O — 18·0 water.
288·2 288·2

The products of this latter reaction decompose themselves together with carbonate of lime according to equation (*c*).

All these reactions go on one after the other, and one by the side of the other, until all the tartar has been transformed into tartrate of lime and bicarbonate of potash. The pressure, which at the commencement is rather low, is elevated with the energy of the action up to a maximum, is again lowered, and disappears at the end of the operation. It is a special peculiarity of this process that the carbonic acid required for the decomposition is developed by the mixed matters themselves, and that the mechanical labour necessary for getting the mixture under pressure is furnished without expense by this same carbonic acid.

In practice the best effects are obtained if the raw materials treated are in a finely-divided state, therefore the tartar and the chalk should be previously finely ground. Rather more than is absolutely necessary of the carbonate of lime should be employed, and it may be replaced by other suitable carbonates.

A low degree of pressure is sufficient for carrying out the operation, but a higher pressure should be employed in order that the work may go on more rapidly. High pressure hastens the reaction. The pressure may be regulated by the volume of the vessels employed. If, for instance, in a vessel of about 1000 gallons capacity are treated—

1881 bitartrate of potash.
1000 carbonate of lime.
5720 water.
8601

After the operation are obtained—

$$\begin{array}{l} 2600 \text{ crystallized tartrate of lime.} \\ \left.\begin{array}{l} 1001 \text{ bicarbonate of potash} \\ 5000 \text{ water} \end{array}\right\} \text{solution } 1:5. \\ \hline 8601 \\ \hline \end{array}$$

In consequence, it is preferable to conduct the operation in the smallest possible space in order to obtain a pressure as high as possible. As mixing vessels, the well-known apparatus used in the manufacture of aërated waters can be employed, with the modification that the openings for filling in the substances and for getting out the mixture must be wider, and the stirring apparatus must be of greater strength. The apparatus is provided with a pressure gauge and safety valve, and is connected with a conduit pipe for carbonic acid. The substances are rapidly filled in, the apparatus closed, the stirrer moved, and the operation may be observed by means of the pressure gauge. When all pressure has disappeared, carbonic acid is to be pumped in. As by the mixture and the filling in of the matters a small quantity of carbonic acid is lost, and also neutral tartrates (generated by the decomposition) may be present in the raw material, and as the reaction can only be terminated if there be a sufficient quantity of carbonic acid for converting the whole quantity of potash into bicarbonate, this addition of carbonic acid is indispensable. In consequence carbonic acid is pumped in until the pressure in the apparatus has become constant, and no carbonic acid is confined. It is not necessary to defer pumping in carbonic acid until all pressure has disappeared, but the pumping in can be begun if the indicator of the pressure gauge continues to fall. The addition of carbonic acid is stopped when the pressure has become constant, at which moment the operation is terminated. The freely developed carbonic acid is blown off, or the pressure of the same is used for transferring the contents of the vessel to other rooms. The apparatus is emptied and the mixture separated in any known manner. A precipitate of tartrate of lime and a solution of bicarbonate of potash are obtained. The precipitate is washed, and then transferred for the manufacture of tartaric acid. The washing water still contains a certain quantity of bicarbonate of potassa, and in order that this carbonate may also be obtained, this water is used in a further operation in lieu of pure water. The solution of bicarbonate of potash is evaporated in the ordinary way.

The small quantity of carbonic acid wanted for the work is to be borne in mind during the evaporation of the leys of carbonate. As for every atom of tartar one atom of carbonic acid is developed, the greater part of this gas remains for any desired use. Upon the same principle neutral tartrates of alkali may be decomposed, and the mother leys of the manufacture may be used.

Neutral tartrate, together with carbonate of lime and carbonic acid under pressure, furnishes tartrate of lime and bicarbonate. In this case the whole intermediate carbonic acid is of course taken from outside, and the operation must take place under a strong pressure of from 5 to 10 atmospheres, more or less, if the decomposition is to be terminated within a suitable time. Without such pressure the decomposition of the neutral tartrates cannot be effected.

Messrs. Jouette and Pontièves have endeavoured to make tartaric acid from the pressed out or distilled grape skins which at present have a value only as manure. They proceed as follows:—The skins are mixed with 2 per cent. of sulphuric acid and boiled for several hours. The tartaric acid present is then liberated, while the unfermented part of the sugar, as well as the appreciable quantity that may be formed by the action of the sulphuric acid on the cellulose residue after, undergoing fermentation and subsequent distillation, will yield a not inconsiderable amount of alcohol. After decanting the sugary fluid, milk of lime is added, forming a tartrate of lime, from which the tartaric acid can be recovered in the usual way. According to these investigators, the residue from making 22 million gallons of wine, when treated as above, will yield nearly 200 tons of tartaric acid, worth about 24,000*l*.

German Method of Manufacture.—The following details of the modern process adopted in South Germany, obtained from a very reliable source, are not without a considerable degree of interest.

The conduct of the manufacture may be divided under two heads: 1. The making of the tartrate of lime; 2. The production of the tartaric acid from the salt. The raw materials consist of crude tartar, wine lees, and the residue from the manufacture of Rochelle salts and tartar refining.

1. *Making the Tartrate of Lime (a) from Crude Tartar.*— Raw tartar 10 to 15 cwt., according to quality, is put into a vat of some 2200 gallons capacity, four-fifths filled with water. The water is heated by steam nearly to the boiling point, during which time it is kept in motion by a revolving spindle. When this temperature is reached, the steam is cut off, and the free part of the tartaric acid neutralized, for which purpose powdered chalk may be used. This settles out as tartrate of lime, and the easily soluble neutral tartrate of potash remains in solution. Carbonic acid escapes in streams, for which reason abundant ventilation must be provided. Theoretically, this reaction requires that for 18·8 parts of tartar there shall be 5 parts of chalk; as, however, the crude tartar

seldom contains more than 80 per cent. of acid tartrate of potash, this proportion is not found to be necessary in practice. Further, it is not imperative to completely neutralize, because the magnesia, clay, oxide of iron, &c., which might be very troublesome in subsequent operations, then fall out as well. It is even advisable, when the tartar is very rich in such matters, or in colouring bodies, to add 25 to 50 lb. of muriatic acid at the beginning of the operation, and yet not altogether to neutralize, on account of the subsequent formation of Epsom salt and alum.

For converting the tartrate of potash into tartrate of lime, gypsum is best suited, as this salt is generally much cheaper than chloride of lime. The quantity of gypsum necessary may be calculated from the amount of chalk used, 5 parts of chalk = 8·6 parts of gypsum. Of course it makes no difference whether the gypsum be added previously or during the neutralization by the chalk, neither will any harm arise from an excess of it.

As the tartrate of lime extracted from the lees is very clean and, on conversion to tartaric acid, leaves a very clean gypsum as a bye-product, in many works the gypsum thus produced is preferably used for turning the tartrate of potash into tartrate of lime. The reaction of the gypsum on the neutral tartrate of potash manifests itself slowly and requires several hours, especially if the liquid be very concentrated. In order to see if the reaction be finished, a cooled sample is filtered and decomposed with acetic acid. When a precipitate is no longer given the reaction is finished.

When this point is reached, the contents of the vat are cooled to about 50° (122° F.) and run into another vessel, for the deposition of the tartrate of lime, which is allowed to pass through a sieve to retain the foreign bodies accidentally present in the crude tartar, as wood chips, dust and pieces of molten sulphur. After three or four hours the fluid is cooled down to about 25° (77° F.), and the tartrate of lime deposits itself, so that the supernatant liquid can be syphoned off.

A triple washing is generally sufficient to make the tartrate of lime pure enough for further operations. In the first ley which is drawn from the tartrate of lime much sulphate of potash is found, which may be recovered if the needful plant be at hand and the market value will repay the cost of evaporation.

(*b*) *From Wine Lees.*—In the spring following the principal fermentation of new wine, the wine is drawn off from the deposit that has formed, which will amount to about five per cent. of the quantity of the wine. This residue may be pressed and will yield about $\frac{5}{8}$ of its bulk as so-called press wine, which, in Austro-Hungary for instance, is coloured with cheap dark red Dalmatian wine and mixed with the requisite quantity of glycerine, and is very largely drunk. About $\frac{3}{8}$ will be left behind as a dough-like lees. Formerly this lees was only used as a manure, for which it is valuable as possessing potash salts and phosphates. Probably Mr. E. von Seibel, at Liesing, near Vienna, was the first to utilize the tartrates (7 to 20 per cent.) in lees for the production of tartaric acid, and many manufacturers have followed him.

In tartaric acid works the lees is partly pressed and partly used without being pressed, so long as the deposit of the wine continues; for working during the greater part of the year the lees is very strongly pressed and dried.

(*i*) *Working with Wet Lees.*—Both the pressed and unpressed lees is first used for making brandy, of which it yields 1 to 4 per cent. and the resulting schnapps—so-called "lager brandy"—is much esteemed by some people. As this lager brandy is considerably dearer than the spirit from other sources (potatoes, maize, &c.) it is the custom to add to the lees before distillation, at least as much spirit as it is expected to derive from the lees as lager brandy, and the properties of the lager brandy are so strong that this may be done with impunity. If, however, the lager brandy by itself be rectified, a pure spirit is the result, which is better adapted than any other to liqueur making, and is much used for that purpose.

After the distillation is complete, the lees is run into a large vat of about 2000 to 3500 gallons capacity, and is thinned with water by means of a pump. About 50 cwt. of lees are put into the vat, which is then almost filled with water, and to this about 1 cwt. of muriatic acid is added. The agitating machinery is then set in motion, and the liquor heated by steam nearly up to the boiling point. When this is attained the steam and the agitator are suspended, and the contents of the vat are left for some time to settle. By far the greater portion of the liquid then becomes clear; this is drawn off by a syphon into a second vat of suitable proportions, and then mixed with powdered chalk, and constantly agitated till neutralized to a weak acid reaction. Through the chloride of lime formed all the tartaric acid will be deposited. Then the liquid is put into a third vat, where the tartrate of lime is itself deposited, and afterwards washed. The slimy deposit from the first-mentioned vat is pressed by steam or compressed air through a filter press, such as is used in sugar works, and afterwards the tartaric acid contained in it is recovered. The press residue can be used for Frankfort black, or for potash making.

(*ii.*) *With Dry Lees.*—The pressed lees is cut into pieces the size of a fist and dried in the air, and then serves for material in autumn and winter when no wet lees is to be had. Before making it into tartrate of lime it is generally ground to powder in a meal mill, about which there is no difficulty. From 18 to 25 cwt. of this ground lees are put into a vat holding 2000 to 3500 gallons, the vessel is filled up with water, 50 to 100 lb. of crude muriatic acid are added, and the mixture is stirred up and heated by steam till it nearly boils. When this point is reached, the agitator is stopped, the mixture is allowed to settle, and is then treated as in the former method.

The tartrate of lime procured from lees is distinctly recognizable from that obtained from tartars; it is cleaner, whiter, and easier to wash; the tartaric acid made from the lime tartrate thus produced is considerably more crystallizable, while the gypsum resulting from the decomposition with sulphuric acid is also much whiter, and separates out much more easily than that yielded in the treatment of tartars.

The treatment of the residues for making Rochelle salts, &c., is analogous to that adopted with lees.

It is not necessary that the manufacture of the tartrate of lime and the tartaric acid be carried on at the same place; on the contrary, the tartrate of lime is often separated first, on account of the cost of transport of the bulky lees. In this case, the tartrate is pressed and dried, because it ferments easily when preserved in a wet state.

2. *Extracting the Tartaric Acid from the Tartrate of Lime.*—To get the acid out of the tartrate of lime, the latter is treated with sulphuric acid. Theoretically, to decompose 9·4 parts of tartrate of lime, 4·9 parts of monohydrated sulphuric acid are necessary, but practically more is needed. This is because tartaric acid crystallizes much better in a solution containing strong mineral acids, while small quantities of non-decomposed tartrate of lime, or of sulphate of potash resulting from an imperfect washing of the tartrate of lime, greatly impede the crystallization. When the tartrate of lime is freshly prepared, sometimes as much concentrated sulphuric acid may be added as is equal to the amount of chalk used at the commencement of the operation. The tartrate of lime is gradually mixed with the sulphuric acid in a suitable vessel, and enough water is added to produce a semi-liquid paste; it is heated to 75° (167° F.) by steam, and agitated by suitable apparatus. The mass foams considerably at first, but this soon ceases, when a sample may be taken for treatment with a solution of chloride of calcium, at about 38° Tw. (23° B.) The volume precipitated will suffice, after a little experience, to show when enough acid has been added. It is important that it should always be a little in excess. The whole mixture is then put through filters of wood lined with lead, containing straw and felt. The filtered solution is heated by steam in leaden vessels, and will deposit still a little gypsum. When the liquor is concentrated, the temperature must not rise above 70° to 75° (158° to 167° F.), as the sulphuric acid would then exercise a carbonizing influence on the tartaric acid.

When the liquor reaches about 75° Tw. (40° B.) it is put to crystallize in large tanks of wood, lined with lead, or in earthenware pots. The crystallization proceeds three times as rapidly in the latter as in the former, but the crystals are very small, which is of no importance, however, if they be still coloured. The mother liquors are then evaporated a second and a third time. The crystals obtained are passed through the turbine, re-dissolved, the solution decolorized and filtered through wicker-work, a little sulphuric acid added, the solution evaporated down to about 63° to 75° Tw. (35° to 40° B.), and crystallized out in leaden vessels. Very fine needle-shaped crystals are thus obtained. These are passed through the turbine, dried and sifted. They always contain a little lead and sulphuric acid. For pharmaceutic purposes they are re-dissolved without addition of sulphuric acid, evaporated to 63° Tw. (35° B.), and crystallized in earthenware jars. It then suffices to dry the crystals in the air. These crystals are distinguishable in form and size from the others, the hemihedral faces are less developed, and they contain less lead and sulphuric acid. As to the residue of the sifting, this is reduced to powder, and appears in commerce as "prepared" tartaric acid. This is generally the most impure.

3. *Refining the Tartar.*—The crude tartar is pulverized in large vessels with water and hydrochloric acid, and dissoved by boiling; bone black is added, and the liquid is filtered under pressure. This yields a tartar which, after crystallization, may be considered as pure. Excess of bone black must be avoided, for otherwise the crystals will be grey.

Much commercial unsifted tartar is adulterated with sand, or with dry lees, and many tartars contain 10 per cent. of tartrate of lime.

Adulterations and Impurities.—Although the nature of the ordinary impurities contained in this acid is well known, and most books on analysis profess to give methods for their detection, Alfred H. Allen has found some of the processes very unreliable, and others to require special precautions not always observed. The following remarks from his valuable paper communicated at a recent meeting of the Society of Public Analysts, will be of great interest.

The principal accidental impurities of tartaric and citric acids are salts of potassium and calcium, together with iron, lead, and copper, derived from the vessels used for the evaporation or crystallization of the acid liquids. The presence of all these impurities is indicated by the proportion of ash left on igniting the specimen. A number of samples of commercial tartaric and citric acids recently examined gave an amount of ash varying from ·05 to ·25 per cent.

The ignition is readily effected in a porcelain crucible over a Bunsen burner. Platinum vessels should be avoided, lest lead be present. 5 to 10 grm. should be taken for ignition. When the proportion of ash is small it is of no interest to examine it further, except for poisonous metals. Very sensible quantities of lead and copper are sometimes present. Of course their existence will be easily indicated on dissolving the ash in a few drops of nitric acid, diluting largely, and passing sulphuretted hydrogen. A very fair approximative estimation of the lead or copper present may be obtained by placing the solution of the ash in a tall glass cylinder, and comparing the depth of tint produced by sulphuretted hydrogen with the tint obtained by treating an equal bulk of a very weak standard solution of lead or copper, in a similar manner. The plan is identical with that recommended by Wanklyn for estimating the lead in water, except that sulphuretted hydrogen is substituted for ammonium sulphide. Experience has shown this to be necessary, owing to the frequent presence of iron which of course gives a dark colour in an alkaline solution. Some stress is laid by him (Allen) on this well-known fact, as some recently examined samples of aërated waters gave a deep brown coloration with ammonium sulphide, apparently indicating the presence of poisonous quantities of lead, but which further inquiry proved to be merely due to a considerable quantity of iron. The author prefers to examine the ash for poisonous metals, instead of using the original sample of acid. The presence of copper is indicated on treatment of the ash with nitric acid in the crucible by the production of a blue colour. Of course the presence of poisonous metals in tartaric and citric acid is always accidental; but as they are occasionally present in dangerous amounts, it behoves manufacturers to take every precaution to avoid their introduction, as the product containing them must be regarded as adulterated.

Many samples of citric acid contain free sulphuric acid, which may be known by the highly deliquescent character of the crystals. In testing citric acid for sulphates with chloride of barium, it is desirable to acidify rather strongly with hydrochloric acid.

The most common adulterant of citric acid, and almost the only substance purposely mixed with it, is tartaric acid, which is frequently found in the powdered samples sold in the shops. Many plans of detecting tartaric acid in admixture with citric acid have been proposed, but some seem to have been tried merely in the separate acids, and not in mixtures containing a comparatively small proportion of the power. The ordinary method described in text books of precipitating the tartaric acid from a cold neutral solution by addition of calcium chloride, Allen has found far from delicate, 10 per cent. of tartaric acid in a sample escaping certain detection.

Messrs. Chapman and Smith found that a citrate when boiled with a very alkaline solution of potassium permanganate (such as is used for the estimation of albuminoid ammonia) merely gave a green solution of alkaline manganate; but a tartrate when similarly treated caused a precipitation of brown manganese dioxide. Allen says, however, that he has been unable to verify these results, having failed to find any decided difference in the behaviour of the two acids.

Another proposed method of detecting this adulterant is to add excess of precipitated ferric hydrate to the aqueous solution of the sample, and to raise the liquid slowly to the boiling point. The undissolved portion is allowed to settle, and the clear liquid is decanted off and evaporated to a syrup at steam heat. If tartaric acid be present, even in very small proportion, it is said to cause the deposition of a pulverulent precipitate of ferric tartrate, while the liquid obtained from pure citric acid remains clear. Allen has not succeeded in detecting moderate percentages of tartaric acid by this test.

The best test for detecting an admixture of tartaric acid is the well-known one of a salt of potassium. It is remarkable how very few of the ordinary works on analysis make any mention of the precautions necessary for the successful detection of tartrates of potassium by their mutual reaction. If aqueous tartaric acid be added to a strong solution of the chloride or nitrate of potassium, a precipitate of the acid tartrate will often occur, but its formation is greatly impeded by the mineral acid set free. This may be proved by filtering off the liquid, and treating it with a strong solution of sodium acetate, when a copious additional precipitation takes place, owing to the replacement of the free hydrochloric or nitric acid by acetic acid and the insolubility of the acid potassium tartrate in the latter. Of course the same object is attained by using excess of acetate of potassium as the precipitant, instead of the nitrate or chloride. The precipitation is greatly promoted by stirring, forming well-defined and characteristic streaks in the track of the glass rod. Of course the liquid must be quite cold. The delicacy of the reaction is greatly increased by the addition of alcohol.

A recognition of this fact suggested the possibility of rendering the best quantitative and delicate by using alcoholic instead of aqueous solutions of the sample and reagent. Tartaric and citric acids are both soluble in absolute alcohol, but the potassium salts are insoluble. Acid tartrate of potassium is also practically insoluble in proof spirit, while the citrates of potassium are pretty readily soluble in weak alcohol. In the following experiments a proof spirit (made by diluting ordinary methylated spirit with water till it had a density of 920) was employed.

Some pure potassium hydrogen tartrate was prepared, and its solubility in proof spirit at 15° was shown to be 0·05 per cent., or 1 grm. in 2000 cc. of spirit.

A saturated cold solution of potassium acetate in proof spirit was prepared; 100 cc. contained about 36 grm. of the salt, so that 5 cc. sufficed for the precipitation of nearly 3 grm. of tartaric acid.

A series of samples of citric acid were prepared, containing 5 to 50 per cent. of tartaric acid. Quantities of 2 grm. of each of these adulterated samples were dissolved in 20 cc. of proof spirit. 5 cc. of the saturated spirituous solution of potassium acetate was added, and the solution stirred and left overnight. It was then filtered, the precipitate was washed with proof spirit saturated with acid potassium tartrate, and then once with ordinary proof spirit. The precipitate was then washed off the filter with hot water into a light porcelain dish, the water evaporated off at steam heat, and the dry tartrate weighed and calculated into tartaric acid.

It was hoped that by proceeding in this manner, very accurate estimations of tartaric acid could be made, as there could be no loss except from the slight solubility of the precipitate in the solution, for which a correction could easily be made on the assumption that the citric acid and potassium acetate present had no influence on the solubility of potassium hydrogen tartrate in proof spirit. It was surprising, however, that the results obtained, even without the correction for solubility, showed sensibly more tartaric acid than had been actually added to the sample. A fresh series of experiments was made, exactly the same method being employed, except that the 2 grm. of the samples were dissolved in 40 cc. of proof spirit instead of 20 cc. as before, thus making the volume of the solution 45 cc. By this proceeding the following results were obtained without the correction for solubility, which would make the numbers 1·1 per cent. higher still:—

No.	Tartaric Acid added.	Tartaric Acid found.	
		By Precipitation.	By Alkalinity of Ash.
1	10	10·55	9·70
2	20	20·70	20·40
3	30	33·35	35·50
4	40	43·50	42·25

In this course of examinations, the results were checked by igniting the precipitate and titrating the ash with standard acid. It was found that the carbon left retained alkali tenaciously, and after dissolving the ash in water it was necessary to ignite the black residue and then add its ash to the main quantity. In the above cases, the amounts of potassium carbonate found by the titration of the ash correspond to the percentages of tartaric acid shown in the last column of the table.

A convenient plan of estimating the tartaric acid volumetrically, is to dissolve the precipitate in hot water and titrate the solution volumetrically. This plan gives results closely according with those obtained by direct weighing when pure tartaric acid is employed.

Another series of experiments was conducted in a similar manner, except that the precipitate was washed with proof spirit, which had *not* been previously saturated with acid potassium tartrate. The following results were obtained, no connection being made for solubility of the precipitates in the mother liquor:—

No.	Tartaric Acid added per cent.	Tartaric Acid found.		
		By Weight of Precipitate.	Means.	By Alkalinity of Ash.
1	10	10·00	10·04	10·50
1A	10	10·25		10·50
1B	10	9·88		..
2	20	20·90	21·30	22·02
2A	20	21·71		..
3	30	31·50	30·73	31·59
3A	30	29·96		..
4	40	43·10	43·91	43·57
4A	40	44·71		..

These estimations were very satisfactory when the proportion of tartaric acid did not exceed 20 or 30 per cent., but there was a uniform tendency towards too high a result. The discrepancies observed seem attributable to (1) the presence of tartaric acid in the sample of citrate employed; (2) precipitation of an acid citrate together with the potassium hydrogen tartrate.

Apart from direct experiment having proved the absence of tartaric acid in the original citric acid used, the invalid nature of the first explanation is shown by the fact that the *less* citric acid used the *greater* was the excess of tartaric acid found over that added.

Experiments were then made with the view of ascertaining whether the discrepancy was due to the second cause. A quantity (2 grammes) of the citric acid was treated in exactly the usual manner, and gave no evidence of the presence of tartaric acid. On the following morning the liquid was again stirred, the temperature being only about 8° (46° F.), when well-defined streaks were produced in the track of the glass rod, and in a few minutes the liquid became semi-solid from the formation of a crystalline precipitate. Either the sample was largely contaminated with tartaric acid, or the cold had induced the separation of potassium citrate. The latter, as might be expected, proved to be the truth; warming causing the precipitate to disappear gradually, while, on decanting off the alcoholic liquid and adding a moderate quantity of cold water, the precipitate dissolved instantly. The fact deserves especial attention, as ignorance of it might readily lead to a sample of citric acid being condensed as largely adulterated with tartaric acid, when the latter substance was entirely absent.

The above observation naturally gave the clue to the anomalous results already obtained. In the concentrated and highly alcoholic solution used, there was a tendency to the precipitation of potassium citrate along with the tartrate. This tendency seemed capable of correction by treating the washed precipitate with a cold saturated aqueous solution of potassium hydrogen tartrate, which would readily dissolve any precipitated citrate, without acting on the acid tartrate. The following figures show the results of this treatment:—

No.	Tartaric Acid added.	Tartaric Acid found.	
		Precipitate washed with Proof Spirit.	Same Precipitate after treatment with Aqueous KHT Solution.
	per cent.	per cent.	per cent.
1	20	21·00	20·96
2	40	44·60	38·77

In this case, the results obtained from the sample containing 20 per cent. of tartaric acid were almost within the limits of error, while the reduction of the weight of the precipitate in No. 2 by an amount equal to nearly 6 per cent. of tartaric acid, conclusively shows that the previous excess was due to citrate carried down by the tartrate precipitate. If, to the results obtained in No. 2 we add 1·1 per cent., as correction for solubility of the potassium hydrogen tartrate in the mother liquor, we obtain 39·87 per cent. of tartaric acid found, as against 40 per cent. added.

An attempt was next made to obtain a precipitation in an *aqueous* solution, using proof spirit merely for washing the product. Two quantities dissolved in ten times their weight of water gave by this method 35·15 and 16·85 per cent. of tartaric acid respectively, instead of 40 per cent. and 20 per cent. added.

Next some experiments were made, in which a cold saturated aqueous solution of potassium hydrogen tartrate was used as the solvent of the sample, but the results were unsatisfactory.

The results of the whole of the above experiments have led to the use of the following process, which, while readily detecting 2 or 3 per cent. of tartaric acid, allows of the estimation of larger proportions with very fair accuracy:—Dissolve 2 grammes of the sample to be tested in 45 cc. of proof spirit, filter from any undissolved calcium or potassium tartrate, add 5 cc. of a cold saturated solution of potassium acetate in proof spirit, stir, and allow to stand for 12 hours. Filter off the precipitate produced and wash it with proof spirit. Rinse off the precipitate from the filter with a saturated solution of potassium hydrogen tartrate in cold water, digest in the cold for a few hours with occasional stirring, then filter, wash once with proof spirit, rinse off the precipitate into a small porcelain dish with boiling water, evaporate at 100°, and weigh the acid potassium tartrate obtained. The weight, multiplied by 0·798 (or roughly, 0·8), gives the quantity of tartaric acid in 2 grm. of the sample examined. As a check, the dry precipitate may be ignited, and the solution of the ash titrated with standard acid; in the same method (substituting standard alkali for acid) may be applied to the purified precipitate on the filter, so as to avoid the trouble of the subsequent evaporation at steam heat.

If any doubt whatever exists as to the precipitate produced by potassium acetate being really the acid tartrate, its insolubility in cold water will readily settle the question, but positive proof is easily obtained by the silver test, which is extremely delicate when carefully applied, but remarkably liable to failure if the proper conditions be not carefully observed. The following plan of operation gives very good results:—A small quantity of the precipitate of acid potassium tartrate is washed with a little cold water, and then treated with a slight excess of ammonia. The resultant solution is boiled till neutral, allowed to cool, and then precipitated with *excess* of argentic nitrate. To the liquid containing the precipitate, dilute ammonia is added till the precipitate has almost disappeared, when the solution is filtered. On heating the filtrate nearly to boiling, for a few minutes, a brilliant mirror of metallic silver is produced on the sides of the tube. Citric acid does not reduce silver under similar circumstances, except on continued boiling.

After the precipitation of the tartaric acid in a solution by addition of potassium acetate, the citric acid may readily be detected in the filtrate (after evaporating off the alcohol) by applying the ordinary tests.

Wigner has suggested that the power possessed by solutions of tartaric acid of altering the plane of polarization of a transmitted beam of light would enable an accurate estimation of that acid to be made in the presence of citric acid, which is inactive. The method would evidently give a practised observer very good results in cases in which the adulterant was all *dextro*-tartaric acid, but would fail if the sample contained racemic *lævo*-tartaric or inactive tartaric acid. This objection does not apply to the estimation as a potassium salt.

Oxalic acid is said to be sometimes employed as an adulterant of citric acid. This dangerous admixture would, of course, be readily detected by treating the aqueous solution of the sample with excess of ammonia, acidifying with acetic acid, filtering from any precipitated acid-ammonium, and testing the filtrate with calcium sulphate.

A method of separating tartaric from citric acid proposed by Barbet is as follows. Some fragments of the substance to be examined are spread over a thin layer of weak solution of caustic potash on a glass plate. After a few seconds, the crystals of tartaric acid become white and then opaque, and finally of almost microscopic size, while the crystals of tartaric acid remain transparent, and partly dissolve in the alkaline solution. This difference is so strongly marked, that it is even possible to estimate the amount of each which is present. The same method may even be employed with a powder of the acids, when, however, a microscope must be used for the observation.

Another plan has been proposed by Dr. Hager. First, a mixture is made consisting of 4 grm. of fused caustic potash, 60 cc. of water, and 30 cc. of alcohol at 90 per cent. This liquid is poured into a glass basin placed on a piece of black paper so as to form a layer of some 6 mm. high; next, crystals of the acid to be tested are placed in this fluid so that they do not touch each other and are some 3 to 5 centimetres apart. After having been left quietly standing for about three hours, the crystals of citric acid will be found either entirely, or at least nearly, dissolved, there being left only a whitish speck where they had lain; but the crystals of tartaric acid, if any, where present, will have been left undissolved, and covered as well as surrounded with a whitish crystalline mass.

With a view to obtaining a trustworthy and easily executed quantitative test for tartaric acid, Dr. Martenson, First Assistant in the chemical laboratory of the Pharmaceutical Institute of Dorpat, in Russia, has made many experiments. First, he ascertained by a number of tests that tartrate of lime is not nearly so soluble in water as is commonly stated in books, but that one part of this salt requires 2388·26 parts of water at 18° (64° F.) for complete solution, and afterwards discovered the almost absolute insolubility of the tartrate of lime in alcohol of 85 per cent. strength. In order to estimate the tartaric acid in tartrate of potash, for instance, the salt is dried at 100° and dissolved in a small quantity of distilled water; next, pure chloride of calcium solution is added, with the precaution to avoid excess of that compound; then a few drops of pure lime water are introduced, and the porcelain crucible in which this operation has been performed is left standing for some hours. A crystalline precipitate is thus obtained, which is collected on a filter previously dried at 100° and weighed. The supernatant fluid is first poured upon the filter, then the precipitate is collected and washed with strong alcohol; the precipitate and filter are thoroughly dried at 100°, and the precipitate is weighed as $C_4H_4CaO_6 + 4H_2O$.

It is of great importance that the porcelain basin which is used be perfectly free from cracks in the glaze, for the precipitate would have a very strong tendency to adhere to such portions of the crucible. When either hydrochloric or nitric acids are present along with the tartaric, the fluid must first be nearly neutralized with pure carbonate of lime, and warmed to expel carbonic acid, while the last traces of acid are removed with lime water. The presence of either chloride of ammonium or of calcium in excess interferes with the correctness of the results, and makes it necessary to add alcohol to the liquor to be treated. When proper care is manifested, the results are said to be perfectly accurate.

H. J. H. Fenton says, in a recent number of the 'Chemical News,' that he has lately noticed the following reaction, which may, so far as he can judge at present, be proposed as a test for tartaric acid. To a very dilute solution of ferrous sulphate or chloride, a small quantity of a solution of tartaric acid or a tartrate is added, followed by a few drops of chlorine water or hydric peroxide, and lastly, excess of caustic potash or soda, when a fine violet colour is obtained. Fenton tried the same experiment with citric, succinic, malic, oxalic, and acetic acids, and with sugar, but without getting a similar result. If a ferric salt be used instead of a ferrous salt, the colour is not produced. The violet compound formed seems to be potassic or sodic ferrate. It is destroyed at once by sulphurous acid, and is slowly discharged by boiling. Success has not attended attempts to obtain the higher oxides of manganese and chromium in the same way.

Jouette and Pontièves have also paid much attention to this subject, and to them the following observations are due.

Of all acids, tartaric and malic acids alone possess the known property of rendering iron, alumina, manganese, &c., soluble in alkaline liquids. Peroxide of iron in acid solution, containing neither tartaric nor malic acids, is precipitated as soon as the liquid is neutralized by ammonia. If, on the contrary, iron and tartaric acid be mixed in determinate proportions, or if the tartaric acid be in excess, there will be produced, after saturation with ammonia, a tartaro-ferric ammoniacal composition of a fine red colour, soluble in acid or alkaline liquids, provided they do not contain any of the alkaline-earthy metals. The study of this phenomenon has led to a method of estimating either tartaric or malic acids with a standard solution of iron and aluminium, or of these metals by a standard solution of crystallized acid. A given weight of pure iron is dissolved in nitric acid, which is then diluted with distilled water to form a standard liquor containing 0·001 or 0·002 of iron. If to a solution of 100 milligrammes of iron 45·5 milligrammes, or any larger quantity of tartaric acid be added, and also 1 or 2 cc. of common ammonia to render the liquid decidedly alkaline, the product will be, after vigorous stirring, a red liquid, at first thick, but which, when left to itself, becomes and remains limpid. If, on the contrary, to 100 milligrammes of iron be added 45 milligrammes or more of tartaric acid, and then an excess of ammonia, &c., the liquid, thick at first, deposits the characteristic precipitate of peroxide of iron. The soluble compound produced by a proportion of tartaric acid equal to or exceeding 45·5 to 100 is permanent in the presence of acids, alkalies, and alkaline carbonates, provided they be exempt from lime, and also in the presence of ammoniacal salts, alcohol, ether, &c. If the compound be heated to ebullition the iron is almost entirely precipitated; this may also be done by adding to the liquid, some hours afterwards, ordinary water containing calcareous salts. In practice 0·455 grammes of the substance to be assayed are dissolved in acidulated water, which is then diluted with common water to form a determinate volume, such as, for instance, 100 cc.; 10 cc. are deducted, and according as the matter contains 1, 2, 3, ... n hundredths of tartaric acid, 1, 2, 3 . . . . n milligrammes of iron may be added, which will remain undissolved. Thus, in a simple manner, by two trials, two different results are obtained, viz.:—

With n milligrammes of iron .. .. limpid solution,
„ $n + 1$ „ „ .. .. precipitate,

n is the number of hundredths of tartaric acid contained in the substance.

The estimation of tartaric acid in crystallized bitartrates and neutral tartrates gives to nearly 0·01 the proportion of tartaric acid indicated by the formula.

Tartaric acid crystallizes with two molecules of water in large, colourless, transparent, oblique prisms of highly sour yet agreeable taste, which melt at 170° (338° F.). They dissolve easily in water, which solution turns mouldy by keeping, then yielding a minute proportion of acetic acid. A remarkable feature of the acid consists in its turning the plane of polarization of a ray of light towards the right, the degree of the angle being exactly in proportion to the acid through which the ray passes.

Sulphuric acid gently heated with tartaric acid converts it into tartralic acid, $C_8H_{10}O_{11}$, and tartrelic acid $C_4H_4O_5$, but at a strong heat carbonic oxide and sulphurous acid only are produced. By the action of nitric acid, acetic, oxalic, and saccharine acids are formed.

Simple heat is capable of exerting remarkable influence on this acid. At a temperature from 170° to 180° (338° to 356° F.) it becomes first metatartaric acid, an isometric acid with itself, but differing from it in forming a gummy transparent mass, which ultimately yields opaque crystals. If the heat be continued for a short time a certain amount of water is disengaged, and the resulting acid is known as tartralic, isotartaric or bitartaric. It is very soluble and quite uncrystallizable, as well as the salts which it forms, which latter are all soluble in water.

By maintaining the temperature for a still longer time a further proportion of water escapes, and the monobasic, tartrelic, soluble anhydrous or dehydrated tartaric acid is obtained. No more water will be liberated by continuing the heat beyond this point, but the anhydrous acid is rendered insoluble and neutral. This, when heated suddenly and very strongly, resolves itself into carbonic oxide, carbonic acid and acetic acid.

Salts of Tartaric Acid.—The commercially important salts formed by tartaric acid are three in number, known respectively as Cream of tartar, Rochelle or Seignette's salts, and Tartar emetic.

(*i.*) *Cream of tartar.*—This derives its name from the Venetian method of preparation. The impurities are first removed by repeated solutions and crystallizations of the granulated tartar. During the last solution, a certain proportion of wood ashes and white of eggs is added to the boiling liquor. This occasions effervescence, which brings the remaining impurities to the surface so that they can be removed by skimming the liquid. When allowed to cool, suddenly the surface will be covered with a thin coating of very fine crystals.

The French plan varies somewhat from the foregoing. The granulated tartar is reduced to powder, saturated with water and placed in vats holding water at a temperature of 100°. After 2 or 3 days it will be found that the insoluble matters have subsided, and the clear liquid is then run into earthenware vessels and allowed to crystallize. Of these crystals 100 parts are dissolved in water containing 4 to 6 parts of clay and the same quantity of animal charcoal in suspension. This liquid is evaporated till the surface is covered with a film, and is then drained off into coolers. After standing for a week or more, a crop of colourless crystals will be found collected round the sides of the vessels, while the colouring matters, clay and charcoal, will be accumulated at the bottom. The crystals are dried and bleached in the sun.

(*ii.*) *Rochelle salts.*—M. Guido Schnitzer takes equivalent weights of nitrate of soda and crude potashes and heats them, with just sufficient water to produce a solution, in an iron vessel, meanwhile thoroughly agitating the compound. After completion of the mutual decomposition that ensues, enough milk of lime is added to the boiling liquid to convert the carbonate into caustic soda. The solution containing the nitrates of potash and soda is then evaporated, to allow the nitrate of potash to crystallize out, which it is said to do perfectly. The crystals are then drained from the soda solution and washed with water slightly acidulated with hydrochloric acid, to remove the last traces of soda. The soda solution is then boiled in a copper vessel, with a sufficiency of rough tartar to make a neutral solution. Some tartrate of lime will be deposited, and may be washed and used subsequently in the process of making tartaric acid. When filtered from this deposit, the solution is evaporated for the crystals.

(*iii.*) *Tartar emetic.*—This salt consists of white, transparent, inodorous, rhombic octahedral crystals, having a slightly sweet and metallic taste, which dissolves in 14 to 15 parts of water at 15°, and in two parts at 100°. It is represented by the formula

$$KOSbO_3 . C_8H_4O_{10} \text{ or}$$

Potash	47·2	13·83
Teroxide of antimony	153·0	44·84
Tartaric acid	132·0	38·69
Water	9·0	2·64
	341·2	100·00

It is obtained by boiling 3 parts of antimony teroxide with 4 parts of cream of tartar and filtering the hot solution and allowing it to crystallize.

Of the other salts formed by tartaric acid, the tartrate and ammonio-tartrate of iron are used in medicine, the chromium tartrate in calico-printing, the tartrate of potash and tin in wool-dyeing, and the tartrate of potash and copper as a water-colour (Brunswick green).

Tartaric acid is used chiefly as a discharge in calico-printing, and also largely for mordanting woollen goods in conjunction with tin salts and alum. It is also frequently made to take the place of citric acid, which it closely resembles in many respects, in the manufacture of acidulated drinks.

A. L.

ACORUS CALAMUS. The common sweet-flag. This plant belongs to the genus *Acorus*, of the natural orders *Aroideæ* or *Araceæ* (Arum), or, according to some botanists, of the natural order *Orontiaceæ*, which is regarded as a connecting-link between *Aroideæ* and *Junceæ*. The plants of this genus have a leaf-like scape, which bears upon its side a dense, cylindrical, greenish spike of flowers, with sex-partite herbaceous perianth, and six stamina in each flower.

The Acorus Calamus is probably the Calamus Aromaticus of the ancients, to which plant they ascribed very important medicinal virtues. It was originally brought from Asia in the fifteenth century, and was formerly much prized as a garden plant. It has since, however, become naturalized in Britain, in Germany, and in other parts of Europe. In Norfolk it grows abundantly; the marshes, rivers, and ditches of this county furnish the chief supply for the London market.

The root, which is exceedingly aromatic, and has a sharp, sweetish taste, is the only part of the plant required for use. It is cut into strips 4 or 5 in. long, in which form it may be obtained from the druggists. It is occasionally used in medicine as a tonic, especially in cases of weak digestion, when its effect is strong, but transient. It is regarded by the Turks as a remedy against contagion. Continental confectioners make an agreeable sweetmeat by cutting the root into slices and preparing it with sugar.

Under the name of "Calamus root" it is employed by English perfumers as an ingredient in various hair-powders (see Perfumery). Its most important application in Britain is in the preparation of gin (see Gin), to which it imparts a peculiar flavour.

The essential oil (*oleum acori calami*) is used for scenting snuff, and to give an agreeable odour to aromatic vinegar.

ALBUMEN or **ALBUMIN**. (LAT., *albumen*, the white of an egg.)

Albumen, an organic nutritive principle, is a constitnent of all animal fluids and solids. The white of eggs contains 12 per cent. of albnmen, and the fluid portion of blood, or serum, 7 per cent. It occurs also in the flesh, in the brain, and more or less in all serous fluids. Fibrin also may be regarded as coagulated albumen. It occurs in the vegetable kingdom, in the sap or juice of many plants, such as the potato, turnip, carrot, &c., in the seeds of the cereal grasses, and in many nuts.

Albumen exists in two different modifications—soluble and insoluble albumen. It is in the former modification that it occurs in the animal body, but the insoluble modification may readily be prepared from the soluble one by the action of heat. This property of becoming insoluble or *coagulating*, as it is termed, by the action of heat, is especially characteristic of this substance.

Albumen contains carbon, hydrogen, oxygen, and nitrogen, together with traces of sulphur and phosphorus. Its chemical composition is as follows:—

Carbon	53·3	per cent.
Hydrogen	7·1	„
Oxygen	22·1	„
Nitrogen	15·7	„
Sulphur	1·8	„
Phosphorus	trace.	
	100·0	

Animal albumen is always associated with certain inorganic salts and free soda. It exists in the animal body in solution, in the form of an alkaline albuminate. If the white of eggs, or the serum of blood, or any animal liquid containiug albumen be incinerated, the residue is chiefly carbonate of soda. This alkali may readily be removed, and the albumen rendered insoluble, or coagulated, by the action of heat. Exposed to a gentle heat, soluble albumen gives off a peculiar, characteristic odour. On raising the heat to 54° (130° F.), white fibres of insoluble albumen begin to appear; at 70° (160° F.) it becomes a solid, jelly-like mass, and at 100° (212° F.) it dries up, turning yellow and brittle, like horn. When in this condition, five times its weight of water will re-dissolve it bringing it once more to its original consistency. The only change which the albumen undergoes during the process of coagulation is the removal by the hot water of the alkali and soluble salts. Its chemical composition remains the same throughout.

Albumen may be prepared in a pure state from white of eggs, by the following method:—The white of eggs is beaten up well with water and filtered. To the filtrate is added a small quantity of sub-acetate of lead, in order to remove the mineral substances. The whole of the albumen is now precipitated as albuminate of lead. This is stirred up with water, and carbonic acid gas is passed through, by which the albuminate of lead is decomposed; carbonate of lead is precipitated, and the albumen remains in solution. The carbonate of lead is now filtered off through paper which has been washed with dilute acid. Traces of lead still remain, and to remove these the filtrate is treated with a few drops of aqueous sulphuretted hydrogen, and gently heated. The first flocks of albumen which appear, retain the whole of the lead as sulphide. This is filtered off, and the filtrate evaporated gently in a basin, the residue consisting of pure soluble albumen.

Albumen may be obtained from the serum of blood by precipitating with lead acetate, washing and decomposing the precipitate while suspended in water, with carbonic anhydride. A cloudy solution of albumen is obtained on filtration; this is evaporated at a temperature of about 50°, and a yellow transparent substance is left, consisting of nearly pure albumen. It is partly soluble in water, but entirely so on addition of a little acetic acid. Alcohol precipitates it from its aqueous solution.

Albumen is insoluble in alcohol and ether. Strong alcohol, in large excess, precipitates it from its aqueous solutions; so also does ether,'but in smaller quantities. Nearly all acids, except acetic acid, in which it is soluble, coagulate albumen. The alkaline earths form with it insoluble compounds which harden on drying. A useful cement, which when dry sets as hard as stone, may be made by mixing slaked lime with white of eggs.

Albumen forms precipitates with salts of lead, mercury, silver, tin, and bismuth. It is therefore an effective antidote in cases of poisoning by sugar of lead, corrosive sublimate, or nitrate of silver, as it forms with these insoluble compounds, and thereby prevents the poison from entering the system.

Albumen is used chiefly for clarifying vinous and syrupy liquids. It is mixed with the liquid, to be clarified, and heat is applied. The albumen coagulates, and in doing so retains all the minute insoluble impurities which rendered the liquid turbid, and which may now be skimmed off with it from the surface, leaving the liquid clear and bright. This process is largely used by sugar refiners (see Sugar). It is also used by calico printers as a mordant for fixing colours (see Dyeing, and Calico Printing), and in photography (see Photography).

The following method has been recommended by M. Berg for the preservation of egg-albumen for photographic purposes. The whites, separated from the yokes, are evaporated to dryness in zinc or porcelain basins, at a temperature of 45°, the operation being conducted *in vacuo* to quicken the evaporation. The solid albumen thus obtained is afterwards reduced to powder, which, if kept perfectly dry, may be preserved for a long time without alteration, and may be employed for all the purposes of the ordinary article, such as the clearing of wines, &c. It is probable that it would serve equally well for the manufacture of albumenized paper.

Albumen, Vegetable.—Vegetable albumen is identical in composition with animal albumen. It may be prepared from potatoes, by cutting them into slices and covering them with water containing about 2 per cent. of sulphuric acid. This is allowed to stand for twenty-four hours, when more potatoes are added, and the operation is repeated. The liquid is afterwards neutralized with potash and boiled, when vegetable albumen separates out in thick white flocks. Albumen prepared in this way is identical in composition and properties with the albumen of serum or white of eggs.

ALCOHOL. (Fr., *alcool;* Ger., *alkohol.*) Formula, C_2H_6O.

Pure alcohol is a liquid substance, composed of carbon, hydrogen, and oxygen, in the following proportions:—

C	52·17
H	13·04
O	34·79
	100·00

It is the most important member of an important series of organic compounds, all of which resemble each other closely, and possess many analogous properties. They are now classed by the chemist under the generic title of "Alcohols." The substance of which this article treats, or *vinous alcohol*, is the principle of all spirituous, fermented liquors. The intoxicating properties of these liquors, due to the presence of this principle, have been known since the flood, but it was not until about the beginning of the fourteenth century that it was isolated in a pure state.

Alcohol does not occur in nature; it is the product of the decomposition of sugar, or, more properly, of *glucose*, which, under the influence of certain organic, nitrogenous substances, called *ferments*, is split up into alcohol and carbonic anhydride. The latter is evolved in the form of gas, alcohol remaining behind mixed with water, from which it is separated by distillation. The necessary purification is effected in a variety of ways.

Pure, absolute alcohol is a colourless, mobile, very volatile liquid, having a hot, burning taste, and a pungent and somewhat agreeable odour. It is very inflammable, burning in the air with a bluish-yellow flame, evolving much heat, leaving no residue, and forming vapours of carbonic anhydride and water. Its specific gravity at 0° is ·8095, and at 15·5° (60° F.), ·794; that of its vapour is 1·613. It boils at 78·4° (173° F.). The boiling points of its aqueous mixtures are raised in proportion to the quantity of water present. Mixtures of alcohol and water when boiled give off at first a vapour rich in alcohol, and containing but little aqueous vapour; if the ebullition be continued, a point is ultimately reached when all the alcohol has been driven off and nothing but pure water remains. Thus, by repeated distillation, alcohol may be obtained from its mixtures with water in an almost anhydrous state.

The following table by Otto gives the boiling points of alcoholic liquids of different strengths, and the proportions of alcohol in the vapours given off:—

Proportion of Alcohol in the Boiling Liquid in 100 vols.	Temperature of the Boiling Liquid.	Proportion of Alcohol in the Condensed Vapour in 100 vols.	Proportion of Alcohol in the Boiling Liquid in 100 vols.	Temperature of the Boiling Liquid.	Proportion of Alcohol in the Condensed Vapour in 100 vols.
90	78·8	92	15	90·0	66
80	79·4	90·5	12	91·3	61
70	80·0	89	10	92·5	55
60	81·3	87	7	93·8	50
50	82·5	85	5	95·0	42
40	83·8	82	3	96·3	36
30	85·0	78	2	97·5	28
20	87·5	71	1	98·8	13
18	88·8	68	0	100·0	0

Absolute alcohol has a strong affinity for water. It absorbs moisture from the air rapidly, and thereby becomes gradually weaker; it should therefore be kept in tightly-stoppered bottles. When brought into contact with animal tissues, it deprives them of the water necessary for their constitution, and acts in this way as an energetic poison. Considerable heat is disengaged when alcohol and water are brought together; if, however, ice be substituted for water, heat is absorbed, owing to the immediate and rapid conversion of the ice into the liquid state. When 1 part of snow is mixed with 2 parts of alcohol, a temperature as low as − 21° is reached.

When alcohol and water are mixed together, the resulting liquid occupies, after agitation, a less volume than the sum of the two original liquids. This contraction is greatest when the mixture is made in the proportion of 52·3 volumes of alcohol and 47·7 volumes of water, the result being, instead of 100 volumes, 96·35. A careful examination of the liquid when it is being agitated reveals a vast number of minute air-bubbles, which are discharged from every point of the mixture. This is due to the fact that gases which are held in solution by the alcohol and water separately are less soluble when the two are brought together; and the contraction described above is the natural result of the disengagement of such dissolved gases. The following table represents the contraction undergone by different mixtures of absolute alcohol and water.

100 Volumes of Mixture at 15°.					
Alcohol.	Contraction.	Alcohol.	Contraction.	Alcohol.	Contraction.
100	0·00	65	3·61	30	2·72
95	1·18	60	3·73	25	2·24
90	1·94	55	3·77	20	1·72
85	2·47	50	3·74	15	1·20
80	2·87	45	3·64	10	0·72
75	3·19	40	3·44	5	0·31
70	3·44	35	3·14		

Alcohol is termed "*absolute*" when it has been deprived of every trace of water, and when its composition is exactly expressed by its chemical formula. To obtain it in this state, it must be subjected to a series of delicate operations in the laboratory, which it would be impossible to perform on an industrial scale. In commerce, it is known only in a state of greater or less dilution.

Alcohol possesses the power of dissolving a large number of substances insoluble in water and acids, such as many inorganic salts, phosphorus, sulphur, iodine, resins, essential oils, fats, colouring matters, &c. It precipitates albumen, gelatine, starch, gum, and other substances from their solutions. These properties render it an invaluable agent in the hands of the chemist.

Alcohol is found in, and may be obtained from, all substances—vegetable or other—which contain sugar. As stated above, it does not exist in these in the natural state, but is the product of the decomposition by fermentation of the saccharine principle contained therein; this decomposition yields the spirit in a very dilute state, but it is readily separated from the water with which it is mixed by processes of distillation, which will subsequently be described. The amount of alcohol which may be obtained from the different unfermented substances which yield it varies considerably, depending entirely upon the quantity of sugar which they contain.

The following are some of the most important sources of alcohol which have been employed in Europe:—Grapes, rice, beet-root, potatoes, carrots, turnips, molasses, and grain. On the continent, many fruits are used for the production of alcohol besides the grape, such as apricots, cherries, peaches, currants, gooseberries, raspberries, strawberries, &c.; figs, too, are used extensively in the East. In America, nearly the whole of the spirit of commerce is obtained from potatoes, Indian corn, and other grains. In India, Japan, and China, rice and *sorghum* are the chief sources. Among a variety of other substances which have been and are still used for the production of alcohol in smaller quantities, are roots of many kinds, such as those of asphodel, madder, &c. Seeds and nuts have been made to yield it; and even woody fibre, old linen, cotton, and hemp have been successfully converted into cellulose, sugar, and thence into alcohol. It will thus be seen that the sources of this substance are practically innumerable; anything, in fact, which contains or can be converted into sugar is what is termed "alcoholisable."

Alcohol has become a substance of such prime necessity in the arts and manufactures, and, in one form or other, enters so largely into the composition of the common beverages consumed by all classes of people, that its manufacture must, of necessity, rank among the most important industries of this and other lands. The traffic in spirituous liquors in this country has during the last few years developed, and is still developing, rapidly; and with the demands of an increasing population it is reasonable to expect that a still further impetus will be given to the production of wines and spirits in England. The manufacture of ale and porter is confined to our own country, and forms the staple industry in some extensive districts, where it gives employment to many thousands of men, and handsome profits to the manufacturer. The production of whiskey is also monopolised by Great Britain, the Scotch and Irish distilleries supplying the entire demand for this article. Wines, brandy, and liqueurs are not produced in any quantity in the British Isles.

FERMENTATION.—Fermentation is a spontaneous change undergone, under certain conditions, by any animal or vegetable substance under the influence of ferments, by which are produced other substances not originally found in it. There are several kinds of fermentation, the most important being that by which alcohol is formed from glucose, or *alcoholic* fermentation. If this process be not carefully conducted, other fermentations ensue, resulting in the formation of acetic, lactic, and butyric acids, and sometimes of saccharine and viscous matters, which are productive of much annoyance to the distiller. These may be called the accidents of fermentation, and must be very carefully guarded against.

Glucose is said, therefore, to be subject to four principal kinds of fermentation—alcoholic, acetous, lactic, and viscous. There are others of a less important nature to which glucose is liable, but only the above four will be examined in this article.

The real nature of the process of fermentation, though it has been made the subject of much investigation, is still shrouded in a good deal of obscurity. Many theories have been put forward to account for it, of which the most probable is that of M. Pasteur, who tells us that the action of ferments is due to the life and growth of the minute cells of which they are composed. To effect this development, the cells require mineral food, and if this be withheld, no fermentation can take place. M. Pasteur has shown this by placing a small quantity of brewer's yeast, the ferment commonly employed in industrial operations, in an absolutely pure solution of sugar. He observed no sign of fermentation until he had introduced a soluble phosphate and a salt of ammonia, salts which constitute the mineral components of the ferment. The presence of albuminoid matters appears also to be indispensable; but these are contained in the ferment itself, so that in case the liquor is not sufficiently provided with such matter, the ferment will, so to speak, nourish itself with its own substance, throwing off at the same time the useless particles that are not necessary for its own growth. The results of careful microscopical examinations of the minute cellules of which yeast is composed fully bear out M. Pasteur's view of the subject.

The different varieties of fermentation to which glucose is liable will here be treated of separately.

Alcoholic Fermentation.—Five agents, each acting in a different direction, are necessary to produce this; in the absence of any one of them, fermentation cannot proceed. They are (1) Sugar, (2) Water, (3) A ferment, (4) Heat, and (5) Air. The part played by each of these five indispensable agents will now be examined.

Sugar.—Sugar when dissolved and brought into contact with a ferment is decomposed, yielding alcohol and carbonic anhydride. Before fermentation, the sugar has to be converted into *glucose*, by combination with two equivalents of water. This hydration is very easily effected; simple heating of a saccharine solution is sometimes sufficient; the presence of ferments themselves produces it, and a thousand other causes will bring it about when water is present. It is this ready conversion of sugar into glucose that renders saccharine matters so useful in the production of alcohol. The best proportion of sugar in an unfermented liquor or "must" is about 12 per cent. More than this hinders the fermentation.

Water.—The proportion of water employed in dissolving the glucose exercises considerable influence upon the products of the fermentation, as well as upon the time occupied by the process. The operation may be hurried or kept back by adding or subtracting water; the latter is effected by evaporation. The relative amount of water present is ascertained by means of an instrument called a "saccharometer." The water employed should contain no organic matter, and only a small proportion of mineral salts; it should always be clear and bright.

The Ferment.—A ferment is a substance undergoing decomposition, the ultimate particles of which are in a state of continual motion. When brought into contact with sugar, this atomic motion is communicated to the atoms of carbon, hydrogen, and oxygen of which the sugar is made up, the carbon dividing itself between the hydrogen and oxygen in such a manner that in place of the sugar, two more stable compounds are formed, viz., carbonic anhydride and alcohol. The elements of the ferment take no part in the formation of these products, but only act as the stimulant which provokes the change without participating therein chemically.

As stated above, brewers' yeast is the ferment chiefly employed by distillers. It is a frothy substance formed during the fermentation of the worts of beer. It collects on the surface, and is skimmed off and rendered dry and solid by the action of a press. That obtained from a strong beer is much to be preferred, as it is more certain in its action and less liable to engender acetous fermentation. It is best when newly prepared: old yeast should never be used when fresh can be obtained.

The best yeast for fermenting grain spirit is the London porter yeast, which is bought up by the grain distillers for this purpose. The proportions of yeast and sugar for quick fermentation are 5 parts of sugar to 1 part of yeast, although the same quantity of yeast will ferment a much larger quantity of sugar. Any nitrogenous substance, such as albumen, fibrin, gluten, &c., possesses the power of converting sugar into alcohol, when in a state of incipient decomposition, though in a less degree than yeast.

When required for storing, the yeast is subjected to processes of washing and pressing in order to get rid of the water and other impurities which it contains. It is pressed through linen or through a hair sieve, and the filtered liquid is then allowed to stand until the yeast has settled to the bottom. The clear liquid is then decanted off, and the yeast is washed several times with cold water, and well stirred up, until the wash water exhibits no acid reaction. It is finally mixed with 15·30 per cent. of starch, filled into bags, and pressed.

Heat.—Heat is as necessary to fermentation as water, and, like water, may be the cause of hastening or checking the process. The lowest temperature at which the action is sustained is about 15°, and it becomes more energetic and perfect as the temperature is increased up to 28° or 30°. A higher temperature than this should be avoided, as likely to excite acid fermentation. As a means of cooling the vat rapidly, in case of necessity, a coil of pipe in which cold water circulates is sometimes laid in the bottom of the vats. Since heat is retained longer in large masses than in small, and the heat generated by the rapidity of the chemical action is in proportion to the bulk of liquor, it follows that the temperature should be raised in inverse proportion to the bulk of the liquor undergoing fermentation.

Air.—Air, though indispensable at the beginning of the process, becomes useless, and indeed injurious, during its continuation. It is essentially the initial force, but when once the impulse has been given, it is no longer necessary. Therefore air should be excluded as carefully as possible, by keeping the vat covered and allowing no movement to displace the layer of carbonic anhydride, resting on the surface of the liquor, because contact with the air is certain to produce an acid fermentation in place of the alcoholic; this is especially liable to occur towards the end of the operation.

The whole process of alcoholic fermentation may be briefly described as follows:—

The liquor in the vat having been heated to the right temperature, the ferment, previously mixed with a small quantity of the saccharine liquor and then left to stand until fermentation begins, is thrown in, and the whole is well stirred together. In about three hours' time, the commencement of the fermentation is announced by small bubbles of gas which appear on the surface of the vat, and collect round the edges. As these increase in number, the whole contents are gradually thrown into a state of motion, resembling violent ebullition, by the tumultuous disengagement of carbonic anhydride. The liquor rises in temperature and becomes covered with froth. At this point, the vat must be covered tightly, the excess of gas finding an exit through holes in the lid; care must now be taken to prevent the temperature from rising too high, and also to prevent the action from becoming too energetic, thereby causing the contents of the vat to overflow. In about twenty-four hours, the action begins to subside, and the temperature falls to that of the surrounding atmosphere. An hour or two later, the process is complete; the bubbles disappear, and the liquor, which now possesses the characteristic odour and taste of alcohol, settles out perfectly clear. The whole operation, as here described, usually occupies about forty-eight hours, more or less. The duration of the process is influenced, of course, by many circumstances, chiefly by the bulk of the liquor, its richness in sugar, the quality of the ferment, and the temperature.

Acetous Fermentation.—This perplexing occurrence cannot be too carefully guarded against. It results, as mentioned above, when the fermenting liquor is exposed to the air. When this is the case, the liquor absorbs a portion of the oxygen, which unites with the alcohol, thus converting it into acetic acid as rapidly as it is formed. When acetous fermentation begins, the liquor becomes turbid, and a long stringy substance appears which after a time settles down to the bottom of the vat. It is then found that all the alcohol has been decomposed, and that an equivalent quantity of acetic acid remains instead. It has been discovered that the presence of a ferment and a temperature of 20° to 35° are indispensable to acetous fermentation, as well as contact with the atmosphere. Hence, in order to prevent its occurrence, it is necessary not only to exclude the air, but also to guard against too high a temperature and the use of too much ferment. The latter invariably tends to excite acetous fermentation. It should also be remarked that it is well to cleanse the vats and utensils carefully with lime water before using, in order to neutralize any acid which they may contain; for the least trace of acid in the vat has a tendency to accelerate the conversion of alcohol into vinegar. A variety of other circumstances are favourable to acetification, such as the use of a stagnant or impure water, and the foul odours which arise from the vats; stormy weather or thunder will also engender it.

Lactic Fermentation.—Under the influence of lactic fermentation, sugar and starch are converted into lactic acid. When it has once begun, it developes rapidly, and soon decomposes a large quantity of glucose; but as it can proceed only in a neutral liquor, the presence of the acid itself speedily checks its own formation. Then, however, another ferment is liable to act upon the lactic acid already formed, converting it into *butyric acid*, which is easily recognized by its odour of rank butter. Carbonic anhydride and hydrogen are evolved by this reaction. The latter gas acts powerfully upon glucose, converting it into a species of gum called *mannite*, so that lactic fermentation—in itself an intolerable nuisance—becomes the source of a new and equally objectionable waste of sugar. It can be avoided only by keeping the vats thoroughly clean; they should be washed with water acidulated with 5 per cent. of sulphuric acid. An altered ferment, or the use of too small a quantity, will tend to bring it about. The best preventives are thorough cleanliness, and the use of good fresh yeast in the correct proportion.

Viscous Fermentation.—This is usually the result of allowing the vats to stand too long before fermentation begins. It is characterized by the formation of viscous or mucilaginous matters, which render the liquor turbid, and by the evolution of carbonic anhydride and hydrogen gases, the latter acting as in the case of lactic fermentation, and converting the glucose into mannite. Viscous fermentation may generally be attributed to the too feeble action of the ferment. It occurs principally in the fermentation of white wines, beer, and beet-juice, or of other liquors containing much nitrogenous matter. It may be avoided by the same precautions as are indicated for the prevention of lactic fermentation.

It remains now to describe briefly the vessels or vats employed in the processes of fermentation. They are made of oak or pine, firmly bound together with iron bands, and they should be somewhat deeper than wide and slightly conical, so as to present as small a surface as possible to the action of the air. Their dimensions vary, of course, with the nature and quantity of the liquor to be fermented. Circular vats are preferable to square ones as being better adapted to retain the heat of their contents. The lid should close securely, and a portion of it should be made to open without uncovering the whole. For the purpose of heating or cooling the contents when necessary, it is of great advantage to have a copper coil at the bottom of the vat, connected with two pipes, one supplying steam and the other cold water. The diameter of the coil varies according to the size of the vat.

The room in which the vats are placed should be made as free from draughts as possible by dispensing with superfluous doors and windows; it should not be too high and should be enclosed by thick walls in order to keep in the heat. As uniformity of temperature is highly desirable, a thermometer should be kept in the room, and there should be stoves for supplying heat in case it be required. Every precaution must be taken to ensure the most absolute cleanliness; the floors should be swept or washed with water daily, and the vats, as pointed out above, must be cleaned out as soon as the contents are removed. For washing the vats, lime-water should be used when the fermentation has been too energetic or has shown a tendency to become acid; water acidulated with sulphuric acid is used when the action has been feeble and the fermented liquor contains a small quantity of undecomposed sugar. Care must be taken to get rid of carbonic anhydride formed during the operation. Buckets of lime-water are sometimes placed about the room for the purpose of absorbing this gas; but the best way of getting rid of it is to have a number of holes, 3 or 4 in. square, in the floor, through which the gas escapes by reason of its weight. The dangerous action of this gas and its effects upon animal life when unmixed with air are too well known to necessitate any further enforcement of these precautions.

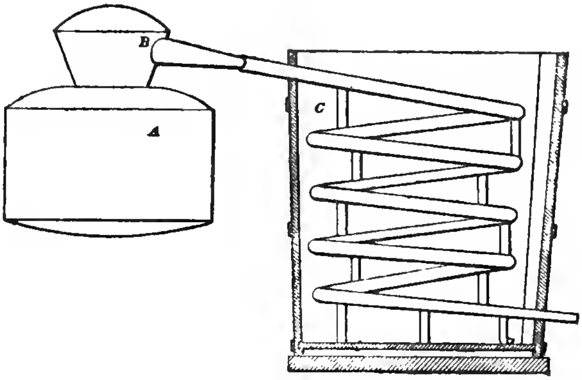
DISTILLATION.—The fermented liquors obtained in the manner described above, are composed essentially of volatile substances, such as water, alcohol, essential oils and a little acetic acid, and of non-volatile substances, such as cellulose, dextrine, unaltered sugar and starch, mineral matters, lactic acid, &c.

The volatile constituents of the liquor possess widely different degrees of volatility; the alcohol has the lowest boiling point, water the next, then acetic acid, and last the essential oils. It will thus be seen that the separation of the volatile and non-volatile constituents by evaporation and condensation of the vapours given off is very easily effected, and that also by the same process, which is termed *distillation*, the volatile substances may be separated from one another. As the acetic acid and essential oils are present only in very small quantities, they will not require much consideration. The aim of the process is to separate as completely as possible the alcohol from the water which dilutes it. At the beginning of this article, we have given a table showing the amount of alcohol contained in the vapours given off from alcoholic liquids of different strengths, and also their boiling points. A glance at this table will show to what an extent an alcoholic liquor may be strengthened by distillation, and how the quantity of spirit in the distillate increases in proportion as that contained in the original liquor diminishes. It will also be seen that successive distillations of spirituous liquors will ultimately yield a spirit of very high strength. As an example, suppose that a liquid containing 5 per cent. of alcohol is to be distilled. Its vapour condensed gives a distillate containing 42 per cent. of alcohol, which, if re-distilled, affords another containing 82 per cent. This, subjected again to distillation, yields alcohol of over 90 per cent. in strength. Thus three successive distillations have strengthened the liquor from 5 per cent. to 90 per cent. This, of course, is speaking theoretically; in practise it is possible to obtain results so absolutely perfect, only by leaving behind a considerable quantity of spirit in the distilling apparatus after each distillation.

It will thus be clear that the richness in alcohol of the vapours given off from boiling alcoholic liquids is not a constant quantity, but that it necessarily diminishes as the ebullition is continued. For example, a liquor containing 7 per cent of alcohol yields, on boiling, a vapour containing 50 per cent. (see table, p. 192). The first portion of the distillate will, therefore, be of this strength. But, as the vapour is proportionally richer in alcohol, the boiling liquor must become gradually weaker, and, in consequence, must yield weaker vapours. Thus, when the proportion of alcohol in the boiling liquid has sunk to 5 per cent., the vapours condensed at that time will contain only 40 per cent.; at 2 per cent. of alcohol in the liquor, the vapours yield only 28 per cent., and at 1 per cent., they will be found when condensed to contain only 13 per cent. From this it will be understood that if the distillation be stopped at any given point before the complete volatilization of all the alcohol, the distillate obtained will be considerably stronger than if the process had been carried on to the end. Moreover, another advantage derived from checking the process before the end, and keeping the last portions of the distillate separate from the rest, besides that of obtaining a stronger spirit, is that a much purer one is obtained also. The volatile, essential oils, mentioned above, are soluble only in strong alcohol, and insoluble in its aqueous solutions. They distil also at a much higher temperature than alcohol, and so are found only among the last products of the distillation, which result from raising the temperature of the boiling liquid. This system of checking the distillation and removing the products at different points is frequently employed in the practice of rectification.

The apparatus employed in the process of distillation is called a *still*, and is of almost infinite variety. The very simplest form is shown in Fig. 174, and consists of two essential parts, the still or boiler A, which is made of tinned copper, and enters the furnace, and the cooler or worm B, a pipe of block-tin or tinned copper, bent into a spiral and connected with the top of the still. The liquid is boiled in the still, and the vapours passing over are condensed in the pipe, which is placed in a tub or vessel containing cold water. This simple apparatus is not much employed in distilling, as it is impossible to get sufficiently pure products from it on a commercial scale. In an arrangement of this kind, the vapours of alcohol and water are condensed together. But if, instead of filling the cooler with cold water, it be kept at a temperature of 80°, the greater part of the water will be condensed; but the alcohol, which boils at 78°, passes through the coil uncondensed. If, therefore, the water be condensed and collected separately in this manner, and the alcoholic vapours be conducted into another cooler, kept at a temperature below 78°, the alcohol will be obtained in a much higher state of concentration than it would be by a process of simple distillation. Supposing, again, that vapours containing but a small quantity of alcohol are brought into contact with an alcoholic liquid of lower temperature than the vapours themselves, and in very small quantity, the vapour of water will be partly condensed, so that the remainder will be richer in alcohol than it was previously. But the water, in condensing, converts into vapour a portion of the spirit contained in the liquid interposed, so that the uncondensed vapours passing away are still further enriched by this means. Here, then, are the results obtained: the alcoholic vapours are strengthened, firstly, by the removal of a portion of the water

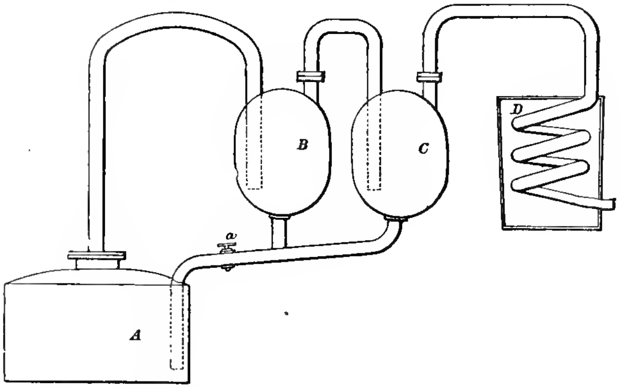
174.



wherewith they were mixed; and then by the admixture with them of the vaporized spirit placed in the condenser. By the employment of some such method as this, a very satisfactory yield of spirit may be obtained, both with regard to quality, as it is extremely concentrated, and to the cost of production, since the simple condensation of the water is made use of to convert the spirit into vapour without the necessity of having recourse to fuel. The construction of every variety of distilling apparatus now in use is based upon the above principles.

The first distilling apparatus for the production of strong alcohol on an industrial scale was invented by Edward Adam, in the year 1801. The arrangement is shown in Fig. 175, in which is a still A to contain the liquor. The vapours were conducted by a tube into the egg-shaped vessel B, the tube reaching nearly to the bottom; they then passed out by another tube into a second egg C; then, in some cases, into a third, not shown in the figure, and finally into the worm D. The liquor condensed in the first egg is stronger than that in the still, while that found in the second and third is stronger than either. The spirit which is condensed at the bottom of the worm is of a very high degree of strength. At the bottom of each of the eggs, there was a tube connected with the still, by which the concentrated liquors could be run back into it. In the tube, was a stop-cock *a*, by regulating which, enough liquor could be kept in the eggs to cover the lower ends of the entrance pipes, so that the alcoholic vapours were not only deprived of water by the cooling which they underwent in passing through the eggs, but were also mixed with fresh spirit obtained from the vaporization of the liquid remaining in the bottom of the eggs, in the manner already described. Adam's arrangement fulfilled, therefore, the two conditions necessary for the production of strong spirit inexpensively; but unfortunately it had also serious defects. The temperature of the egg could not be maintained at a constant standard, and the bubbling of the vapours through the liquor inside created too high a pressure. It was, however, a source of great profit to its inventor for a long period, although it gave rise to many imitations and improvements of greater or less merit. Among these are the stills of Solimani and Berard which more nearly resemble those of the present day. Utilizing the experience which had been gained by Adam, Solimani, and Berard, and avoiding the defects which these stills presented, Cellier-Blumenthal devised an apparatus which has become the basis of all subsequent improvements; indeed, every successive invention has differed from this arrangement, merely in detail, the general principles being in every case the same. The chief defect in the three stills above-mentioned was that they were intermittent, while that of Cellier-Blumenthal is continuous; that is to say, the liquid for distillation is introduced at one end of the arrangement, and the alcoholic products are received continuously, and of a constant degree of concentration, at the other. The saving of time and fuel resulting from the use of this still is enormous. In the case of the previous stills, the fuel consumed amounted to a weight nearly three times that of the spirit yielded by it; whereas, the Cellier-Blumenthal apparatus reduces the amount to one-quarter of the weight of alcohol produced. Fig. 176 shows the whole arrangement, and Figs. 177 to 181 represent different parts of it in detail. In Fig. 176, A is a boiler, placed over a brick furnace; B is the still, placed beside it, on a slightly higher level and is heated by the furnace flue which passes underneath it. A pipe *c* conducts the steam from the boiler to the bottom of the still. By another pipe *d*, which is furnished with a stop-cock and which reaches to the bottom of the still A, the alcoholic liquors in the still may be run from it into the boiler; by opening the valve K, the spent liquor may be run out at *a*. The glass tubes *b* and *f* show the height of liquid in the two vessels. The still is surmounted by a column C, shown in section in Fig. 177. This column contains the arrangement

175.



shown in Fig. 178, which consists of a series of spherical copper capsules, placed one above the other, and kept apart by three metallic rods passing through the series. These capsules are of different diameters; the larger ones, which are nearly the diameter of the column, are placed with the rounded side downwards, and are pierced with small holes; the smaller ones are turned bottom upwards. Into the top capsule, is made to flow a stream of the liquid to be distilled, which, running through the small holes, falls upon the smaller capsule beneath, and from this upon the one next below, and so throughout the whole of the series until it reaches the bottom and falls into the still. The vapours rise up into the column from the still and meet the stream of spirit, converting it partially into vapour and pass out at the top, considerably enriched, into the column D, Fig. 180, which contains a system resembling in principle that of Adam; here the vapours are still further strengthened. Fig. 179 is an interior, and Fig. 180 a sectional view of this column, the "rectifying column," as it is called. It contains six vessels, placed one above the other

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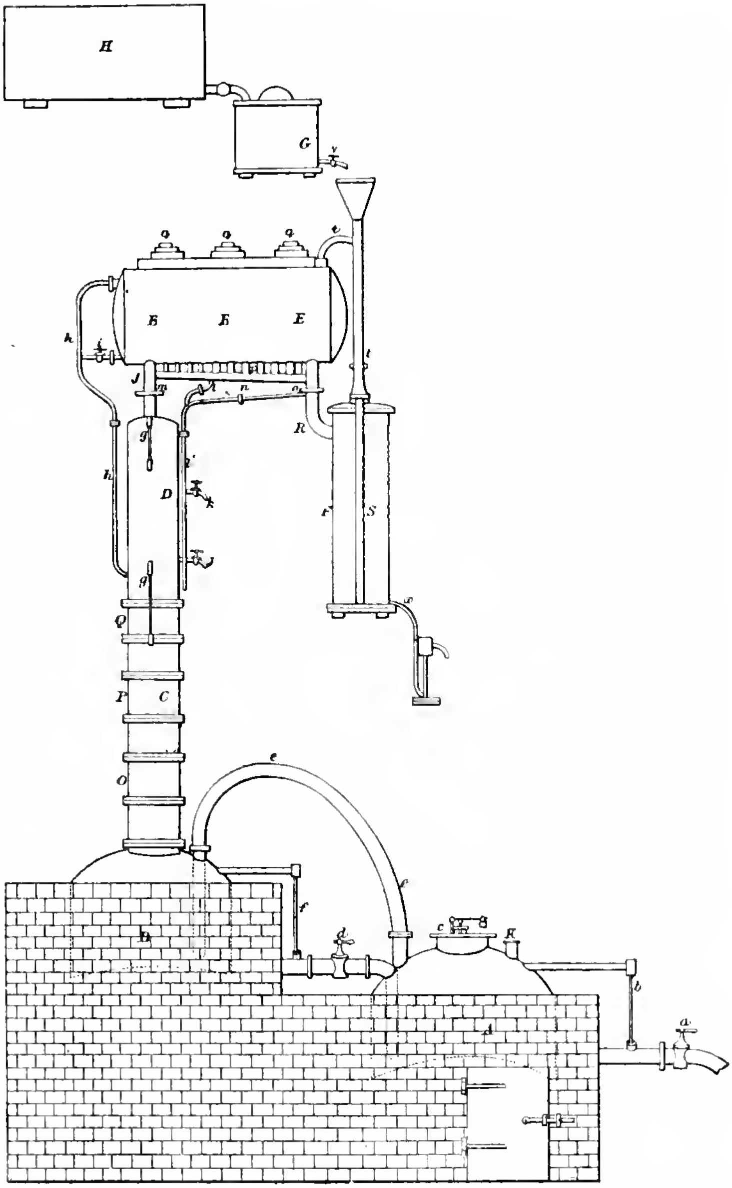
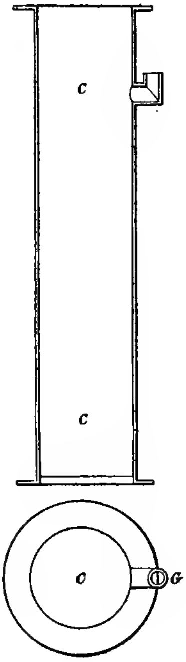


in an inverted position. These are so disposed that the vapours traverse a thin layer of liquor in each. The condensed liquid flows back into the column C, and the uncondensed vapours pass into the next part of the apparatus.

Leaving this column, the vapours are conducted into a horizontal cylinder E, containing a coil S, Fig. 181, which lies in a hot liquid. This liquid is the liquor which has to be distilled.

177.



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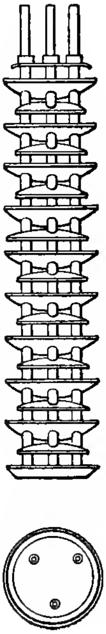

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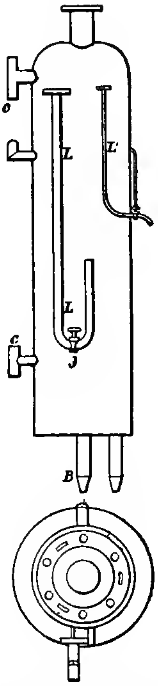

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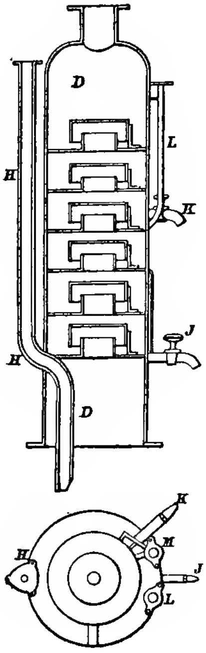
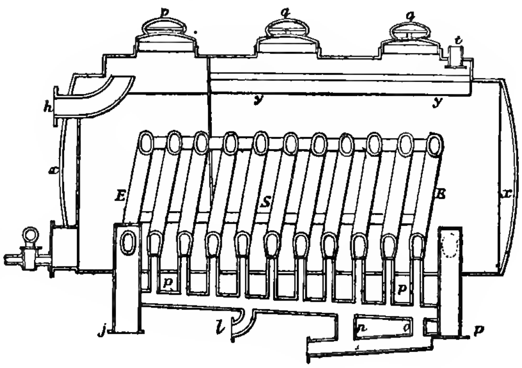


Entering by the pipe *t*, Fig. 181, it is distributed over holes in the plate *y y*, and, falling in drops into the cylinder, is heated by contact with the coil S. The cylinder is divided into two compartments by a diaphragm which is pierced with holes at its lower extremity; through these holes the liquor flows into the second compartment, and passes out at the top, where it runs through the pipe *a*, into the top of the column C. The vapours are made to traverse the coil S, which is kept at an average temperature of 50° in the right-hand compartment and somewhat higher in the other. They pass first through J into the hottest part of the coil, and there give up much of the water with which they are mixed, and the process of concentration continues as they pass through the coil. Each spiral is connected at the bottom with a vertical pipe by which the condensed liquors are run off; these are conducted into the pipe P P. Those which are condensed in the hottest part of the coil, and are consequently the weakest, are led by the pipe L into the third vessel in the column D, Fig. 180, while the stronger portions pass through L′ into the fifth. The stop-cocks *a o* regulate the flow of liquid into these vessels, and consequently also the strength of the spirit obtained.

181.



Lastly, as they leave the cylinder, the highly concentrated vapours are condensed in the vessel F, which contains another coil. This is kept cool by a stream of liquor flowing from the reservoir

H into the smaller cistern G, from which a continuous and regular flow is kept up through the tap *o* into the funnel tube S, and thence into the condenser F; it ultimately flows into the cylinder E through the pipe *t*, there being no other outlet. The finished products run out by the pipe *x* into suitable receivers.

ALCOHOL FROM WINE.—The most important of the many sources from which alcohol is obtained on an industrial scale, is wine. The distillation of alcohol from wines is confined exclusively to France, where the best wines for this purpose are prepared. The spirit obtained from them is used very extensively in the same country for the production of all kinds of brandy. As the wines employed are generally of special preparation and must be chosen with much care, we shall here devote a little space to the details of their preparation from the grape, as carried on in France.

Of all the fruits employed as sources of alcohol, the grape must occupy the first place. Not only does it present the advantage of containing in itself the sugar, the water, and the ferment necessary for the conduct of the fermenting process, but the spirit which it yields is unequalled for fineness, bouquet, or delicacy of aroma. The grapes should be just ripe when gathered, a period recognized by the softening of the fruit, the brownness of the stem, and the sweetness and stickiness of the expressed juice. Much care is requisite in the performance of cutting, in order to avoid bruising the fruit; this should be performed with shears or scissors, not with a knife.

The next operation is the *crushing*, the object of which is to mix up and to bring into contact with each other all the constituent elements of the grape. If this be not done, it withers and dries up without undergoing the necessary fermentation. It may be conducted advantageously in a square box, open at the top and with holes pierced in the bottom; this box is fixed upon the edges of the vat. Inside it, the fruit is trampled under foot by a man wearing wooden boots, and the juice pressed out flows through the perforated bottom of the box into the vat; this is continued until the vat is full. The refuse, or *marc*, as it is called, may either be fermented in the vat with the juice, or in a separate vessel. This plan is much to be preferred to that of crushing the grapes in the vat, as, in the latter case, much of the fruit floats about in the must untouched, and thus escapes fermentation. It is an advantage not to stem the grapes before crushing, as the presence of the stems in the vat promotes and regulates the fermentation; moreover, they contain an astringent principle, which assists in preserving wines containing but little alcohol. Sufficient room must be left in the vat to allow for the increase in volume undergone by its contents, in consequence of the elevation of temperature resulting from the fermentation.

In some cases, when the process is being conducted on a very large scale, and the vats employed are of great size, it is necessary to conduct the pressing of the grapes upon a wide floor, surrounded by a trench or gutter, connected with a cistern, from which the expressed juice is run into the vats. In other places, it is customary to press the grapes between two rollers placed sufficiently far apart to avoid breaking the seeds. Every distiller, however, varies the *modus operandi* according to the scale upon which he is working.

The vats are round in shape, and may be either of oak, hooped together with iron hoops, or of masonry. The latter is preferable in the case of wines intended for distillation. In the course of a day or two, fermentation sets in, and the must undergoes the changes described on p. 195, the resulting liquid bearing the name of wine. The room in which the process is conducted should have a temperature of about 15°, and the fruit should be at the same degree at the time of crushing. The vats may be heated before being filled.

In some cases, when the grapes have been grown on moist land, or the season has been a rainy one, it happens that the must contains too small a proportion of sugar, and it is, therefore, necessary to diminish the quantity of water present by artificial evaporation; or the excess of water may be counteracted (and this is by much the better method) by the addition of the theoretical quantity of sugar required to bring the must to the ordinary strength; this quantity is determined by the degree of concentration of the must as shown by the saccharometer. When ascertained, the necessary quantity is dissolved in a little of the must by boiling over a fire, and then poured into the vat. The whole is well stirred together and then covered up.

When the process is complete, the wine is drawn off, or *racked*. As the quality of the wine depends in a great measure, upon the performance of this at the right moment, much care must be employed to determine it. The only sure guide consists in observing, by means of the saccharometer, the progress of the conversion of sugar into alcohol, so as to note the exact moment when the whole of the saccharine principle is decomposed. After racking the wine, a certain quantity is always left in the marc, at the bottom of the vat. This is obtained by submitting the marc to the action of a wine-press, of which there are many varieties. The wine expressed is harsher and more tart than that previously drawn off, and should therefore be kept separate.

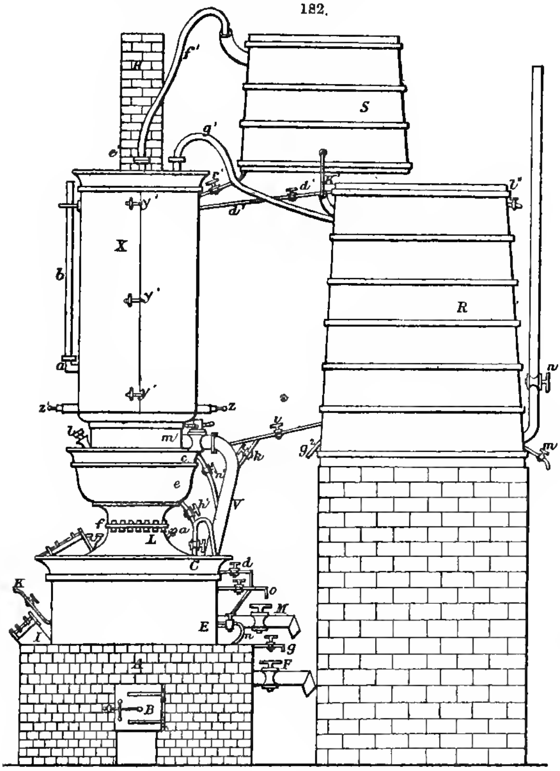
Wine contains alcohol in proportions varying from 7 to 24 per cent., a large proportion of water, small quantities of undecomposed sugar, besides traces of albumen, pectin, and tannin, tartaric and malic acids, colouring matters, essential oils, &c.

In making choice of the wines to be distilled, the first consideration is the amount of alcohol which they contain, and then the quality of the spirit which they will yield. Their richness in alcohol is readily determined by means of Guy Lussac's *test-still.* One-third of the wine is distilled off and two volumes of water are added to the remainder; the strength may then be read off by means of an alcoholometer. As regards the quality of the brandy obtained, much depends upon the purity, fineness, and age of the wine employed. White wines, or those made from the juice alone of the grape, are to be preferred; all the best varieties of "Cognac" brandy are distilled from these wines.

Another variety of spirit, called in France *Eau-de-vie de marc,* is prepared from the marcs or refuse of the wine-press. After the grapes have been pressed, the marcs contain a certain amount of sugar, if the grapes were pressed before fermentation, and of wine, if this process was carried on, as is sometimes the case, after fermentation. The marcs are transferred to vats where they are covered with water and stirred up vigorously. Weighted sieves are then placed in the vats in such a manner that the marc is pressed down to the bottom, leaving a layer of clear liquor above it. Air is then excluded by covering the vat securely. After fermentation, which occupies about five days, the clear liquor is drawn off and distilled. On account of its rough, unpleasant taste and odour, the spirit so obtained is seldom used for direct consumption, but is generally added to the fermenting vats for the purpose of increasing the strength of liquors which contain a small proportion of sugar. Employed in this way, the spirit loses its objectionable qualities, and is found to enhance the colour and strength of the wine to which it is added.

The still most commonly used in France for distilling brandy from wines, is known as the "Allègre" still, and is represented in elevation in Fig. 182, and in vertical section in Fig. 183. A B is the furnace; E the boiler, which is partly enclosed in brickwork, and having an emptying-cock F near the bottom. A try-cock *g* for ascertaining the level of the liquid in the interior should be placed at about the height of the dotted line in the section. K is another try-cock for ascertaining the end of the operation; at this point, the vapours emitted on turning the cock, will no longer take fire. L is another boiler, placed above the previous one, fitted with an emptying cock M, a try-cock *o*, and a small pipe *n*, which puts the two boilers in communication. Q is a plate separating the two boilers. In its centre there is a pipe *r*, surrounded by a series of concentric cylinders *s t u* and *v*, disposed as shown in the figure. These cylinders form a system by which

182.



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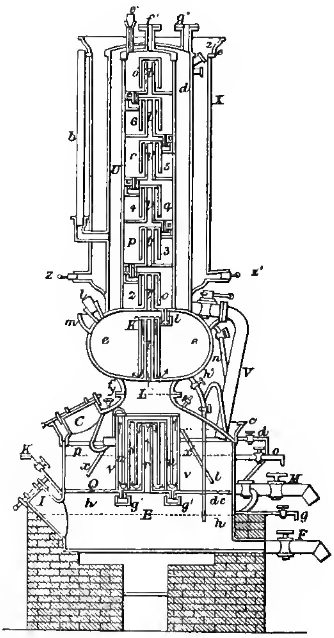


the vapours of spirit and water are condensed at different temperatures and thereby effectually separated from each other; the liquor formed is conducted away by the pipe *g g*. The vapours from the boilers are thus made to travel through the spaces between these concentric cylinders, and finally pass out at the openings *k k*, coming again into contact with the liquor in L. A curved tube *y*, connected with the interior of the system, is filled with water, and permits the entrance of air in case of too sudden condensation. *a* is a try-cock corresponding to K in the boiler E. C is a manhole for the purpose of cleaning the boiler. The vapours from the upper boiler pass upwards into the circular rectifier *e* which rests upon the neck of the boiler L; this vessel may be cleaned out by means of the opening at *l*. Six compartments, *o p q r s o′*, arranged as shown in the figure, are placed above the rectifier *e* in the form of a column. Communication between these compartments is established by means of the pipes *l′ l′*; besides this, the compartments are also connected by the small pipes 1, 2, 3, 4, 5 and 6, which reach down to within 5 centimetres of the bottom of each, falling into a little trough similar to *g g* in the boiler E. U is a cylinder surrounding the column. The wine circulates in this, condensing and concentrating the ascending vapours, and afterwards escaping through *r* into the boiler L. S is a cistern containing the wine, which is run into the cylinder U by a little pipe *f*. Through another pipe *f′* the vapours escape from the column in order to condense, while the vapours from the cylinder U are led away through *f″* into the coils contained in the vats S and R. X is an outer covering to prevent the loss of heat by radiation. In grain distilleries, this is used for drying malt, which is placed in the interior. An opening at *c*, serves for the admission of water when it is required to clean the column.

The operation of distilling is performed by this apparatus in the following way:—All the cocks are closed excepting those at *o* and *g*. The cooler R is filled with water, and the cock at *x″* opened. The upper condenser S is filled with the wine to be distilled; this condenser contains a coil in which the vapours passing through *f′* are partially condensed, and which communicates by K′ with the large coil in the cooler R. When R is filled, the water is run through *i* into the boiler *c*, when it is made to boil by passing steam through the apparatus until the wine in S has reached a temperature of about 40°. The cock in the pipe *c′* is then opened to allow the wine to run from S into the cylinder U, S being re-filled with cold wine. The cocks in the pipe *h* are then opened in order to allow the water in the compartments of the column and in the rectifier to run out. These cocks are then closed again, and the heat is diminished as far as possible, by means of a damper, to allow the water to run out from the two boilers and from the rectifier by the cocks F M and *h*.″ While this is going on, the manhole I is opened and the boiler thoroughly cleaned out. This cleansing of the apparatus is not necessary every time that the process is interrupted, but only when the interruption is of some duration. When work is stopped for a length of time, the apparatus is left full of water until the work is resumed. As soon as the hot water has run out, the cocks F, M, and *h″* are closed, and the lower boiler is filled up as far ss the cock *g*; *g* and I are then closed, and heat is again applied to the apparatus. When the water begins to boil, the boiler L is filled from the pipe *r* with the wine previously heated in the cylinder U, up to the point *o*; *o* and *r* are then closed, and *c′* is opened in order to refill U with the contents of the cistern S. The water in E soon begins to boil, and the steam generated heats the lower part of the boiler L, and passing up *r*, around the cylinder, and out at *k k*, it passes through the wine into the upper part of L. The wine is thus gradually heated to the boiling point, and the vapours given off are led by *i* into the rectifier *c*, where it is partly concentrated; the remainder passes into the upper column by the pipes *l′ l′ l′*. Here the chief part of the condensation is carried on; as the vapours gradually rise they are deprived of water, until they ultimately find their way through *f* into the coil contained into the cistern S, and from that into the cooler R, where they are completely condensed. The finished spirit is run out at *m′*.

The weak liquors from the several compartments of the upper column return through the pipes numbered 6, 5, 4, 3, 2, 1, until they reach the boiler L. The whole operation, as above described, occupies three hours; but when the apparatus has become properly heated in all parts, two hours only are required.

Alcohol from Molasses.—Another common source of alcohol is molasses or treacle. Molasses is the uncrystallizable syrup which constitutes the residuum of the manufacture and refining of cane and beet sugar. It is a dense, viscous liquid, varying in colour from light yellow to almost black, according to the source from which it is obtained; it tests usually about 40° by Baume's hydrometer. The molasses employed as a source of alcohol must be carefully chosen; the lightest in colour is the best, containing most uncrystallized sugar. The manufacture is extensively carried on in France, where the molasses from the beet sugar refineries is chiefly used on account of its low price, that obtained from the cane sugar factories being considerably dearer. The latter is, however, much to be preferred to the former variety as it contains more sugar. Molasses from the beet sugar refineries yields a larger quantity and better quality of spirit than that which comes from the factories. Molasses contains about 50 per cent. of saccharine matter, 24 per cent. of other organic matter, and about 10 per cent. of inorganic salts, chiefly of potash. It is thus a substance rich in matters favourable to fermentation. When the density of molasses has been lowered by dilution with water, fermentation sets in rapidly, more especially if it has been previously rendered acid. As, however, molasses from beet generally exhibits an alkaline reaction, it is found necessary to acidify it after dilution; for this purpose sulphuric acid is employed, in the proportion of about 4½ lb. of the concentrated acid to 22 gallons of molasses, previously diluted with 8 or 10 volumes of water. Three processes are thus employed in obtaining alcohol from molasses: dilution, acidification, and fermentation. The latter is hastened by the addition of a natural ferment, such as brewers' yeast. It begins in about eight or ten hours, and lasts upwards of sixty.

In Germany, where duty is imposed upon the distilleries according to the capacity of the fermenting vats, the molasses is not diluted to such an extent as in France, where the duty is upon the manufactured article. In the former case the liquor, before fermentation, tests usually as high as 12° Baumé, whereas in France it is diluted until it tests 6° or 8°, a degree which is much more favourable to rapid and complete fermentation. In consequence of this difference in the concentration of the unfermented liquor, the degree of temperature at which the process is begun is higher in the case of the strong liquor than when it is more dilute. In Germany, the temperature at which fermentation begins is about 25°, and this is raised during the operation to 30°, whilst in France a much lower temperature suffices. Moreover, owing to the enormous size of the French vats, the temperature rises so quickly that it must be moderated by passing a current of cold water through a coil of pipe placed on the bottom of the vat. Two cwts. of molasses at 42° Baumé will furnish about 6 gallons of pure spirit. The spirit of molasses has neither the taste nor the odour of spirit from wine; it is sweeter, and when the distillation and rectification have been properly conducted, it may be considered as a type of alcohol in its purity, for it has neither taste nor any peculiar aroma. In this state it is called *fine spirits*, and may be employed in the manufacture of liqueurs, for improving common brandies, and especially for refining the *trois-six* (rectified spirit) of Montpellier. In those districts of France where the beet is largely cultivated for the manufacture of sugar, and the molasses is converted into alcohol, the waste liquor is made a source of no inconsiderable profit by concentrating it and incinerating the residue, from which is obtained, for the use of the soap-boiler, a caustic potash of superior quality. In addition to the alcohol, good beet molasses will yield 10 or 12 per cent. of commercial, or from 7 to 8 per cent. of refined potash. In addition to this a method has lately been proposed by M. Camille Vincent of collecting the ammonia water, tar, and oils given off when this residue is calcined, and utilizing them for the production of ammonia and *chloride of methyl*, which latter substance possesses considerable commercial value. The process has been made the subject of a paper read by Professor Roscoe before the Royal Institution, who prophesies for it the most complete success when tried on an industrial scale. "Chloride of methyl," he says, "has up to this time, indeed, not been obtained in large quantities; but it can be employed for two distinct purposes: (1) it serves as a means of producing artificial cold; (2) it is most valuable for preparing methylated dyes, which are at present costly, inasmuch as they have hitherto been obtained by the use of methyl iodide, an expensive substance."

Besides the molasses of the French beet sugar refineries, large quantities result from the manufacture of cane sugar in Jamaica and the West Indies. This is entirely employed for the distillation of *rum*. As the pure spirit of Jamaica is never made from sugar, but always from molasses and skimmings, it is advisable to notice these two products, and, together with them, the exhausted wash commonly called *dunder*.

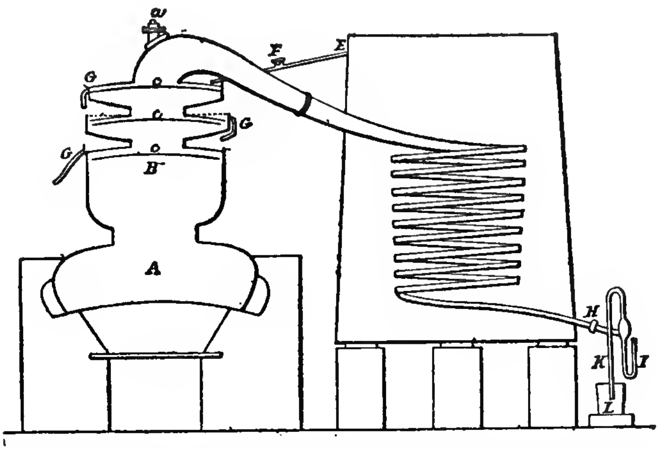
The molasses proceeding from the West Indian cane sugar contains crystallizable and uncrystallizable sugar, gluten, or albumen, and other organic matters which have escaped separation during the process of defecation and evaporation, together with saline matters and water. It therefore contains in itself all the elements necessary for fermentation, i. e. sugar, water, and gluten, which latter substance, acting the part of a ferment, speedily establishes the process under certain conditions. *Skimmings* comprise the matters separated from the cane juice during the processes of defecation and evaporation. The scum of the clarifiers, precipitators, and evaporators (see Sugar Manufacture), and the precipitates in both clarifiers and precipitators, together with a proportion of cane sugar mixed with the various scums and precipitates, and the "sweet-liquor" resulting from the washing of the boiling-pans, &c., all become mixed together in the skimmings-receiver, and are fermented under the name of "skimmings." They also contain the elements necessary for fermentation, and accordingly they very rapidly pass into a state of fermentation when left to themselves; but, in consequence of the glutinous matters being in excess of the sugar, this latter is speedily decomposed, and the second, or acetous fermentation, commences very frequently before the first is far advanced. *Dunder* is the fermented wash after it has undergone distillation, by which it has been deprived of the alcohol it contained. To be good, it should be light, clear, and slightly bitter; it should be quite free from acidity, and is always best when fresh. As it is discharged from the still, it runs into receivers placed on a lower level, from which it is pumped up when cool into the upper receivers, where it clarifies, and is then drawn down into the fermenting cisterns as required. Well-clarified dunder will keep for six weeks without any injury.

Good dunder may be considered to be the liquor, or "wash," as it is termed, deprived by distillation of its alcohol, and much concentrated by the boiling it has been subjected to; whereby the substances it contains, as gluten, gum, oils, &c., have become, from repeated boilings, so concentrated as to render the liquid mass a highly aromatic compound. In this state it contains at least two of the elements necessary for fermentation, so that, on the addition of the third, viz. sugar, that process speedily commences.

The first operation is to clarify the mixture of molasses and skimmings previous to fermenting it. This is performed in a leaden receiver holding about 300 or 400 gallons. When the clarification is complete, the clear liquor is run into the fermenting vat, and there mixed with 100 or 200 gallons of water (hot, if possible), and well stirred. The mixture is then left to ferment. The great object that the distiller has in view in conducting the fermentation is to obtain the largest possible amount of spirit that the sugar employed will yield, and to take care that the loss by evaporation or acetification is reduced to a minimum. In order to ensure this, the following course should be adopted. The room in which the process is carried on must be kept as cool as it is possible in a tropical climate; say, 24° to 27°. Supposing that the fermenting vat has a capacity of 1000 gallons, the proportions of the different liquors run in would be 200 gallons of well-clarified skimmings, 50 gallons of molasses, and 100 gallons of clear dunder; they should be well mixed together. Fermentation speedily sets in, and 50 more gallons of molasses are then to be added, together with 200 gallons of water. When fermentation is thoroughly established, a further 400 gallons of dunder may be run in, and the whole well stirred up. Any scum thrown up during the process is immediately skimmed off. The temperature of the mass rises gradually until about 4° or 5° above that of the room itself. Should it rise too high, the next vat must be set up with more dunder and less water; if it keeps very low, and the action is sluggish, less must be used next time. No fermenting principle besides the gluten contained in the wash is required. The process usually occupies eight or ten days, but it may last much longer. Sugar planters are accustomed to expect 1 gallon of proof rum for every gallon of molasses employed. On the supposition that ordinary molasses contains 65 parts of sugar, 32 parts of water, and 3 parts of organic matter and salts, and that, by careful fermentation and distillation, 33 parts of absolute alcohol may be obtained, we may then reckon upon 33 lb. of spirit, or about 4 gallons, which is a yield of about $5\frac{2}{5}$ gallons of rum, 30 per cent. over-proof, from 100 lb. of such molasses.

The operation of distilling is often carried on in the apparatus represented in Fig. 184. It is termed the Patent Simplified Distilling Apparatus; it was originally invented by Corty, but it has since undergone much improvement. A is the body of the still, into which the wash is

184.



put; B, the head of the still; *c c c* three copper plates fitted upon the upper part of the three boxes; these are kept cool by a supply of water from the pipe E, which is distributed by means of the pipes G G G. The least pure portion of the ascending vapours is condensed as it reaches the lowest plate, and falls back, and the next portion as it reaches the second plate, while the purest and lightest vapours pass over the goose-neck, and are condensed in the worm. The temperature of the plates is regulated by altering the flow of water by means of the cock F. For the purpose of cleaning the apparatus, a jet of steam or water may be introduced at *a*. A gas apparatus is affixed at the screw-joint H, at the lower end of the worm, which addition is considered an important part of the improvement. The part of the apparatus marked I becomes filled soon after the operation has commenced: the end of the other pipe K is immersed in water in the vessel L. The advantage claimed for this apparatus is that the condensation proceeds in a partial vacuum, and that there is therefore a great saving in fuel. One of these stills, having a capacity of 400 gallons, is said to work off four or five charges during a day of twelve hours, furnishing a spirit 35 per cent. over-proof.

185.

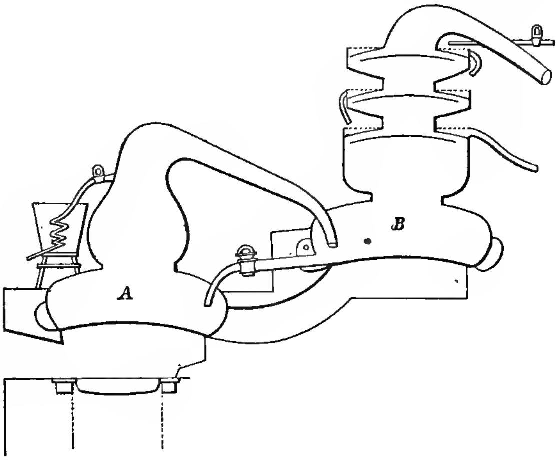
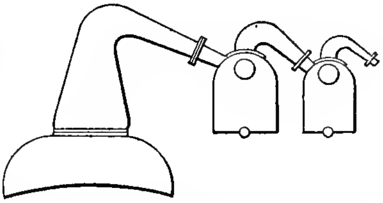


Fig. 185 represents a double still which is largely employed in the colonies. It is simply an addition of the common still A to the patent still B. From time to time the contents of B are run off into A, those of A being drawn off as dunder, the spirit from A passing over into B. Both stills are heated by the same fire; and it is said that much fine spirit can be obtained by their use at the expense of a very inconsiderable amount of fuel. In Jamaica, however, nothing is likely to supersede the common still and double retorts, shown in Fig. 186. It is usually the custom to pass the tube from the second retort through a charger containing wash, by which means the latter is heated previous to being introduced into the still; the tube then proceeds directly to the worm-tank. With an arrangement of this kind, a still holding 1000 gallons should produce 500 gallons of rum (30 to 40 per cent. over-proof), between the hours of five in the morning and eight in the evening. The first gallon of spirit obtained is termed "low wines," and is used for charging the retorts, each of which contains 15 to 20 gallons. After this, rum of 40 to 45 per cent. over-proof flows into clean cans or other vessels placed to receive it.

186.



Alcohol from Grain.—The different cereals constitute a very important source of alcohol in this country and also in Belgium, Holland, Germany, and America. The spirit obtained from them is termed "grain spirit;" large quantities of that distilled in England are sent to London for the preparation of gin, the remainder going to the Scotch and Irish whiskey distilleries. The cereals contain an amylaceous or starchy substance, which, under the influence of diastase, is converted into fermentescible sugar. The quantity of sugar, and consequently the yield of alcohol, produced from each variety differs widely. The following table shows the results which may be obtained from good workmanship:—

100 kilos.	wheat	give	32	litres	pure alcohol.
„	rye	„	28	„	„
„	barley	„	25	„	„
„	oats	„	22	„	„
„	buckwheat	„	25	„	„
„	maize	„	25	„	„
„	rice	„	35	„	„

From this it will be seen that rice, wheat, rye, and maize are more frequently employed than the rest; barley and buckwheat are added to these in some proportions. Oats, owing to their high price, are rarely used, except for the purpose of giving an aroma to the alcoholic products of the other grains. Some care is requisite in making choice of the grains for fermentation. The wheat selected should be farinaceous, heavy, and dry. The barley should be free from chaff, quite fresh, and in fine large grains of bright colour. Rice, which of all grains is the most productive to the distiller, should be dull white, slightly transparent, without odour, and of a fresh farinaceous taste; the rice of commerce is chiefly supplied from the East Indies, Piedmont, and the United States.

The flour, or farinaceous part of grain, is composed essentially of starch, gluten, albumen, mucilage, a little sugar, and traces of inorganic salts.

The following table shows the proportions of these substances in the commonest grains:—

Grains.	Starch.	Gluten and other Azotized Substances.	Dextrine, Glucose, and similar Substances.	Fatty Matter.	Cellulose.	Inorganic Salts. (Silica, Phosphates, &c.).
Wheat (average of five varieties)	65·99	18·03	7·63	2·16	3·50	2·69
Rye	65·65	13·50	12·00	2·15	4·10	2·60
Barley	65·43	13·96	10·00	2·76	4·75	3·10
Oats	60·59	14·39	9·25	5·50	7·06	3·25
Indian corn	67·55	12·50	4·00	8·80	5·90	1·25
Rice	89·15	7·05	1·00	0·80	1·10	0·90

Under certain conditions, the albumen or gluten contained in the grain has the power of converting starch into saccharine matter; this change is, however, better effected by a mineral acid, by germinated barley, or by diastase. This latter substance is a principle developed during the germination of all cereals, especially of barley. It has the remarkable property of reacting upon starchy matters, converting them, first, into a gummy substance, called *dextrine*, and then into glucose, or grape sugar. This principle does not exist in the grain before germination. Its action upon starch or flour made into a paste is very remarkable; 50 grains of diastase are sufficient to convert 100 kilos. of starch into glucose. The rapidity with which the change is effected depends upon the quantity of water employed, and the degree of heat adapted to the operation. Diastase is generally prepared from barley, as this grain germinates more readily and develops a larger proportion than any other.

There are six processes to which the grain must be subjected before it is ready for fermentation. They are—(1) Steeping, (2) Germination, (3) Drying the malt, (4) Grinding, (5) Mashing, and (6) Infusion. We shall briefly notice each of these operations.

Steeping.—This operation, which requires much attention, is conducted in a wooden vat, or stone tank, lined with hydraulic cement. The grain is placed in the tank and covered with river or well water for a space of 30 or 40 hours, according to the temperature of the atmosphere, the quality or dryness of the grain, and the character of the water. In very warm weather, the water should be changed every four or six hours, by running it out through a hole in the bottom of the vat, and running in fresh at the top; this is done in order to prevent fermentation from setting in prematurely. When the grain swells, and yields readily when crushed between the fingers, it has been sufficiently steeped, and the water is run off finally.

Germination.—After the water has run off, the grain is allowed to drain for a few hours, and is then conveyed to the malt-house. This is kept constantly at a temperature of 12°, and is always paved with stone. Here the grain is arranged in beds of two or three feet in thickness, until it becomes sensibly heated. Some hours after these beds have been prepared, a vital movement commences in the grain, attended by a considerable elevation in temperature, which increases gradually until it is about 7° or 8° higher than that of the room itself. During this time the grain absorbs oxygen, and gives out carbonic acid with much rapidity; it also becomes moist, and gives out a peculiar, somewhat agreeable, odour. The grain must not be allowed to become too warm, and should be turned over every six or eight hours, until germination begins, and then every three, four, or five hours, according to the temperature; this should always be maintained at about 15° or 16°. The whole process occupies from eight to fifteen days, according to the season; it is over when the little roots have attained a length equal to about two-thirds of that of the grain.

Drying the Malt.—This is effected in a room called a *kiln.* Here the grain is spread out in a layer about 12 in. thick, and subjected to a temperature beginning at 35°, but increasing to 55° or 60°, until the grain is nearly dry, when it may be still further raised to 80° or 90°. The germinated and dried barley is called *malt;* it is known to be of good quality when the grain is round and full of flour; when the skin is very thin; and when it has an agreeable odour and sweetish taste. Pale malt, or that which has not been altered in colour by heat, is the heaviest and best for distillation.

Grinding.—The dried malt must be coarsely ground on a mill, in order that none of the grains may escape fermentation; it is not necessary that they should be reduced to flour. If the grain be raw or unmalted, it must be ground more finely, so that it may be thoroughly penetrated by water, in the subsequent operations, and the starch more readily converted into sugar by the action of the diastase. The grain must not be ground until it is required for use, as it is liable to become musty, in which condition it loses much of its fermentescible property.

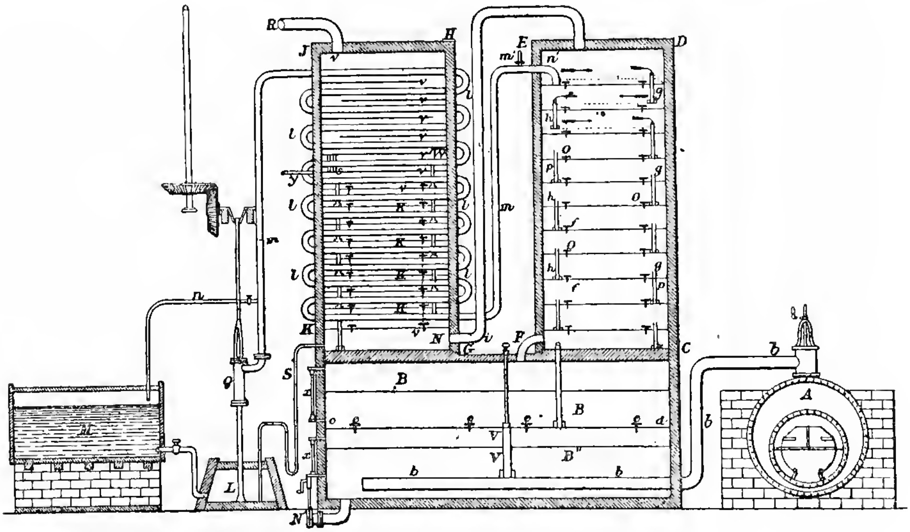
Mashing.—After being crushed, the malt, together with the other grains, is placed in a vat, and warm water is run in, in small quantities at a time, in about the proportion of a litre to every kilo. of flour; its temperature should be about 35° to 38°. During the entrance of the water the mass is well stirred, so as to cause the whole of the grain to be thoroughly soaked, and to prevent the formation of lumps. The vat must then be covered tightly and left for twenty or thirty minutes.

It usually requires three mashings to extract the whole of the saccharine and fermentescible matters contained in the grain. In some places, it is customary to boil down the liquors from the three mashings until they have acquired a specific gravity of about 1·05, the liquor from a fourth wash being kept back for the next mashing. Some distillers use enough water in the first two mashings to bring the whole to the correct degree for fermentation, the liquors from the third and fourth being boiled down to the same density and then added to the rest. In a large Glasgow distillery, the charge for the mash-tun is 260 cwts. of grain together with the proper proportion of malt. Two mashings are employed, about 28,300 gallons of water being required; the first washing has a temperature of 60°, and the second that of 80°. In Dublin, the proportion of malt employed is only about one eighth of the entire charge. One mashing is employed, and the temperature of the water is kept at about 62°. The subsequent mashings are kept for the next day's brewing.

Infusion.—The object of this important operation is the conversion of the starch of the grain into sugar by means of the diastase contained in the malt. To effect this, boiling water must be poured into the vat until the temperature of the mass reaches about 60° or 70°, the whole being well stirred meanwhile: when this temperature has been reached, the vat is again covered and left to stand for four hours, during which time the temperature should, if possible, be maintained at 60°, and on no account suffered to fall below 50°, in order to avoid the inevitable loss of alcohol consequent upon the acidity always produced by so low a temperature. In cold weather the heat should, of course, be considerably greater than in hot. It should be also remarked that the greater the quantity of water employed, the more complete will be the saccharification, and the shorter the time occupied by the process.

Having undergone all the above processes, the wash is next drawn from the mash tin into a cistern, and from this it is pumped into coolers placed at the top of the building. These coolers consist of shallow iron vessels, or, in some cases, of copper tubes kept cool by water. When the wash has acquired the correct temperature—viz. from 20° to 26°, according to the bulk operated upon—it is run down again into the fermenting vats situated on the floor beneath. 5 or 6 litres of liquid, or 2½ to 3 kilos. of dry brewer's yeast are then added for every 100 kilos. of grain; the vat is securely covered, and the contents are left to ferment. The process is complete at the end of four or five days, and if conducted under favourable conditions there should be a yield of about 28 litres of pure alcohol to every 100 kilos. of grain employed.

187.



The apparatus used in England for the distillation of grain-spirit is known as "Coffey's" still; and is shown in Fig. 187. It consists of two columns, C D E F and G H J K, placed side by side, and above a rectangular chamber, containing a steam-pipe *b* from the boiler A. This chamber is divided into two compartments by a horizontal partition, pierced with small holes, and furnished with four safety-valves *e e e e*. The column C D E F, called the *analyzer*, is divided into twelve small compartments, by means of horizontal partitions similar to the one beneath, also pierced with holes and each provided with two little valves *f*. The spirituous vapours passing up this column are led by a pipe to the bottom of the second column or *rectifier*. This column is also divided into compartments in precisely the same way, except that there are fifteen of them, the ten lowest being separated by the partitions *k*, which are pierced with holes. The remaining five partitions are not perforated, but have a wide opening as at *w*, for the passage of the vapours. Between each of these partitions passes one bend of a long zig-zag pipe *m*, beginning at the top of the column, winding downwards to the bottom, and finally passing upwards again to the top of the other column, so as to discharge its contents into the highest compartment. The apparatus works in the following way:—The pump Q is set in motion, and the zig-zag pipe then fills with the wash or fermented liquor until it runs over at *n'*. The pump is then stopped, and steam is introduced through *h*, passing up through the two bottom chambers and the short pipe *z* into the analyzing column C D E F, finally reaching the bottom of the other column by means of the pipe *i*. Here it surrounds the coil pipe containing the wash, so that the latter becomes rapidly heated. When several bends of the pipe have become heated, the pump is again set to work, and the hot wash is driven rapidly through the coil and into the analyzer at *n'*. Here it takes the course indicated by the arrows, running down from chamber to chamber until it reaches the bottom; none of the liquor finds its way through the perforations in the various partitions, owing to the pressure of the ascending steam. In its course downwards the wash is met by the steam, and the whole of the spirit which it contains is thus converted into vapour. As soon as the chamber B' is nearly full of the spent wash, its contents are run off into the lower compartment by opening a valve in the pipe V. By means of the cock N, they are finally discharged from the apparatus. This process is continued until all the wash has been pumped through.

The course taken by the steam will be readily understood by a glance at the figure. When it has passed through each of the chambers of the analyzer, the mixed vapours of water and spirit pass through the pipe *i* into the rectifying column. Ascending again, they heat the coiled pipe *m*, and are partially deprived of aqueous vapours by condensation. Being thus gradually concentrated, by the time they reach the opening at W they consist of nearly pure spirit, and are then condensed by the cool liquid in the pipe falling upon the partition *s*, and being carried away by the pipe *y* to a refrigerator. Any uncondensed gases pass out by the pipe R to the same refrigerator, where they are deprived of any alcohol they may contain. The weak liquor condensed in the different compartments of the rectifier descends in the same manner as the wash descends in the other column; as it always contains a little spirit, it is conveyed by means of the pipe S to the vessel L in order to be pumped once more through the apparatus.

Before the process of distillation commences, it is usual, especially when the common Scotch stills are employed, to add about 1 lb. of soap to the contents of the still for every 100 gallons of wash. This is done in order to prevent the liquid from boiling over, which object is effected in the following way:—The fermented wash always contains small quantities of acetic acid; this acts upon the soap, liberating an oily compound which floats upon the surface. The bubbles of gas as they rise from the body of the liquid are broken by this layer of oil, and hence the violence of the ebullition is considerably checked. Butter is sometimes employed for the same purpose.

When the still contains a charge of about 8000 gallons, distillation is carried on as quickly as possible until about 2400 gallons have passed over. This portion possesses but little strength, and is known as "*low wines*." The remainder of the 8000 gallons is received in another vessel for re-distillation, and the low wines are also re-distilled in another still, until the product acquires an unpleasant taste and smell; these, which are then called "*faints*," are collected in a vat called the "*faints back*," mixed with the impure portions of the first distillation, diluted with water, and re-distilled. The product of a further distillation then yields finished spirit.

In addition to the apparatus already described, the following vessels are employed in the British grain distilleries:—

A *wash charger*, or close-covered vat, the capacity of which must not be less than half that of the largest fermenting vat. This vessel is connected with the still by a close metal pipe, with a branch to each still provided with cocks. One end of this pipe is fixed to the bottom of the wash charger, and the end of each branch is fixed into the still. The wash charger has also another pipe fitted with a cock, one end of which is fixed to the pipe or trough communicating with the fermenting vats; it also communicates with another vessel, called the faints receiver, by means of a close pump or metal pipe and stopcock.

If the still used be of such kind that the products of the first distillation are *low wines*, another vessel, called a *low wines receiver*, must be used. This is a covered vessel, having a pump and discharging cock fixed in it for the conveyance of low wines from the receiver into the low wines and faints charger. There is also a close metal pipe, attached to and leading directly from a *safe* at the end of the worm, and fixed into the low wines receiver, so that all low wines running into this pipe from the safe shall immediately be discharged into the receiver. This safe is a close vessel into which the low wines, faints, and spirits are made to run as they leave the worm; it is kept enclosed and secured for the inspection of the excise officers whenever necessary.

The *faints receiver* is a covered vessel with a pump or discharging cock fixed in it for the conveyance of faints into the low wines and faints charger, and there is a close metal pipe attached to and leading from the safe mentioned above, and fixed into the faints receiver, so that all faints running into this pipe from the safe shall be immediately discharged into the receiver. The *low wines and faints charger* alluded to above is another covered vessel connected with the still by a close metal pipe and cock; one end of this pipe is fixed into the bottom of the charger and the other into the still. This charger communicates directly with the low wines and faints receiver respectively, by pipes, one end fixed to the charger, and the other to the pump or discharging cock.

The *spirit receiver* is another covered vessel, communicating only with the safe by means of a metal pipe. The *spent lees receiver* is a vessel connected with the low wines still by a pipe. This vessel has another opening at about one-third of its depth from the top, covered and secured by an internal metal plate, perforated with circular holes of not more than four-tenths of an inch in diameter. When intermediate still chargers are used, they are covered vats, and are connected by pipes with the wash charger and the still.

ALCOHOL FROM BEET.—Beet contains 85 per cent. of water, and about 10 per cent. of sugar, the remainder being woody fibre and albumen. The conversion of the sugar into alcohol is effected in several different ways, of which the following are the principal:—(1) By rasping the roots and submitting them to pressure, and fermenting the expressed juice; (2) By maceration with water and heat; (3) By direct distillation of the roots.

By Rasping and Pressure.—The spirit obtained by this process is much preferable to that obtained by the others, but it is considerably higher in price, as it requires a larger stock and much more labour. The process is adopted chiefly in the large sugar factories, where all the necessary utensils are always at hand, and the only additional expense incurred is the distilling apparatus. The roots are washed, rasped, and pressed exactly as in the manufacture of sugar (see Sugar). By this means, 80 or 85 per cent. of juice is obtained, but this proportion is much increased by permitting a stream of water to flow upon the rasping instrument. The utmost cleanliness is essential to these processes; all the utensils employed should be washed daily with lime-water to counteract acidity. Before fermentation, the juice from the rasp and the press is brought into a boiler and heated by steam to about 28°; at this temperature it is run off into the fermenting vats. Here it is necessary to add to the juice a small quantity of concentrated sulphuric acid, for the purpose of neutralizing the alkaline salts which it contains, and of rendering it slightly acid in order to hasten the process; this quantity must not exceed 2½ kilos. to every 1000 litres of juice, or the establishment of fermentation would be hindered instead of promoted. The addition of this acid tends also to prevent the viscous fermentation to which the juice obtained by rasping and pressure is so liable. Although the beet contains albumen, which is in itself a ferment, it is necessary, in order to develop the process, to have recourse to artificial means. A small quantity of brewer's yeast—about 50 grammes per 100 litres of juice—is sufficient for this; the yeast must previously be mixed with a little water. An external temperature of about 20° must be carefully maintained.

The fermentation of acidulated beet-juice sets in speedily. The chief obstacle to the process is the mass of thick scum which forms upon the surface of the liquor. This difficulty is sometimes obviated by using several vats and mixing the juice, while in full fermentation, with a fresh quantity. Thus, when three vats are employed, one is set to ferment; at the end of four or six hours, half its contents are run into the second vat and here mixed with fresh juice. The process is arrested, but soon starts again in both vats simultaneously; the first is now allowed to ferment completely, which is effected with much less difficulty than would have been the case had the vat not been divided. Meanwhile the second vat, as soon as the action is at its height, is divided in the same manner, one-half its contents being run into the third. When this method is employed, it is necessary to add a little yeast from time to time when the action becomes sluggish.

By Maceration.—The object of this process is to extract from the beets by means of water or spent liquor all the sugar which they contain, without the aid of rasping or pressure Spirit is thus produced at considerably less expense, although it is not of so high a quality as that yielded by the former process. The operation consists in slicing up the beets with a root-cutter, and then allowing the slices to macerate in a series of vats at stated temperatures. It is essential that the knives by which the roots are cut should be so arranged that the roots are divided into slices having a width of 1 centimetre and a thickness of 1 millimetre, and a variable length; the roots are, of course, well washed before being placed in the hopper of the cutter. When cut, the beets are covered with boiling water in a macerator of wood or iron for one hour; the water should contain 2 kilos. of sulphuric acid to every 1000 kilos. of beets. After this, the water is drawn off into a second vat in which are placed more beets, and allowed to macerate again for an hour. This is repeated a third time in another vat, and the juice, which has now acquired a density equal to that obtained by rasping, is run off into the fermenting vat. When the first vat is empty it is immediately refilled with boiling water and fresh beets; the juice from this operation is run into the second vat, when the contents of that one are run into the third. To continue the operation, the beets are completely exhausted by being macerated for an hour with a third charge of boiling water (acidulated as in the former case). The exhausted pulp is removed to make room for fresh slices; and the first vat is then charged with juice which has already passed through the second and third vats. After macerating the fresh beets for one hour, the charge is ready for fermentation. In ordinary weather, the juice should now be at the right heat for this process, viz. about 22° or 24°, but in very cold weather it may require some re-heating. The fermentation is precisely similar to that of the pressed juice and calls for no special remark. It is usually complete in from 24 to 30 hours.

By direct Distillation of the Roots.—This process, commonly called "Leplay's method," consists in fermenting the sugar in the slices themselves. The operation is conducted in huge vats, holding as large a quantity of matter as possible, in order that the fermentation may be established more easily. They usually contain about 36 hectolitres, and a single charge consists of 1000 kilos. of the sliced roots. The slices are placed in porous bags in the vats, containing already about 20 hectolitres of water acidulated with a little sulphuric acid; and they are kept submerged by means of a perforated cover, which permits the passage of the liquor and of the carbonic acid evolved; the temperature of the mixture should be maintained at about 25° or 27°. A little yeast is added, and fermentation speedily sets in; it is complete in about twenty-four hours or more, when the bags are taken out and replaced by fresh ones; fermentation declares itself again almost immediately, and without any addition of yeast. New bags may, indeed, be placed in the same liquor for three or four successive fermentations without adding further yeast or juice.

The slices of beets charged with alcohol are now placed in a distilling apparatus of a very simple nature. It consists of a cylindrical column of wood or iron, fitted with a tight cover, which is connected with a coil or worm, kept cool in a vessel of cold water. Inside this column are arranged a row of perforated diaphragms or partitions. The space between the lowest one and the bottom of the cylinder is kept empty to receive the condensed water formed by the steam, which is blown into the bottom of the cylinder in order to heat the contents. Vapours of alcohol are thus disengaged from the undermost slices, and these vapours as they rise through the cylinder vaporize the remaining alcohol, and finally pass out of the top at a considerable strength and are condensed in the worm. When all the contents of the still have been completely exhausted of spirit, the remainder consists of a cooked pulp, which contains all the nutritive constituents of the beet except the sugar.

Alcohol from Potatoes.—The distillation of spirits from potatoes is chiefly carried on in Germany and has of late years assumed considerable dimensions. Potatoes contain from 16 to 20 per cent. of starch, which is capable of being converted into glucose by the action of sulphuric acid or of malt. Three principal methods of effecting the saccharification of potato-starch are in use: (1) the potato may be baked, and then crushed into a pulp; or (2) it may be rasped to bring about the same result; or (3) the starch may be extracted and converted into sugar afterwards.

1. In the first method, there are several different operations, viz. cooking the potatoes; crushing them; converting the starch into sugar by means of malt; and, finally, fermentation and distillation.

The operation of *cooking* is carried on in an apparatus consisting of a boiler set in brickwork, which is surmounted by a tun or vat, made of oak staves firmly bound together. The bottom of the tun, which must be of solid wood, is perforated with a large number of small square holes, to give admittance to the steam from below. The potatoes placed in this tun are rapidly cooked by the ascending steam; they are then withdrawn and crushed into a thick pulp between two rollers, commonly made of oak, and placed below the level of the tun. As the potatoes swell considerably during the steaming, the tun should never be completely filled.

The pulp or paste thus made is now placed in a vat, holding about 30 or 40 hectolitres, in which the saccharification takes place. About 1000 kilos. of the crushed potatoes and 70 kilos. of broken malt are introduced, and immediately afterwards water is run in at a temperature of about 36° to 40°, the contents being well stirred with a fork meanwhile. The vat is then carefully closed for half an hour, after which boiling water is added until the temperature reaches 60°, when the whole is left for three or four hours. The process of fermentation is conducted in the same vat. Alternate doses of cold and boiling water are run in upon the mixture, until the quantity is made up to 32 or 35 hectolitres, according to the size of the vat, and so as finally to bring the temperature to 24° or 26°. Two and a half or three litres of liquid brewer's yeast are then added, and fermentation speedily sets in. This process complete, the fermented pulp is distilled in the apparatus devised by Cellier-Blumenthal for distilling materials of a pasty nature; the product has a very unpleasant odour and taste.

2. By rasping the potatoes in a machine, the expensive operations of cooking and separating the starch are avoided. In this operation, the potatoes, after having been washed, are thrown into a

rasping machine similar to those employed in the sugar manufactories. If 1000 kilos. of potatoes be worked at once, a vat must be employed having a capacity of 22 to 25 hectolitres and a perforated false bottom on which is spread a layer of straw. The vat is charged with 1000 kilos. of potatoes, which are allowed to stand for half an hour in order to get rid of a portion of the water they contain. After this, 1000 to 1200 litres of boiling water are run in, and then 70 kilos. of malt are added; the whole is stirred up and left to macerate for three or four hours. This done, the liquid is drawn off from beneath into the fermenting vat; the pulp is drained for a quarter of an hour, and the drainings are added to the liquor previously run off. Five hundred litres of boiling water are now run in upon the pulp, which is again stirred up energetically. After remaining some little time, the water is again drawn off, the pulp drained and washed anew with 500 litres of cold water, with agitation. This is again drawn off, and the whole of the water with the drainings is mixed up in the fermenting vat. Two kilos. of yeast are then added, and the contents of the vat are left to ferment. Only the *liquor* is fermented by this process, but the spirit yielded is nearly as unpleasant to taste and smell as that obtained by the former process.

3. The only means of obtaining alcohol of good quality from the potato is to extract the starch and to convert it into sugar separately. The saccharification of the starch may be effected either by means of sulphuric acid or of diastase, the latter being decidedly preferable. In a vat of 30 hectolitres capacity are mixed together 1000 litres of cold water, 500 kilos. of dry or 750 kilos. of moist starch. The mixture is well agitated, and 1700 litres of boiling water are run in, together with 75 to 80 kilos. of malt; the whole is stirred up energetically for ten minutes and then left to saccharify for three or four hours. The saccharine solution obtained must be brought to 6° or 7° Baumé at a temperature of 22° or 24°, and 500 grm. of dry yeast are added for every 1000 litres of must. Fermentation is soon established and occupies usually about thirty-six hours. After remaining at rest for twenty-four hours, the must is distilled. One hundred kilos. of starch ought to yield 35 to 40 litres of pure alcohol, or 40 to 45 litres of alcohol at 90°.

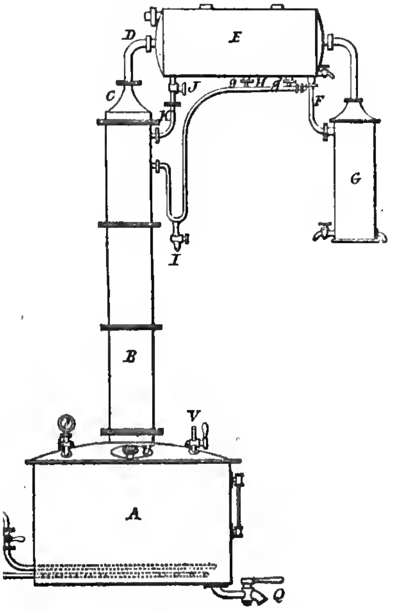
RECTIFICATION.—The product of the distillation of alcoholic liquors, termed *low wine*, does not usually contain alcohol in sufficient quantity to admit of its being employed for direct consumption. Besides this it always contains substances which have the property of distilling over with the spirit, although their boiling points, when in the pure state, are much higher than that of alcohol. These are all classed under the generic title of *fusel-oil:* owing to their very disagreeable taste and smell, their presence in spirit is extremely objectionable. In order to remove them, the rough products of distillation are submitted to a further process of concentration and purification. Besides fusel-oil, they contain other substances, such as aldehyde, various ethers, &c., the boiling points of which are lower than that of alcohol; these must also be removed, as they impart to the spirit a fiery taste. The whole process is termed *rectification*, and is carried on in a distillatory apparatus. Heat is first applied gradually, in order to remove the most volatile impurities, and to concentrate them in the first portion of the distillate. When the spirit coming over possesses no objectionable odour, it is caught separately as long as it is of sufficient strength. The receiver is then changed again and the remainder is collected apart, as weak spirit which contains much fusel-oil; the first and last runnings are then mixed together and re-distilled with the next charge. When a strong spirit is required, rectification may be repeated several times. It is customary, however, with the improved apparatus of modern times, to produce at the outset spirit containing but little fusel-oil and at least 80 per cent. of alcohol; this is then purified and concentrated in the above manner, and afterwards reduced with water to the required strength.

Another cause of the offensive flavour of the products of distillation is the presence of various acids, which exist in all fermented liquors; they are chiefly tartaric, malic, acetic, and lactic acids. The excessive action of heat upon liquors which have been distilled by an open fire has also a particularly objectionable influence upon the flavour of the products.

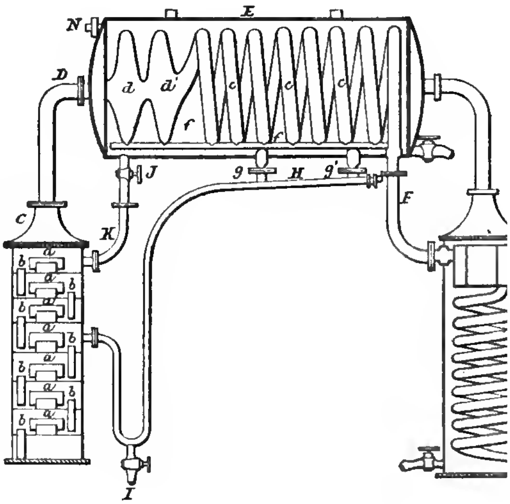
The first operation in the process of rectification is to neutralize the above-mentioned acids; this is effected by means of milk of lime, which is added to the liquor in quantity depending upon its acidity; the point at which the neutralization is complete is determined by the use of litmus paper. In the subsequent process of distillation, the determination of the exact moments at which to begin and to cease collecting the pure spirit is very difficult to indicate. It must be regulated by the nature of the spirits; some may be pure twenty or thirty minutes after they have attained the desired strength; and some only run pure an hour, or even more, after this point. The product should be tasted frequently, after being diluted with water, or a few drops may be poured into the palm of the hand, and after striking the hands together, it will be known by the odour whether the spirit be of good quality or not; these two means may be applied simultaneously.

The process of rectification is usually carried on in the apparatus shown in Figs. 188 and 189. A is a still which contains the spirit to be rectified; it should be four-fifths full. The condenser E and the cooler G are filled with water. After closing the cocks F and I, the contents of the still are heated by steam, which is introduced at first slowly. The vapours of spirit given off pass above the plates *a* of the column B, and escape through C and D into the condenser E, where they are condensed on reaching the lentils *d d'*, and return in a liquid state through *f f'* and *g g'* to the upper plates of the column B. In these return pipes the liquid is volatilized, and constantly recharged with alcohol to be again condensed. until the water in the condenser is hot enough to permit the lighter alcoholic vapours to pass into the coil *c c c*, without being reduced to the liquid state. When this is the case, the vapours pass through F into the cooler G, where it undergoes complete condensation. Great care must be taken that the heat is not so great as to permit any of the vapours to pass over uncondensed, or to flow away in a hot state; and also to keep up a constant supply of water in the cooler without producing too low a temperature; the alcoholic products should run out just cold. The highly volatile constituents of the spirit come over first, that which follows becoming gradually purer until it consists of well-flavoured alcohol; after this comes a product containing the essential oils. The more impure products are kept apart from the rest and re-distilled with the next charge. Some hours generally elapse before alcohol begins to flow from the cooler. The purest alcohol is obtained while its strength is kept between 92° and 96° Baumé, and the operation is complete when the liquid flowing through the vessel marks not more than 3° or 4° Baumé; it is better, however, to stop the still when the backing or "faints" indicate 10°, because the product after this point contains much fusel-oil, and is not worth collecting.

188.



189.



In order to cleanse the apparatus—which should be performed after each working—the still A is emptied of water by opening the cock C. The contents of the condenser are then emptied in like manner by opening the cock J, through which they flow upon the plates in the column B, and wash out essential oils which remain in them. These two cocks are then closed, and the door U is removed. The water in the cooler G is then run by means of a pipe into the still A, so as partially to cover the steam-coil in the latter. After again securing the door U, a strong heat is applied, and the water in the still is well boiled, the steam evolved thoroughly cleansing all the different parts of the apparatus; this is continued for fifteen or twenty minutes, when the heat is withdrawn and the still left to cool gradually.

The capacity of the rectifying apparatus has a good deal of influence upon both the quantity and the quality of the spirit obtained. Besides being much more difficult to manage, a small apparatus will not yield so large a proportion of spirit as a more capacious one, nor will its products be of equally good flavour. The proportion of alcohol which may be obtained from a successful rectification is very variable; it depends upon the nature of the spirit rectified, the method of extracting the sugar, and the manner of conducting the distillation; it will also be in inverse proportion to the quantity of fusel-oil contained in the raw spirit. The average loss of pure alcohol during the process of rectification is generally estimated at about 5 per cent.

The uses of alcohol are very numerous and varied, the principal being, of course, for the production of all alcoholic liquors, such as brandy, gin, rum, whiskey, liqueurs, &c.; that distilled in

England from grain is almost entirely consumed in the manufacture of whiskey, gin, and British brandy. In the arts, strong alcohol is employed by the perfumers and makers of essences for dissolving essential oils, soaps, &c., and for extracting the odour of flowers and plants; by the varnish-makers for dissolving resins; by photographers in the preparation of collodion; by the pharmaceutists in the preparation of tinctures and other valuable medicaments; by chemists in many analytical operations, and in the manufacture of numerous preparations; by instrument makers in the manufacture of delicate thermometers; by the anatomist and naturalist as an antiseptic; and in medicine, both in a concentrated form (rectified spirit), and diluted (proof spirit, brandy, &c.), as a stimulant, tonic, or irritant, and for various applications as a remedy. It is largely consumed in the manufacture of vinegar; and in the form of methylated spirit it is used in lamps for producing heat. It has, in fact, been employed for a multitude of purposes which it is almost impossible to enumerate.

The common form of alcohol known as "methylated spirit" consists of alcohol to which one-tenth of its volume of wood spirit, or methylic alcohol, has been added, for the purpose of rendering the mixture undrinkable through its offensive odour and taste. Methylated spirit being sold duty free, is applied by chemical manufacturers, varnish makers, and many others, to a variety of uses, to which, from its greater cost, duty-paid spirit is commercially inapplicable. Its use, however, in the preparation of tinctures, sweet spirits of nitre, &c., has been prohibited by law, the Pharmacopeia Committee of the Medical Council having expressed a decided opinion against the substitution of methylated spirit for rectified spirit in any of the processes of the Pharmacopeia. It has often been attempted to separate the wood spirit from the alcohol, and thus to obtain pure alcohol from the mixture, but always unsuccessfully, as, although the former boils at a lower temperature than the latter, when boiled they both distil over together, owing probably to the difference of their vapour densities.

As we have already stated, nearly all the alcohol made in England is distilled from grain. The whiskey distilleries are confined to Ireland and Scotland; but large quantities of the plain spirit is prepared in the distilleries in the West of England. Of these, there are several situate in Bristol and Plymouth, besides those in London and the neighbourhood. The manufacture of brandy, beet spirit, and liqueurs is carried on almost exclusively in France, that of potato spirit in Germany, of rum in Jamaica and the West Indies, of gin in Holland and the neighbourhood of London; the former is called Hollands gin, to distinguish it from the latter, or British gin. Spirits from rice, sorghum, molasses, &c., are all prepared in the East. In all countries, the manufacture of alcohol in its various forms is distributed among a few distillers.

All spirits distilled in England, Scotland, or Ireland, are called by the Board of Excise "British spirits," those which have not had any flavour communicated to them being known as "plain British spirits;" those which have been flavoured, and all liquors mixed with such spirits, are called "British brandy;" and those which have been re-distilled or mixed with juniper berries, caraway seeds, aniseed, or any other such preparation or ingredient, and all liquors which have been mixed with such spirits, are called "British compounds." British spirits 43 per cent. over proof, as denoted by Syke's hydrometer, and all spirits of a higher degree of strength, except those in a distiller's stock or duty-free warehouse, are called "spirits of wine."

There are certain restrictions imposed upon the manufacture of spirits in Great Britain, which it may be well to mention here. According to Act of Parliament, all distilleries must be situated in, or within a quarter of a mile of, a market town; but the commissioners may, if they think fit, grant a licence for a distillery, if the distiller undertakes to provide lodging for the residence of the officers to be placed in charge of the distillery. No distiller in England may keep or use a still for making low wines or spirits, the body of which without the head shall be of less than 400 gallons capacity.

For every 100 gallons of wash made in any distillery, the distiller is charged with duty for a quantity of spirits at the rate of 1 gallon of proof spirit for every 5° of gravity with which the wash is attenuated. Duty is also payable upon the quantity of proof spirits found by the officer in the low wines made from the distillation of any wash, after making an allowance of 5 per cent. on that quantity. It is further charged by the strength of the produce on the re-distillation of low wines into spirits and faints.

The duty levied upon spirits is, at the present time, 7*s.* 10*d.* a gallon, proof strength.

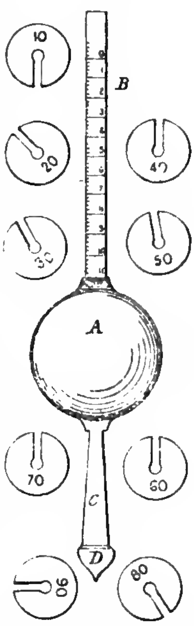
ALCOHOLOMETRY.—The name given to a variety of methods of determining the quantity of absolute alcohol contained in spirituous liquors. It will readily be seen that a quick and accurate method of making such determinations is of the very utmost importance to those who are engaged in the liquor traffic, since the value of alcoholic liquors depends entirely upon the percentage of alcohol which they contain. When such liquors consist of simple mixtures of alcohol and water, the test is a simple one, the exact percentage being readily deducible from the specific gravity of the liquor; this is obtained either by means of the *specific gravity bottle* (see Specific Gravity), or of hydrometers of various kinds, specially constructed.

At the latter end of the last century, a series of arduous experiments were conducted by Sir C. Blagden, at the instance of the British Government, with a view to establishing a fixed proportion between the specific gravity of spirituous liquors and the quantity of absolute alcohol contained in them. The result of these experiments, after being carefully verified, led to the construction of a series of tables, reference to which gives at once the percentage of alcohol for any given number of degrees registered by the hydrometer; these tables are invariably sold with the instrument. They are also constructed to show the number of degrees over- or under-proof, corresponding to the hydrometric degrees. Other tables are obtainable which give the specific gravity corresponding to these numbers.

The measurement of the percentage of absolute alcohol in spirituous liquors is almost invariably expressed in volume rather than weight, owing to the fact that such liquors are always sold by volume. Nevertheless, the tables referred to above show the percentage of spirit both by volume and weight.

The standard liquor known as *proof spirit* contains 49·5 per cent. by weight, and 57·27 per cent. by volume, of absolute alcohol; it has a specific gravity of ·9186 at 15°. The strength, and therefore the value, of spirituous liquors is estimated according to the quantity by volume of anhydrous spirit contained in the liquor with reference to this standard. Thus the expressions "20 *per cent. overproof*," "20 *per cent underproof*," mean that the liquor contains 20 volumes of water for every 100 volumes over or under this fixed quantity, and that in order to reduce the spirit to *proof*, 20 per cent. of water by volume must be subtracted or added, as the case may be. Any hydrometer constructed for the measurement of liquids of less density than water may be employed. That known as "Syke's" is most commonly used in this country for alcoholometric purposes, as it is the instrument prescribed for use by the Board of Excise. It is shown in Fig. 190, and consists of a spherical brass ball A, to which is fixed two stems; the upper one B is also of brass, flat, and about 3½ in. in length; it is divided into ten parts, each being subdivided into five, and the whole being numbered as shown in the figure. The lower stem C is conical, and slightly more than an inch long; it terminates in a weighted bulb D. A series of circular weights, of the form shown in the figure, accompany the instrument; these are slipped upon the top of the lower stem C, and allowed to slip down until they rest upon the bulb D. The instrument is used in the following way:—It is submerged in the liquor to be tested until the whole of the upper stem is under the surface, and an idea is thus gained of the weight that will be required to *partly* submerge the stem. This weight is added, and the hydrometer again placed in the liquor. The figure on the scale to which the instrument has sunk when at rest is now observed, and added to the number on the weight used, the sum giving, by reference to the tables, the percentage by volume of absolute alcohol above or below the standard quantity.

190.



In exact estimations, the temperature of the liquor tested must be carefully registered, and the necessary corrections made. In Jones's hydrometer, which is an improvement upon Syke's, a small spirit thermometer is attached to the bulb, and by noting the temperature of the liquor at the time of the experiment, and referring to the tables accompanying the instrument, the strength is found at once without the need of calculation.

On the Continent, Gay-Lussac's hydrometer and tables are chiefly used for alcoholometric testing. This instrument is precisely similar in construction to those of Twaddle and Baumé, described in the article on Acidimetry. On the scale, zero is obtained by placing it in pure distilled water at 15°, and the highest mark, or 100, by placing it in pure alcohol at the same temperature, the intermediate space being divided into 100 equal divisions, each representing 1 per cent. of absolute alcohol. The correction for temperature, as in the above cases, is included in the reference tables.

Another hydrometer, used in France for alcoholometric determinations, is Cartier's. In form it is precisely similar to Baumé's hydrometer. Zero is the same in both instruments, but the point marked 30° in Cartier's is marked 32° in Baumé's, the degrees of the latter being thus diminished in the proportion of 15 or 16. Cartier's hydrometer is only used for liquids lighter than water.

In France, particular names have been adopted to denote spirituous liquors of different degrees of strength. The first products of distillation, registering 16° to 20° Cartier, are called "Eau-de-vie." At 19°, the spirit is called "Eau-de-vie ordinaire." From 21° to 22°, it is called "Eau-de-vie forte." Beyond this degree the alcoholic products take the name of "esprits,' and the quantity of water which they contain is expressed by numbers in the form of a fraction. These numbers show the quantity of water which must be added to every part of spirit to bring it to the state of "Eau-de-vie ordinaire," at 19°. Thus, spirit at 29° is called "*Esprit trois-cinq,*" because by taking three volumes of this liquor and adding thereto two volumes of water, five volumes of spirit at 19° are obtained. Spirit at 33° is called "*Esprit trois-six*" because three volumes mixed with three volumes of water, produce six volumes of spirit at 19° Cartier.

The above hydrometric methods can be safely employed only when the spirit tested contains a very small amount of solid matter, since, when such matter is contained in the liquor in quantity, the density alone cannot possibly afford a correct indication of its richness in alcohol. Many methods have been proposed for the estimation of alcohol in liquor, containing saccharine colouring and extractive matters, either in solution or suspension. Undoubtedly the most accurate of these, though at the same time the most tedious, is to subject the liquor to a process of distillation by which a mixture of pure alcohol and water is obtained as the distillate. This mixture is carefully tested with the hydrometer, and the percentage of alcohol in it determined by reference to the tables as above described; from this quantity and the volume of the original liquor employed the percentage by volume of alcohol in that liquor is readily found. The condensing arrangement must be kept perfectly cool, if possible in a refrigerator, as the alcohol in the distillate is very liable to be lost by re-evaporation. When great accuracy is desired, and time is at the operator's disposal, the above method is preferable to all others.

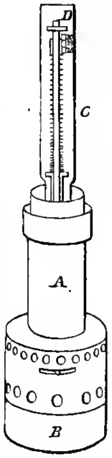
It is performed in the following manner:—Three hundred parts of the liquor to be examined are placed in a small still, or retort, and exactly one-third of this quantity is distilled over. A graduated glass tube is used as the receiver, in order that the correct volume may be drawn over without error. The alcoholic richness of the distillate is then determined by any of the above methods, and the result is divided by three, which gives at once the percentage of alcohol in the original liquor. The strength at proof may be calculated from this in the ordinary way.

If the liquor be acid, it must be neutralized with carbonate of soda before being submitted to distillation. From 8 to 10 per cent. of common salt must be added, in order to raise the boiling point, so that the whole of the spirit may pass over before it has reached the required measure. In the case of the stronger wines it is advisable to distil over 150 parts and divide by two instead of three. If the liquor be stronger than 25 per cent. by volume of alcohol, or above 52–54 per cent. underproof, an equal volume of water should be added to the liquid in the still, and a quantity distilled over equal to that of the sample tested, when the alcoholic strength of the distillate gives, without calculation, the correct strength required. If the liquor be stronger than 48–50 per cent. underproof, three times its volume of water must be added, and the process must be continued until the volume of the distillate is twice that of the sample originally taken. In each case the proportionate quantity of common salt must be added.

For the estimation of alcohol in wines, liqueurs, &c., the following method is employed in the Inland Revenue and Customs laboratories:—A measuring flask is filled up to a mark on its neck with the liquor under examination, which is then transferred to a retort; the flask must be carefully rinsed out with distilled water, and the rinsings added to the liquor in the retort. About two-thirds are then drawn over into the same measuring flask, and made up to its previous bulk with distilled water, at the same temperature as that of the sample before distillation. The strength is then determined by means of Syke's hydrometer, and this, if underproof, deducted from 100, gives the true percentage of proof-spirit in the wine.

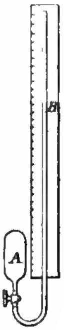
A quick, if not always very exact, method consists in determining the point at which the liquor boils. The boiling point of absolute alcohol being once determined, it is obvious that the more it is diluted with water the nearer will the boiling point of the mixture approach that of water; moreover, it has been proved that the presence of saccharine and other solid matters has but an almost inappreciable effect upon this point. Field's alcoholometer, since improved by Ure, is based upon this principle. It is shown in Fig. 191, and consists, roughly speaking, of a cylindrical vessel A, to contain the spirit; this vessel is heated from beneath by a spirit lamp, which fits into the case B. A delicate thermometer C, the bulb of which is introduced into the spirit, is attached to a scale divided into 100 divisions, of which each represents one degree over- or under-proof. This method is liable to several small sources of error, but when a great many determinations have to be made, and speed is an object rather than extreme accuracy, this instrument becomes exceedingly useful. It does not answer well with spirits *above* proof, because the variation in their boiling points are so slight as not to be easily observed with accuracy. But for liquors underproof, and especially for wines, beer, and other fermented liquors, it gives results closely approximating to those obtained by distillation, and quite accurate enough for all ordinary purposes. Strong liquors should therefore be tested with twice their bulk, and commercial spirits with an equal bulk, of water, the result obtained being multiplied by two or three, as the case may be.

191.



Another very expeditious, but somewhat rough, method was invented by Geisler. It consists in measuring the tension of the vapour of the spirit, by causing it to raise a column of mercury in a closed tube. The very simple apparatus is shown in Fig. 192, A is a small glass bulb, fitted with a narrow tube and stop-cock. This vessel is completely filled with the spirit, and is then screwed upon a long, narrow tube B, bent at one end and containing mercury. This tube is attached to a graduated scale showing the percentage of absolute alcohol above or below proof. To make the test the cock is opened, and the bulb, together with the lower part of the tube, is immersed in boiling water, which gradually raises the spirit to its boiling-point. When this is reached, the vapour forces the mercury up the tube, and, when stationary, the degree on the scale to which it has ascended gives directly the percentage of alcohol.

192.



Another method, which is not to be relied on for very weak liquors, but which answers well for cordials, wines, and strong ales, is that known as Brande's method. The liquor is poured into a long, narrow glass tube, graduated centesimally, until it is half-filled. About 12 or 15 per cent. of subacetate of lead, or finely powdered litharge, is then added, and the whole is shaken until all the colour is destroyed. Powdered anhydrous carbonate of potash is next added until it sinks undissolved in the tube, even after prolonged agitation. The tube is then allowed to rest, when the alcohol is observed to float upon the surface of the water in a well-defined layer. The quantity read off on the scale of the tube and doubled, gives the percentage by volume of alcohol in the original liquid. The whole operation may be performed in about five minutes, and furnishes reliable approximative results. In many cases it is necessary to add the lead salt for the purpose of decolorizing the liquid.

ALCOHOLIC LIQUORS.—By "alcoholic liquors" is understood those spirituous drinks which are obtained by *distillation*, such as brandy, whiskey, rum, &c.: these only will be treated of in the present articles. The spirituous drinks which are the immediate products of fermentation, such as beer, cider, wine, &c., will be discussed later in the articles entitled "Beverages." Of the former class, some, as brandy and rum, are the immediate products of distillation; others, as gin, and the various liqueurs, are prepared from alcohol previously obtained from the still.

Absinth. (Fr., *Absinthe;* Ger., *Wermuthextract*).—Absinth is the name given to an infusion of the *Artemisia Absinthium*, or wormwood plant, in strong alcohol. It is of a greenish colour, intensely bitter, and has a peculiar, penetrating odour.

The manufacture of absinth is carried on chiefly in Switzerland in the town of Neufchâtel, and at Lyons, Portarlier, and Montpellier. It is prepared by steeping the leaves and tops of wormwood in brandy or proof spirit; other aromatic substances are added, and the whole is allowed to digest for some days. The leaves are then strained, and the liquid is distilled and flavoured with some essential oil. The following is a recipe for the absinth of Neufchâtel:—

The leaves and tops of the wormwood plant, 4 lb.; angelica root, calamus root, aniseed and dittany leaves, 1 oz. of each; brandy or spirit (12 underproof), 4 gallons; macerate for ten days, add a gallon of water, distil 4 gallons at a gentle heat, and dissolve in the distilled spirit 2 lb. of crushed white sugar; flavour with a few drops of oil of anise.

Absinth is constantly coloured with indigo, and occasionally with sulphate of copper; chloride of antimony has also been found in it in small quantities.

The following are receipes for absinth, as manufactured in different French towns:—

Absinth of Lyons. (For 1 hectolitre):—

Large absinth (dried)	3 kilos.
Green anise	8 ,,
Fennel	4 ,,
Angelica seed	500 grm.
Alcohol (at 85°)	95 litres.

Digest these ingredients for twelve hours in a water bath; add 45 litres of water, close the apparatus, and distil off 95 litres; continue the distillation until all the spirit has passed over, and keep the remainder for another operation. The distillate is then coloured by means of the following mixture:—

Small absinth (dried)	1 kilo.
Lemon balm (dried)	1 ,,
Hyssop tops and flowers (dried)	500 grm.
Dried veronica	500 ,,

The small absinth is cut up fine, and the balm and hyssop are reduced to powder; they are then mixed with 40 litres of the spirit in a water-bath, and heated gently, but not so as to distil any of the contents. After a short time, they are allowed to cool, passed through a hair-sieve, and added to the remainder of the spirit from the preceding operation. About 5 litres of water are then added to make the whole up to 1 hectolitre.

Absinth of Portarlier.

Large absinth (dried and ground)	2½ kilos.
Green anise	5 „
Fennel	5 „
Alcohol (at 85°)	95 litres.

Digest and distil as in the previous operation, and colour with the following:—

Small absinth (dried)	1 kilo.
Hyssop tops and flowers	1 „
Lemon balm (dried)	500 grm.

Absinth of Montpellier.

Large absinth (dried)	2½ kilos.
Green anise	6 „
Florentine fennel	4 „
Coriander	1 „
Angelica seed	500 grm.
Alcohol (at 85°)	95 litres.

Colouring.

Dried hyssop (herb and flowers)	750 grm.
Dried balm of Moldavia	750 „
Small absinth	1 kilo.

The quantities of the ingredients in the above recipes may, of course, be varied to suit the taste of the manufacturer, or the quality and price of the product required. Nothing but age, however, will afford to absinth the qualities which are so much valued by consumers of this drink.

Much care is required in the choice of the materials, and especially of those used for colouring. The plants should be green and dry, and free from black or mouldy leaves. They are finely divided or reduced to powder, covered with the perfumed spirit from the distillation, and heated gently in order to extract the *chlorophylle*, or colouring principle. After cooling, the coloured spirit is drawn off clear, and the plants are drained and re-distilled, in order to collect the spirit still adhering to them. The vessels in which the colouring is conducted are made of tinned copper, and hold about 20 hectolitres. They are hermetically closed, and heated by steam to 60°.

The mixture of colouring and spirit is tested, and reduced to 74°. It is not sold above 72°, but a slight loss occurs on keeping, which must be provided against. By age, absinth loses its green colour, becoming yellowish; this tinge is preferred by consumers. The spirit is considered to be of good quality when, on being diluted with water, it becomes whitish or opalescent, owing to the presence of the essential oils from the seeds, and the resinous and colouring matters of the plants, which, on the addition of water, are set at liberty, and thus afford the milky colour so highly prized by connoisseurs. In this state it should be agreeable, odorous, and sweetish.

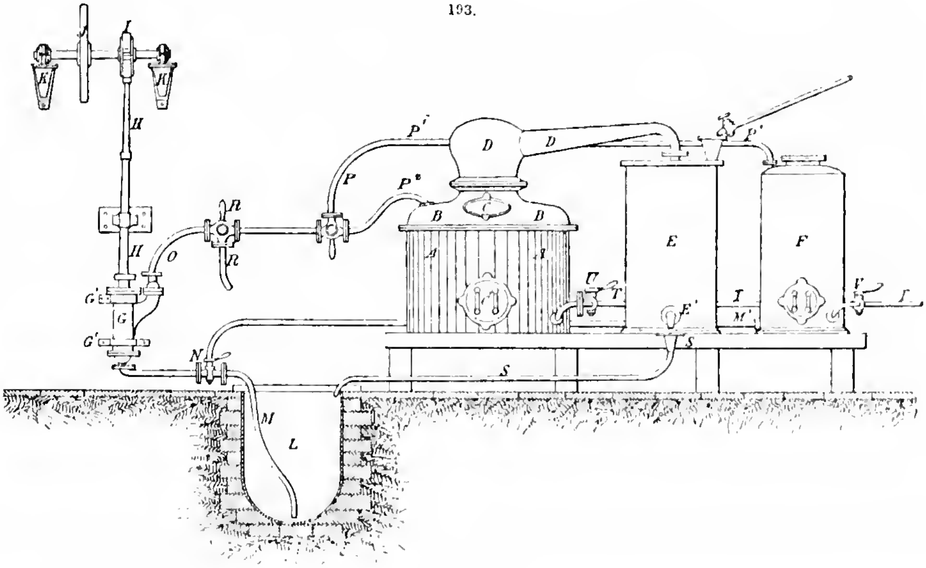
Absinths of an inferior and very pernicious quality are frequently met with in the market. These are chiefly manufactured without distillation, essences being used instead of the seeds and plants. Others are prepared from old or damaged materials, while others again have had added to them aromatic resins, such as benzoin, guaiacum, &c., after the distillation, in order to increase the opalescence.

Absinthine, the bitter principle of wormwood, is an energetic poison, acting especially upon the nervous system, and very injurious effects are invariably consequent upon the long-continued use of this drink.

Fig. 193 represents the apparatus used in Neufchâtel and other places for the manufacture of absinth and other perfumed spirits. It consists of the following parts:—

A is a kettle enclosed in a wooden jacket, acting as a water-bath enclosing another kettle, which contains the ingredients to be distilled. B is the top or cover of the still; C an opening closed by a plug for charging the still; C′ a similar opening for discharging the plants after distillation. D is the cap of the still, fastened on by a circular collar, and terminating in a neck which conducts the alcoholic vapours to the cooling coil. E is the cooler with its coil, and E′ the discharge pipe of the coil. F is the colourer, furnished, like the still, with plugs through which to fill and empty at. G is a pump fastened firmly to the wall by the collars G′. H is a piston rod; I, the eccentric for driving the pump; J, a pulley on which a band runs to connect with the power; and K, bearings from the pulley shaft. L is a tank or well of metal sunk into the floor. M is a suction pipe, and M′ another, connected with the colourer. N is a three-way cock attached to the suction pipe to draw any liquid from the tank to deliver it into the still, into the colourer, or to the store-room, or to draw the finished liquor from the colourer, and deliver it to the store-room. N′ is a pipe for drawing off the coloured product; O is a force or delivery pipe; P, a three-way cock, which directs liquids at pleasure into the still or the colourer; P′, a pipe delivering the liquid into the colourer, and P″ a pipe conveying the liquor into the still. R is a cock and pipe for delivering the manufactured product into the store-room; S, a funnel and pipe to convey the distilled product to the tank; T, the main steam-pipe connected with the steam boiler; U, the steam-cock for the kettle of the still; and V the steam-cock for the colourer.

193.



The apparatus is worked in the following manner:—

The tank L having been filled with water and alcohol in the correct proportion, and the boiler of the still with the ingredients necessary for the preparation of the absinth, the cock P P′ is opened and the pump set to work. The boiler A is immediately filled with the contents of the tank L. As soon as the tank is empty, the pump is stopped and the cock P closed. Steam is turned on by opening the cock U, and the product soon begins to flow over from the condensing coil into S, and again fills the tank L; it now consists of spirits perfumed by the plants placed in the still; it is white in colour, and possesses already many of the properties peculiar to the manufactured article. In order to colour it, the pump again draws up the liquor into the colourer F, which has been previously filled with the proper quantity of the colouring plants. After this operation, the pump fulfils its third office by raising the coloured absinth from the colourer through the pipe N′, and the cock and pipe R into its final receptacles.

Arrack or Rack. (Fr., *Arac*; Ger., *Arrack*.) Any alcoholic liquor is termed "arrack" in the East; but arrack proper is a liquor distilled either from toddy, the fermented juice of the cocoa-nut palm, or from rice. In the latter case, the rice is covered with water in large vats and agitated with a long rake. Great care must be taken in order to effect this without breaking the seed, and so causing the rice to decay, which would greatly impede its fermentation. This agitation is carried on until about half the rice has begun to germinate, when the water is run off from below. Molasses, or toddy, or a mixture of both, is now added, and the whole is left to ferment. When this process is complete, the fermented rice is distilled in the ordinary way.

The arrack of Jamaica and Batavia is prepared in this manner and is considered the best quality; that of Goa and Columbo is distilled from toddy alone. Since arrack may be extracted from the juice of the cocoa nut palm, it may perhaps be worth inquiring how nearly it may be imitated by fermenting and distilling the juices of the birch and sycamore trees. We should, by this means, obtain an English arrack; and perhaps a spirit equal in flavour to that of Batavia.

Arrack is also largely manufactured and consumed by the Chinese in Siam, where the revenues accruing to the Government from its distillation are said to be 58,000*l.* per annum. The revenues derived from this source from Ceylon are also very large, no less than 700,000 gallons being exported annually from this island, of which quantity about 30,000 gallons are sent to this country, where it is much valued for making Punch.

In Java, where large quantities of arrack are also made, the materials are generally used in the following proportions: Rice, 35 parts; molasses, 62 parts; toddy, 3 parts; from which, on distillation, a yield of 23½ parts of proof arrack is obtained.

Arrack is colourless, or nearly so; but if kept long in wooden casks, it acquires, like many other spirits, a yellowish tinge. When the cask in which arrack is imported happens to be decayed, or the liquor touches any nails, or other iron, it dissolves part of it, and at the same time extracts the resinous parts of the oak, by which means the whole liquor in the cask acquires an inky colour. In order to whiten and clarify arrack which has contracted this colour, a large quantity of new or skimmed milk must be put into the cask, and the whole beaten together, as vintners do to whiten their brown wines; by this means, the inky colour will be absorbed by the milk, and fall with it to the bottom, so that the greater part of the arrack may be drawn off fine, and the remainder procured in the same condition by being filtered through a conical flannel bag. The finest qualities have an agreeable taste, and are not unwholesome; they improve much on keeping. Common arrack, or as it is called in India, "pariah-arrack," has a strong and slightly nauseous taste and odour, which is due to the presence of a volatile oil which distils from the rice. If slices of ripe pine apple be put into good arrack, and the spirit kept for a considerable time, it mellows down and acquires a very delicious flavour. This quality is much valued for making "rack-punch."

The arrack of Batavia and Jamaica is the finest quality, the second best being the varieties made in Madras, China and Siam. Other varieties are considered inferior. That which is distilled from rice is narcotic, intoxicating, and very unwholesome. Hemp leaves, poppy heads, and other objectionable substances are sometimes added in order to render the spirit more intoxicating.

Brandy. (Fr., *Eau-de-vie*; Ger., *Branntwein.*) Brandy is the direct product of the distillation of French wines, as described under Alcohol from Wine (p. 201). The better qualities are distilled from white wines, the inferior varieties being the products of the dark-red Spanish and Portuguese wines, or of the marcs or refuse of the wine-press, called *eau-de-vie de marcs.* The variety made in England, and known as British brandy, is a spirit compounded in several different ways by the rectifying distiller.

Good brandy should be clear and sparkling; white if new, slightly yellow if a few years old, and brownish-yellow if very old; its flavour is sweet, mellow and ethereal, and not in the least degree, fiery or earthy. When held in the mouth, it creates an agreeable, warm sensation on the tongue, quite different from the harsh flavour and unpleasant after-taste which are common to brandies of an inferior quality. The following list represents the different French brandies in their order of merit:—

1. Cognac fine Champagne.
2. „ Champagne.
3. „ petite Champagne.
4. „ premier bois.
5. „ deuxième bois.
6. „ Saintonge.
7. „ Saint-Jean d'Angely.
8. „ Bas-Armagnac.
9. Eau-de-vie de Tenarèze.
10. Cognac (Surgères).
11. Eau-de-vie Haut-Armagnac.
12. Rochelle Aigre feuille.
13. Rochelle.
14. Marmande.
15. Pays (Marmande).
16. Trois-six Languedoc.

Originally, the cultivation of the vines producing the cognac brandy was confined to the neighbourhood of the town of that name; but they are now the produce of a very extensive vine-growing district. Unfortunately, only a very small proportion of the brandy which is sold as cognac is genuine. The remainder consists generally of mixtures of alcohol and water to which different colouring and aromatic substances have been added. These liquors have neither the agreeable flavour nor the mellowness of natural brandies; it is possible, nevertheless, by the aid of certain harmless chemical preparations, to give them a bouquet and an aroma which renders them quite fit for consumption as beverages.

As the depth of colour in natural brandies is in proportion to the length of time they have remained in the cask, it is customary to give a high colour to the fictitious varieties. To imitate this natural colour, caramel dissolved in an infusion of tea is added to them; the mixture affords to the spirit a peculiar, agreeable taste, which often deceives inexperienced judges. The addition of caramel may be detected by boiling a little of the brandy to dryness; a residue is left which on ignition yields the characteristic odour of burnt sugar. The colouring matter is also sometimes prepared from the rind of nuts, or from catechu. This latter substance is rarely used alone, but is with other astringent and aromatic substances which give to the spirit colour and bouquet. The following is a recipe frequently employed by rectifiers in the preparation of fictitious brandy:—

Powdered catechu	100 grm.
Sassafras wood	10 „
Balsam of tolu	10 „
Vanilla	5 „
Essence of bitter almonds..	1 „
Well-flavoured alcohol (at 85°)	1 litre.

The vanilla is triturated in 125 grm. of brown sugar, and the whole is macerated for eight days with frequent shaking. It is then to stand for twenty-four hours, and the clear liquor is drawn off to be added to the brandy to be improved. Sulphuric acid to the extent of 1 per cent. is sometimes added for the purpose of affording to the spirit a peculiar bouquet; but this adulteration is very reprehensible. In order to tone down and remove the harshness from new brandy, it is in some places the custom to add 10 grm. ammonia per hectolitre, stirring it well in; white soap has sometimes been used for the same purpose.

In order to ascertain the purity and genuineness of brandy, a few drops may be poured into the palm of the hand, and the two hands rubbed together. The liquid, if genuine, exhales a sweet and pleasant odour: if counterfeit, the odour is on the other hand penetrating and disagreeable, and is readily recognized by those who are accustomed to make use of this test. Or a small quantity may be poured into a saucer and left to evaporate spontaneously; the foreign substances, consisting of amylic, butylic, and propylic alcohols, which are less volatile than ordinary alcohol, are left behind in the saucer if present in the brandy, and are at once detected by their peculiar smell. Another method frequently employed to detect these impurities is to dilute the spirit with four or five times its volume of water, and to take a portion of the mixture into the mouth without swallowing it. An experienced taster will distinguish with ease between the brandies of Cognac, Armagnac, Languedoc, &c., and will even detect the variety of fruit from which the spirit was distilled.

Since the colour of French brandies is acquired from the oak of the cask, there is no difficulty in imitating it to perfection. A small quantity of the extract of oak, or the shavings or sawdust of that wood, properly digested, will furnish us with a tincture capable of giving the spirit any degree of colour required. But as the tincture is extracted from the cask by brandy, i. e. alcohol and water, it is necessary to use both in extracting the tincture, for each of these menstrua dissolves different parts of the wood. The chips, shavings, sawdust, &c. of the white oak used at Cognac for making brandy casks are soaked in water for eight days. This water is then thrown away, and rain-water containing one-tenth of brandy is substituted; about 10 kilos. of the wood should be employed for every 100 litres of liquid required. After remaining for some months, the water acquires a colour and an aroma which, when the mixture is made in the proper proportions, can hardly be distinguished from that of the best French brandy.

As all new brandies retain a certain sharpness of flavour, which wears off as the spirit is kept, and preserve to some extent the peculiar flavour which characterizes the wines from which they were produced, it is customary to take certain precautions to remove this harshness, to "age" the spirit, and to impart to them the bouquet of different valuable growths. A good recipe for an imitation of the brandy of Armagnac is the following:—

Infusion of hulls of walnuts	1 litre.
,, ,, bitter almonds	2 ,,
Syrup of raisins	3 ,,

This mixture is added to every hectolitre of the trois-six employed, which has been previously diluted with water to the required strength.

Another good imitation of this brandy is:—

Alcohol (of good flavour, at 85°)	56 litres.
Water	40 ,,
Rum	2 ,,
Syrup of raisins (at 36°)	2 ,,
Dried liquorice root	500 grm.
Black tea	60 ,,
Cream of tartar	2 ,,
Boracic acid	1 ,,

Bruise the liquorice root and boil it with half the water intended for reduction; infuse the tea separately in a hermetically closed vessel with 10 litres of boiling water; dissolve the cream of tartar and boracic acid in 2 litres of hot water. When all these preparations have become cold, pass the infusions of tea and liquorice root through a hair cloth, and mix the whole together with the alcohol, rum, syrup of raisins, and enough water to make up to 100 litres; colour the mixture with caramel.

Cognac brandy is the most difficult to imitate; the following recipe being one of the best:—

Alcohol (well flavoured at 85°)	54 litres.
Rum (of good quality)	2 ,,
Syrup of raisins	3 ,,
Infusion of hulls of green walnuts	2 ,,
,, ,, bitter almonds	2 ,,
Water	27 ,,
Powdered catechu	15 grm.
Balsam of Tolu	6 ,,

Dissolve the catechu and balsam of tolu together in a litre of the alcohol, and pour this solution into the remainder of the spirit; mix all the liquids together, stir well, and colour with caramel.

The following recipe is used by one of the largest houses in the spirit trade in Paris:—

Alcohol (good flavoured, at 85°)	68 litres.
Rum	2 ,,
Rain water	30 ,,
Liquorice root	500 grm.
Roman chamomile	125 ,,
Vanilla	10 ,,
Brown sugar	1 kilo.

Bruise the liquorice root, and boil it in a portion of the water intended for the mixture, then make hot infusions of the chamomile and vanilla separately in a hermetically closed vessel. When cold, pass all these infusions through a cloth filter, add them to the spirit, and to the remainder of the water in which the sugar has been dissolved.

When it is required only to "age" or "improve" the genuine new brandies of Cognac, Armagnac, or Montpellier, it is customary to add to them 15 grm. of sugar-candy, or 3 centilitres of syrup of raisins, to a litre. Or the bouquet of the Armagnac brandy may be improved by the addition of a litre of the infusion of green walnut hulls, or a litre of the infusion of the hulls of bitter almonds, or, in the absence of these, of two litres of rum to each hectolitre of brandy.

The brandies of Cognac, Jean d'Angely, Saintonge, &c., may be "aged" by the addition of the following mixture to every hectolitre of the brandy:—

Old rum	2 litres.
Old kirsch	1·75 ,,
Infusion of green walnut hulls	0·75 ,,
Syrup of raisins	2 ,,

In some districts it is customary to "age" new brandies with *low wines* prepared for the purpose by adding 10 or 12 per cent. of brandy at 85° to clear rain-water, in order to preserve it. When the water has been kept for six or eight months in the casks, it is invaluable for imparting the softness and qualities of age to new brandies.

If kept in a cool, but not draughty, place, brandy is capable of being kept for an indefinitely long period. To hinder this evaporation to some extent, the casks should be filled up at least once a month, and twice as often during the heat of summer, or if the cellar be subject to currents of air, which tend to bring about a rapid evaporation. The brandy used for filling up the casks should be as nearly as possible of the same quality as that already contained in them (see Alcohol from Wine).

Gin. (Fr., *Genièvre*; Ger., *Wachholderbranntwein*).—Gin, or geneva, is common grain spirit, aromatized with juniper berries; it is, in fact, nothing more than plain British spirit flavoured with the juice of this berry. A spirit containing this juice was formerly sold by apothecaries, on account of its valuable medicinal virtues, under the name of Geneva. The better varieties are even now prescribed by medical men for use as a diuretic, which property is due solely to the presence of the essential oil of juniper. The proportion employed is variable, depending upon the nature of the spirit and the requirements of the distiller; usually one kilogramme of berries is enough to flavour one hectolitre of raw grain spirit. Before being used the berries are coarsely ground or crushed; they are then either added in that state to the undistilled grain spirit, or, what is much better, interposed in some manner in the course traversed by the spirituous vapour before condensation. In some distilleries it is customary to suspend bags containing the berries in the still, when the condensed liquid is found to be strongly impregnated with the odour and taste of juniper. The berries should be chosen fresh and plump, full of pulp, and of a strong taste and smell; they are usually imported from Germany, though we have a great many of the trees in England.

The finest gin is prepared in Holland, from which country considerable quantities are annually imported into England. In the town of Schiedam alone there are upwards of two hundred gin distilleries, the produce of which is commonly called "Schnaps."

A rough kind of gin is made in Norway and Sweden by digesting the berries for some days in spirits at 50° or 55°. The product, however, has a very disagreeable, sharp taste. It is much preferable to distil the berries after maceration with alcohol at 85° or 90°, and to reduce the product of the operation to 49°.

Gin was originally, and for a long period, imported from Holland under the name of "Geneva" (of which word the common form "gin" is a corruption) from *Genièvre*, the French for juniper. The liquor known by this name in England, or British Gin, is a very different article from that made in Holland. It consists usually of grain spirit flavoured with *Oil of Turpentine*, instead of juniper. This substance closely resembles juniper in taste and smell, and also possesses, but in a less degree, its diuretic properties; being much cheaper, it is almost invariably substituted for juniper in this country. Small quantities of other aromatic substances are introduced into the spirit for the purpose of hiding or "killing" the very unpleasant taste and effects of the unrectified grain spirit. The recipes which are often given in different works for the preparation of gin, are wholly untrustworthy, as they yield a liquor which bears but little resemblance to either British Gin or "Hollands." Indeed, all attempts to make gin from the recipes usually found in books, have invariably resulted in failure. The common impression appears to be that the flavour of this spirit is due entirely to juniper berries, which is not by any means the case, as British gin does not, as a rule, obtain its flavour from this source at all, but from oil of turpentine. Some distillers, however, prefer to heighten the flavour of their products by the addition of a very small quantity of oil of juniper; but in England, this is the exception rather than the rule. Each distiller has his own peculiar recipe, and his product its own characteristic flavour and adherents; the difference between the several varieties, and especially between those of London and Plymouth, is very marked.

In making gin, great care must be taken not to use an excess of flavouring. The following are good recipes for British Gin:—

(1). Grain spirit (proof), 80 gals.; newly rectified oil of turpentine, 1¼ pint; mix well together; add 14 lb. of common salt, dissolved in 40 gals. of water; stir well, and add 3 fluid drs. of creasote; distil over 100 gals., or until the faints begin to rise. The product is 100 gals. of gin (22 u.p). Half-a-pint either of rectified fusel-oil, or of oil of juniper, may be added.

(2). Grain spirit (proof), 80 gals.; oil of turpentine, 1 pint; oil of juniper, 3 fluid oz.; salt, 21 lb., dissolved in 35 gals. of water; oil of caraways, ½ fluid oz.; oil of sweet fennel, ¼ fluid oz.; oil of sweet almonds, 1 dr.; essence of lemons, 4 drs.; distil 100 gals. (22 u.p.), and add 2 drs. of creasote.

(3). Grain spirit (proof), 80 gals.; oil of turpentine, ¾ pint; oil of junipers, ¼ pint; creasote, 2 drs.; oranges and lemons, sliced, 9 of each; macerate for a week, and distil 100 gals. (22 u. p.)

(4.) To make 100 gals. of gin, take 1 oz. oil of juniper; ½ oz. oil of bitter almonds; ½ oz. of oil of caraways; ½ oz. oil of cassia; ¼ oz. of oil of vitriol; put the whole into one pint of spirits of wine, as nearly 60 overproof as possible; shake well together in a bottle, two or three times a day, for two days. This should always be prepared at least a week before it is wanted, so that the oils may be well killed. One ounce of chilies is boiled in three pints of liquor, or water, until reduced to one quart, and then strained off through a fine sieve; the whole is put into the gin with 45 to 50 lb of lump sugar dissolved in as many pints of water, and 15 gals. of water; this will be very strong gin. Twenty gallons of water will not be found too much, as the ingredients in this receipt will give ten gallons more apparent strength and flavour than gin made up with sugar and water only. It may be fined down with 4 oz. of alum, and 2 oz. of cream of tartar dissolved in 1 pint of water. The tartar should be put in with the alum after it is dissolved. If rummaged well together, the whole should be clear and bright in one day's time. If it be required to make up more or less than one hundred gallons, the quantity of ingredients used must be increased or diminished in proportion.

The oil of turpentine used must be of the very best quality. Juniper berries, bitter almonds, or the aromatic seeds may be substituted for the essential oils, though the latter are preferable. Only a small quantity of any of these may be employed. The addition of creasote imparts to the spirit a flavour resembling that of whiskey; the lemons and other aromatics, an agreeable richness or fulness, which may also be enhanced by the addition, in minute quantities, of caraways cardamoms, cassia, &c. Fusel-oil is added to increase the whiskey flavour afforded by the creasote; crude pyroligneous acid is sometimes used for the same purpose. The creaminess and smoothness of Hollands gin is due to age; it is sometimes imitated by British distillers by adding sugar. Occasionally grains of paradise, cayenne pepper, and sulphate of zinc are added by fraudulent dealers, as well as, in some cases, caustic potash, which affords to the spirit a peculiar piquancy, often mistaken by inexperienced consumers as a proof of its quality and strength.

The spirit obtained from the above recipes is termed "unsweetened" gin, but that usually sold in London contains a large proportion of sugar, and is known as "sweetened," or "made up" gin. This addition of sugar is objectionable, inasmuch as it permits very extensive adulteration and dilution of the spirit with absolute impunity.

All the utensils employed in the preparation of gin should be perfectly clean, as gin which has become coloured or stained is much depreciated in value. If the colour be deep, the spirit is rendered unsaleable, and must be redistilled; if very slight, the addition of a spoonful or two of strong acetic acid will probably remove it.

An imitation of gin, made without distillation, may be prepared by simply digesting or dissolving the flavouring ingredients in the spirit. In this case, no salt must be employed (see Alcohol from Grain).

Kirschwasser. (Fr., *Kirschwasser ;* Ger., *Kirschwasser.*) A spirituous liqueur obtained by the distillation of cherries, as its name implies (cherry water); it is commonly contracted into Kirsch. It is made exclusively in Germany and Switzerland, in the following way:—The cherries, preferably the wild variety, are shaken from the trees when ripe, and thrown by children into open hogsheads. Here they are all mashed together, whether unripe, ripe or rotten, and allowed to ferment. When this process is complete, which generally takes from fifteen to thirty days, according to the weather, the whole mass is thrown into an ordinary Turk's head still, and distilled over a naked fire. The result is, of course, a spirit of very unpleasant smell and taste, and is decidedly unwholesome, as the fruit, during fermentation, is constantly allowed to become acid or mouldy. Moreover, the distillation over an open fire tends to produce an empyreumatic flavour which the oils from the crushed seeds often fail to conceal.

The largest quantity, and by far the best quality of kirschwasser is made in the Black Forest. A good variety also comes from the Vosges. In these places, only the perfectly ripe fruit is chosen, that which is rotten or damaged being rejected. It is then crushed by hand, or by a wooden rubber, on a wicker basket or trough supported by a frame resting on a tub. The juice falls into the tub while the pulp and seeds remain in the basket. The latter are afterwards carefully picked out and thrown into the juice. The process of fermentation is carefully attended to; the vats being tightly covered and kept at the correct temperature. The must should be at about 6° or 7°, and the process, which is conducted without the use of an artificial ferment, should occupy four or five days. When complete, the liquor is drawn off and distilled properly by the aid of steam.

The kirsch of the Black Forest is equal in strength to the most powerful spirit, and has a delicate perfume and taste, resembling those of bitter almonds, owing to the presence of a small quantity of prussic acid derived from the kernels.

The product in alcohol from 100 kilos. of cherries is about 7 or 8 litres of kirsch at 55° or from $3\frac{3}{5}$ litres to $4\frac{2}{5}$ litres of pure alcohol.

It is customary to put new kirsch into glass bottles or flasks, which, during the first year, are closed with some substance which will permit a slight evaporation; by this means, the acid principles are volatilized and the spirit is rendered more agreeable; it is afterwards corked tightly to be kept. In the absence of bottles, it is put into small casks or kegs made of ash, in order that the spirit may not receive any colour from the wood, kirsch being of greater value when limpid and colourless. It is, like all other spirits, much improved by age.

Kirsch is constantly met with in the market mixed with brandy, or alchohol from apricot seeds, and reduced to 51°. Sometimes alcohol perfumed with essence of bitter almonds is added to it; but these adulterations are readily detected by the difference in taste. The following, however, is a good recipe for an imitation of kirsch :—

Cherry seeds	9 kilos.
Apricot seeds..	3 „
Dried peach leaves	625 grm.
Myrrh	150 „
Alcohol (at 85°)	62 litres

The seeds are bruised and digested in a water-bath in an ordinary still for twenty-four hours. At the commencement of this process, about 30 litres of water are added, and the still is tightly closed and heat applied. When 60 litres have come over, 40 litres of water must be added to reduce the spirit to 50°. Fifteen grammes of sugar are finally added to correct the sharpness of the product.

Kirsch is sometimes adulterated with a liquid extracted from sloes.

Liqueurs, the French name for all spirituous drinks which are obtained artificially, whether by fermentation, such as rum, gin, kirschwasser, &c., or by mixing various aromatic substances with brandy or alcohol, such as curaçoa, anise cordial, absinth, &c.; in England the name has become restricted to the latter class.

Originally, liqueurs consisted merely of the fermented juice of the grape, flavoured with various aromatic substances. The earliest liqueur on record is a mixture of wine, cinnamon, and honey, which was for a long period a very fashionable beverage, used on all occasions of festivity; it is said to have been first prepared by Hippocrates. At a later period, other liqueurs were prepared by digesting in wine such herbs as hyssop, calamus root, and absinth, and were very popular in the tenth, eleventh, and twelfth centuries, under the generic name of "wine of herbs." The first liqueur which contained alcohol as its basis was simply brandy mixed with sugar; it was more used as a medicine than as a beverage, and was known as "*eau divine.*" The Italians were the first to employ alcohol to extract the flavouring and aromatic principles of plants and flowers, in order to produce agreeable and perfumed liqueurs. These were called "*liquori,*" and were exported largely into other countries, and into France in particular. Shortly afterwards they were manufactured and sold in Paris by Italian compounders on a larger scale. At the beginning of the last century, the Americans introduced their famous ratafia from *cedrat*, which they called *crême des barbades;* and about the same time curaçoa first made its appearance in Amsterdam, and anisette in Bordeaux. Since then they have multiplied enormously, many of them being named after the inventor. Most are obtained by steeping in pure brandy or spirit different fruits or aromatic herbs, and submitting the resulting liquid to distillation. Cochineal, caramel, indigo, and other colouring matters are used to colour liqueurs, and they are also sweetened with sugar. The manufacture of these liqueurs constitutes the trade of the "compounder" or "liquorist."

Some liqueurs are prepared simply by steeping the ingredients in proof spirit for a length of time, without having recourse to distillation; but these do not possess the fine delicate flavour of the other class, and they are of small importance.

The first process in the manufacture is the solution in alcohol of the particular aromatic substances which are to supply the required flavour and aroma. The spirit employed for this purpose must be of the very best and purest quality. Rectified spirit of wine is, owing to its freedom from flavour, best adapted for the use of the liquorist. The ingredients are usually well bruised, and, in some cases, ground to powder. Immediately after this, they are placed in the spirit, and the whole is constantly agitated for a longer or shorter period, as the case may demand; generally, the time occupied is from five days to a fortnight. The distillation is carried on in any ordinary copper still, provided with a suitable condensing arrangement. Salt is sometimes added to the ingredients in the still. The products of distillation are brought to the requisite strength by the addition of pure soft water, or of the syrup used for sweetening. The sugar used must be of the finest quality, and is added in the form of a thin, clear syrup, after the spirit has been clarified or filtered, but never before. If great care has been bestowed upon the selection of the materials, and upon the subsequent operations, the liqueur, when made, will be perfectly clear and bright. Occasionally, however, they may appear clouded or milky: when this is the case, it is necessary to add a little white of egg, or of a solution of alum in water. These are termed "finings," and are generally effectual in removing cloudiness, and rendering the spirit clear and transparent.

Careful attention must be paid to the *amount of flavouring matter* added to the spirit. A very slight excess not only renders the liqueur disagreeably high-flavoured, but the excess of essential oil induces a milkiness also, which is extremely difficult to get rid of. It should be borne in mind that whenever the quantity required is uncertain, *too little* should be added at the outset, as the correct flavour may readily be imparted afterwards by the addition of a little more flavouring.

The process of distilling when applied to liqueurs must be very carefully attended to. The still should be thoroughly cleansed before each operation, and the coil well rinsed with hot water in order to remove the flavour left by the last distillation. When conducted over a naked fire, the still must be placed on an iron grating which rests on the furnace, to prevent the ingredients from adhering to the bottom of the still and becoming burnt, thereby imparting an empyreumatic flavour to the products. The boiler of the still should be only about two-thirds full, and the plants employed, especially if they be dried, should be cut up as small as possible, in order to prevent them from swelling. All joints should be carefully closed with a paste made of flour and water, over which is placed a strong band of paper or linen, so as to cover the joint completely and closely. Heat is then applied, at first gradually, and afterwards increased as the operation proceeds; on the appearance of the first few drops, it is well to moderate the heat slightly for a few moments. Great care is requisite in the management of the fire in order to produce a regular and even flow of liquid from the coil; if the fire be pushed too rapidly, the faints will come over and an empyreumatic flavour will thereby be produced in the spirit; which flavour is highly objectionable. The water in the cooler must be changed frequently.

Distillation over an open fire, although it progresses with more rapidity, has the disadvantage of altering the product more or less, owing to the unequal distribution of the heat. Distillation over a water-bath is conducted in precisely the same way, but it does not require so much attention. The boiler is placed on the furnace—the grating previously used being removed—and is half filled with water. The water-bath containing the various ingredients is then fixed in its place, the joists are carefully luted, and heat is applied. The products obtained by this method are much purer, and possess a far more delicate flavour, owing to their perfect freedom from empyreuma, than the products of distillation over an open fire. But perhaps the best method in use is that of distillation by steam, which is conducted in the following way:—Fill the steam boiler three-fourths full of water, and boil. When the correct pressure is indicated by the steam-gauge, admit a small jet of steam to the still so as to heat the contents at first gently; the cock may afterwards be opened to the full extent. The still is managed precisely as in the previous operations. This method is employed only in the large liqueur manufactories owing to the expense of erecting boilers, &c., but, when once established, the process is preferable to any other for economy of fuel, facility of working, and quality of the product. The following is a list of plants which should always be distilled by steam:—

Absinth.
Anise.
Caraway.
Citronella.
Fennel.
Juniper.
Hyssop.
Lavender.
Melilot.
Balms.
Mint.
Orange.
Rose.
Sage.
Wild Thyme.
Garden Thyme.

When the first method, namely, that of distilling over a naked fire is employed, the distillate must be subjected to a process of rectification. This consists in pouring the crude distillate into the water-bath of a still and diluting it with water, whereby the excess of volatile oil is liberated, and made to collect in globules upon the surface. By its means, is also effected the removal from the spirit of the empyreumatic flavour acquired during the course of a distillation pushed to excess. In conducting this operation, it is necessary to watch the fire carefully and to frequently renew the water in the cooler.

It is impossible to lay too much stress upon the importance of exercising care in making choice of the ingredients to be employed by the liquorist. A few general hints on this subject will probably be found useful to the reader. All seeds, roots, woods, and other drugs should be purchased ready dried; the seeds should be full and plump, roots sound and very dry, and woods hard and compact. When flowers are used, the freshest, and those possessing most perfume, should be selected; they should also be full-blown and quite dry. Fruits having a good flavour and colour are to be preferred, and those which are perfectly fresh, having been gathered in dry weather, and possessing a sound and smooth skin. The plants used should also have been gathered in dry weather, and they should be healthy and vigorous in growth: when dry, they should be packed in paper and kept in a dry place.

Liqueurs are never perfect in flavour immediately after their preparation; they require time, mellowing and many precautions for their preservation in order to produce the desired result. The room in which they are stored should be kept uniformly at a temperature of 15° or 20°, and this room should be situate as far as possible from all external noises and disturbance. Daylight, and especially the direct rays of the sun, tend to destroy the colour of liqueurs, causing the colouring matter to fall to the bottom of the bottles. When in large quantities, it is far better to store them in casks, which should be as large as possible.

We subjoin various recipes for the best known and most highly esteemed liqueurs.

Anisette.

Spirit of Anise	5 litres.	Sugar	12·5 kilos.
Alcohol (at 85°)	20 „	Water	66 litres.

Place the spirit of anise and the alcohol in a can; add the sugar dissolved in a little of the water; pour in the rest of the water; size with white of egg or solution of alum; allow to stand and filter.

Cedrat cordial.

Fresh cedrats (outer rind)	150	Alcohol (at 85°)	50 litres.

Digest, distil, and rectify, to obtain 40 litres of spirit; add:—

White Sugar	56 kilos.	Water	22 litres.

Colour to a bright yellow with caramel.

Chartreuse. (Green).

Dried lemon balm	500 grm.	Thyme	30 grm.
Hyssop in flower	250 „	Arnica flowers	15 „
Peppermint (dried)	250 „	Buds of Balsam Poplar ..	15 „
Genepi	250 „	China Cinnamon	15 „
Balsamite	125 „	Mace	15 „
Angelica (seeds)	125 „	Alcohol (at 85°)	62 litres.
Angelica (roots)	62 „		

Digest for 24 hours; distil and rectify to obtain 60 litres; add 25 kilos. of refined white sugar dissolved by heat in 24 litres of water; mix the whole and make up with water to 100 litres. Mellow and colour green with a mixture of blue colouring and infusion of caramel or saffron. Size, allow to repose and filter.

(Yellow).

Lemon balm	250 grm.	Mace	15 grm.
Hyssop in flower (tops) ..	125 „	Coriander	1500 „
Genepi	125 „	Socotrine aloes	30 „
Angelica (seeds)	125 „	Cardamoms (small)	30 „
Angelica (roots)	30 „	Cloves	15 „
Arnica flowers	15 „	Alcohol (at 85°)	42 litres.
China Cinnamon	15 „	Refined white sugar ..	25 kilos.

Make up to 100 litres with water, and proceed as above, colouring yellow with saffron.

(White).

Lemon balm	250 grm.	Cloves	30 grm.
Genepi	125 „	Nutmegs	15 „
Hyssop in flower (tops)	125 „	Cardamoms (small)	30 „
Angelica (seeds)	125 „	Calamus	30 „
Angelica (root)	30 „	Tonka beans	15 „
China Cinnamon	125 „	Alcohol (at 85°)	52 litres.
Mace	30 „	Best refined white sugar	37 kilos.

Make up to 100 litres with water, and proceed as above.

Curaçoa.

(1). Spirit of curaçoa	8 litres.	Sugar	12·5 kilos.
Alcohol (at 85°)	17 „	Water	66 litres.

Proceed in the same way as for the above; colour with caramel.

(2). Spirit of curaçoa	10 litres.	Sugar	25 kilos.
Alcohol (at 85°)	40 „	Water	33 litres.

Colour with caramel to a deep yellow, and proceed as above.

(3). Spirit of curaçoa	12 litres.	Sugar	25 kilos.
Infusion of curaçoa	15 centilitres.	Water	55 litres.
Alcohol (at 85°)	15 litres.		

Colour with caramel, and proceed as above.

Noyeaux.

(1). Spirit of apricot seeds	9 litres.	Sugar	12·5 kilos.
Alcohol (at 85°)	16 „	Water	66 litres.

Proceed as for Anisette.

(2). Spirit of apricot seeds	14 litres.	Sugar	25 kilos.
Alcohol (at 85°)	36 „	Water	33 litres.

Proceed as for Anisette.

(3). Spirit of apricot seeds	14 litres.	Sugar	25 kilos.
Alcohol (at 85)	14 „	Water	55 litres.

Proceed as for Anisette.

Peppermint cordial.

(1). Peppermint water	8 litres.	Sugar	12·5 kilos.
Alcohol (at 85°)	25 „	Water	58 litres.
(2). Peppermint water	12 litres.	Sugar	25 kilos.
Alcohol (at 85°)	50 „	Water	21 litres.
(3). Peppermint water	10 litres.	Sugar	25 kilos.
Alcohol (at 85°)	28 „	Water	15 litres.

Proceed in each case as in the above recipes.

Ratafia.

Pure alcohol	21·25 litres.	Wine of Rousillon or Loire	7 litres.
Infusion of cassis (black currants)	18 „	Alcohol (at 85°)	14 „
		Raw sugar (well clarified)	12·5 kilos.

Add water to make up to 100 litres.

Usquebaugh. (Scotch).

Saffron	60 grm.	China Cinnamon	60 grm.
Juniper berries	250 „	Musk mallow	60 „
Coriander	250 „	Fresh lemons (outer rind)	25 „
Star anise	125 „	Alcohol (at 85°)	40 litres.
Angelica root	125 „		

Digest for a month, with occasional stirring; strain through a hair-sieve, and add:—

Water	41 litres.	Refined white sugar	25 kilos.
Orange flower water	2 „		

Colour a light reddish-yellow, with cochineal.

Vanilla.

Vanilla	200 grm.	Alcohol (at 85°)	40 litres.
Refined white sugar	56 kilos.	Water	22 „

Cut the vanilla up small; bruise it in a mortar with about 5 kilos. of the sugar; pour the spirit and syrup of sugar into a water-bath, and add the vanilla; mix well together in the still, and heat gently so as to digest without distilling. Allow to cool, colour with cochineal, size, allow to stand, and filter.

Rum. (Fr., *Rhum;* Ger., *Rum.*) The name of rum is applied to a spirit obtained from the molasses of the sugar-cane, in the manner described on p. 204. It is a spirit of excellent quality and flavour, and is much valued when old. That which comes from the West Indian Islands, and particularly from Jamaica, is the best. Martinique and Guadaloupe furnish also very good qualities. Considerable quantities of rum are also made in Brazil, and imported into Europe and North America. When new, rum is white and transparent, and has a peculiar, unpleasant flavour, which is generally understood to proceed from the resinous aromatic gum, or essential oil, contained in the rind of the cane; but apart from this, an empyreumatic oil appears to be generated during the fermentation of the wash which Liebig ascribes to the interchange of the elements of sugar and gluten. This flavour is, however, exceedingly undesirable, and has to be removed before the spirit is fit for the market; this may be done by the use of charcoal and lime, the former to absorb, and the latter to combine with the oil, and to precipitate it in the form of a soap. A wooden box, about 2 ft. long and 1 ft. in diameter, with a division running down to within an inch of the bottom, is filled with coarsely powdered charcoal, through which the spirit is made to pass as it runs from the worm. The charcoal absorbs a considerable portion of the oil, and the rum consequently flows from the filter much purified. It is then conveyed to the rum butt (of about 300 or 500 gallons capacity), which is situated at a good elevation, and at once heated with a little caustic lime, and well-stirred up. After an interval of two days, the flavour may be tried, and if found satisfactory, the contents of the butt may be drawn off through a charcoal filter, similar to the first, into the colouring butt to be coloured. But if the lime used be not enough, a little more must be added, mixing the whole together again; and after two days it may be run off as noticed. At this period the lime will be seen at the bottom of the butt in combination with the oil, forming together a kind of soapy precipitate.

When this process has been carefully conducted, quite new rum may be afforded the appearance and flavour of aged spirit. Pineapple juice is sometimes employed by the planters for the purpose of ageing new rum.

The next operation is to colour the rum, and this is a very important part of the process. It frequently happens that really good rum is quite spoilt by being badly coloured, and this should therefore be strictly attended to. The best description of sugar for boiling "colouring" is a well-grained *muscovado,* such as is commonly chosen in Jamaica. It is placed in a large copper or iron boiling pan, to which heat is applied. The contents are well-stirred up by means of a wooden oar or rake throughout the process. As the boiling proceeds, bubbles rise, large and heavy at first, then small and more quickly, the colour of the mass changing from brown to deep black. The fire is then withdrawn, and some strong proof rum is added, the whole being stirred hard meanwhile. When quite cool, it is poured into a cask and allowed to settle. Good colouring is quite thick, clear, and bright; three pints should be sufficient to colour 100 gallons of spirit. When coloured, the rum is filled into hogsheads for sale or shipment.

Pure rum, as made in the West Indies, is not often met with in commerce. The spirit which is so largely drunk in England as rum, is in reality nothing more than mixtures of British spirit, or "silent" spirit, as it is called, with small quantities of genuine rum, and of *essence of rum,* a butyric compound made for the purpose of preparing a fictitious rum. The greater portion probably contains no genuine rum at all, and consists merely of silent spirit, or beet spirit flavoured with this volatile essence. The consumption of rum is steadily declining in England, its place being taken by gin. The duty on the genuine article, if imported direct from any of the British Colonies, is 10*s.* 2*d.* per proof gallon, but if imported from any other part of the world, it is 10*s.* 5*d.* per gallon. It is consumed in considerable quantities in the Royal Navy (see Alcohol from Molasses).

Whiskey. (Fr., *Whisky;* Ger., *Whisky.*) The spirit obtained from the fermented wort of malt or grain, or from a mixture of these. The chief seats of the manufacture are in Ireland and Scotland; the very best of the Irish kinds comes from Dublin, and is known in the market as Dublin whiskey. The difference between the Irish and Scotch varieties lies mainly in the fact that the former is distilled in the common, or so-called "pot still," which brings over, together with the spirit, a variety of flavouring and other ingredients from the grain; while in Scotland, nothing but Coffey's "patent" still is employed, the product of which is a spirit deprived entirely of all essential oils. The Irish distillers claim a distinct advantage in the presence of fusel-oil in their produce, on the ground that, if kept in wood for a certain length of time, this oil is decomposed into a number of volatile ethers, readily recognized by their fragrant perfume, and by their pleasant exhilarating effects when consumed. They assert further that the Scotch produce or "silent spirit" as they agree to term it, undergoes no change on keeping, and possesses no flavour, but only the pungent penetrating odour, peculiar to alcohol; and that in order to convert this silent spirit into whiskey, it has to be flavoured with different substances which have no exhilarating effects upon the systems whatever, but are rather injurious to the habitual consumer. Another argument advanced by the Irish distiller in favour of his own produce is that as the spirit yielded by the patent still is absolutely flavourless, the Scotch manufacturer may, if he will, employ damaged grain, potatoes, molasses refuse, and various other waste products to yield the silent spirit, since, owing to its "silence," there is no possibility of detecting afterwards from what source it has been obtained, and that not only are the distinctive qualities of good whiskey thereby kept out of the spirit, but that the spirit itself may also be of an inferior character.

The Scotch distillers, on the other hand, affirm that Irish, or pot-still whiskey, is less wholesome than their own produce on account of the presence in the former of the large quantities of fusel-oil. They maintain, also, that patent still whiskey *does* improve very much by keeping, and brings a higher price in the market when old; and they strongly repudiate the insinuation that they employ damaged or refuse materials, for the production of their spirit.

The product of the pot-still, as stated above, does not contain merely alcohol and water, but also, in intimate mixture or in solution, other matters yielded by the grain, and either previously existing in it or formed during the processes of fermentation and distillation. These are present chiefly in the form of volatile oils and vegetable acids, and their quantity as well as their nature depends upon the quality of the grain, and the amount of care bestowed upon the fermentation and other subsequent processes. The finest Dublin whiskey, when made, is stored in large casks, at a strength of 25 per cent. overproof. During its sojourn in the cask, the reactions which occur between the above substances, and the alcohol itself lead to the gradual formation of those fragrant volatile ethers which impart to the spirit its characteristic perfume and flavour. It attains its full maturity and highest excellence at an age of from three to five years in the wood; after this period, it may be bottled and preserved for an indefinite length of time without undergoing further change.

Owing to the reputation enjoyed by whiskey of an Irish, or Dublin manufacture, an enormous quantity of both Scotch and English silent spirit finds its way to Dublin or Belfast, in order that it may be falsely palmed off upon purchasers, under cover of an Irish permit, as Irish whiskey. Genuine whiskey is put generally into old sherry casks, by which means a slight flavour and colour are afforded to it. Large quantities of an inferior sherry, known as "Hamburgh Sherry," are also employed in effecting the conversion of silent spirit into whiskey. The actual composition of this "sherry" is not known, except by those who make it, but there is no evidence to show that it is harmful. The process known as "blending" is largely resorted to for the purpose of introducing silent spirit into the market under the name of whiskey. In order to effect this, it is the custom to mix a quantity of coarse, new, strongly-tasted, genuine pot-still whiskey with an equal quantity of silent spirit, the value of which is about one-half that of the former kind, and to sell the mixture as old Irish whiskey. On account of the strong taste of the former spirit, and the absolute tastelessness of the latter, the effect of mixing the two is to produce a spirit which is much milder than the genuine Irish spirit employed, and which may be represented to the consumer as being of greater age and better quality than it really is. This practice has been so widely carried on that enormous quantities of new whiskey, containing fusel-oil and other impurities, which in course of time would have undergone beneficial changes, have been consumed as *old spirit* simply through being diluted with silent spirit. It is possible, however, to distinguish readily between the two varieties. Genuine whiskey of mature age has an exquisite perfume, and when freshly opened soon fills the room with its fragrance. A few drops rubbed upon the palms of the hands retain their fragrance until completely evaporated; whereas, the odour left by silent spirit, or counterfeit whiskey, when submitted to the same test, is of a decidedly unpleasant nature (see Alcohol from Grain).

ALDEHYDE.—A volatile, mobile fluid, discovered by Döbereiner, who obtained it in an impure state, and named it *light oxygen ether*. It was afterwards prepared in a pure state by Liebig, who also demonstrated its constitution and properties.

The composition of aldehyde may be represented by that of alcohol after the abstraction of two atoms of hydrogen; then alcohol being represented by the formula C_2H_6O, that of aldehyde is C_2H_4O; the word "aldehyde" itself is an abbreviation of "*alcohol dehydrogenatum.*" Aldehyde constitutes an intermediate stage in the oxidation of alcohol into acetic acid, and is produced by the destructive distillation of alcohol, and many other organic compounds. There are very many methods by which aldehyde may be prepared, the following, by Liebig, being the best:—Two parts of 80 per cent. alcohol are mixed with two parts of water, three parts of peroxide of manganese, and three parts of oil of vitriol, and the mixture is introduced into a capacious retort fitted with a receiver, which is kept constantly cool. The contents are heated gently until they begin to froth, and the distillation is arrested when the receiver contains about one-third, and the distillate begins to redden litmus. When this is the case, it is mixed with its own weight of chloride of lime and redistilled until $1\frac{1}{8}$ part has been obtained; this product is treated in the same way, and the distillate, amounting to about $\frac{3}{4}$ part is mixed with twice its volume of ether, and saturated with dry ammonia gas. The crystals of aldehyde-ammonia obtained are washed with ether and dried; two parts are then dissolved in water, and a mixture of three parts of sulphuric acid with four parts of water is added; the whole is next distilled at a low heat, on the water-bath, and the vapours of aldehyde are condensed in a receiver surrounded with ice, after being dehydrated by passing over chloride of calcium.

Aldehyde is a thin, colourless fluid; it is very inflammable, burning with a pale, bluish flame. Its specific gravity is 0·800, and its boiling point 21°. It possesses a very pungent odour, mixes in any proportion with water, alcohol, and ether, and readily dissolves iodine, sulphur, and phosphorus. Aldehyde combines with aniline, forming a brilliant violet colouring matter discovered by Charles Louth. It is prepared artificially in an impure state for this purpose.

The word *aldehyde* seems now to signify any compound which yields an alcohol by taking up two atoms of hydrogen, or an acid by taking up two atoms of oxygen. Some compounds which are classed as "aldehydes" (for this reason), enter largely into the composition of various essential oils, such as those of bitter almonds, cinnamon, rue, &c., and, with the knowledge of this fact, it may be possible to prepare these oils artificially on a large scale.

ALKALIES. (Fr., *Alcali;* Ger., *Alkali.*) The name *alkali*, in its widest sense, is given to a large class of compounds which possess certain distinctive properties. In its most restricted sense it is applied to four substances only, viz. potash, soda, lithia, and ammonia; and these four substances are usually called the *alkalies proper.* But under the same title are included the hydrates of the metals barium, strontium, and calcium, which possess alkaline properties to a greater or less degree; these are commonly known as the *alkaline earths.* A large number of organic bodies, both natural and artificial, are also classed as alkalies under the generic title of organic alkalies or *alkaloids.* Each of these classes will be treated of in detail in the following articles, and it will be necessary here only to state the characteristic properties which are common to the three. They are (1) solubility in water; (2) they neutralize the most powerful acids, and with the weaker acids from salts having alkaline properties; (3) they exert a caustic or corrosive action upon animal and vegetable matters; and (4) they alter the colours of many vegetable colouring matters, such as litmus, turmeric, and others.

Organic Alkalies, or **Alkaloids.**—Numerous vegetable, and some animal substances, have been classed as alkalies, on account of the very striking analogy which they present, in constitution with the volatile alkali, ammonia. From the processes by which some alkaloids have been prepared artificially, they are regarded by modern chemists as ammonia in which all or part of the hydrogen is replaced by a compound organic radical, composed usually of carbon and hydrogen. All the alkaloids possess alkaline properties in some degree, and combine directly with acids, forming salts of more or less stability; some have a strongly alkaline reaction with vegetable colouring matters, but in others this reaction is much feebler. By far the larger number of organic alkalies are obtained from the vegetable kingdom, some few from the animal kingdom, while a considerable number have of late years been prepared on a small scale by various chemical processes. Among the vegetable alkaloids are found some of the most valuable medicines, such as *aconite, brucine, cinchonine, morphia, quinine, strychnine, &c.;* among these are also numbered many of the most virulent poisons known.

The method employed for the extraction of vegetable alkaloids from the plants which contain them is in most cases the same. If the alkaloid be soluble in water, as these compounds usually are, a strong infusion of the plant in pure water is made; but if the alkaloid be insoluble, a little mineral acid is added to the water. This solution is filtered and concentrated, after which the alkaloid is precipitated with carbonate of lime, ammonia, or carbonate of soda. The precipitate is collected on a filter, washed, and dried. When thoroughly dry, it is treated with alcohol to dissolve the alkaloid, and the solution is filtered and evaporated. The alcoholic solution usually requires decolorizing and purifying, which are effected in a variety of ways. Some of the most important alkaloids employed in medicine will be considered below.

Aconitine.—This alkaloid is obtained from the leaves of the *Aconitum napellus.* The leaves are infused in alcohol, and the solution is treated with milk of lime, which liberates the alkaloid in solution. To the filtered liquid a little sulphuric acid is added, and the precipitated sulphate of lime is filtered off. The filtrate is evaporated until free from alcohol, when the aconitine is precipitated by an alkaline carbonate. This precipitate is re-dissolved in alcohol, and the solution is decolorized by animal black, and evaporated to dryness. The residue is re-dissolved in sulphuric acid, and precipitated anew with an alkaline carbonate; the precipitate thus obtained yields pure aconitine on treatment with ether. It is deposited from this solution in a white powder, or sometimes in the form of a compact, transparent, vitreous mass. It is inodorous, intensely bitter, and dissolves in fifty parts of boiling water; its solution is powerfully alkaline. A very small quantity causes death with violent tetanic convulsions.

Atropine.—Atropine is found in the belladonna (*Atropa belladonna*), and in the roots of the *Datura stramonium.* It is obtained from the latter by exhausting the roots with alcohol and adding milk of lime to the solution. The liquid is filtered and saturated with a slight excess of dilute sulphuric acid; it is then boiled till free from alcohol and precipitated with carbonate of potash, filtered and allowed to stand; the atropine is deposited in fine, silky needles, and subsequently purified by frequent crystallization in alcohol. Care must be taken not to raise the temperature too high in these processes, as atropine is extremely volatile. It is slightly soluble in water, and considerably so in alcohol and ether. It is very alkaline, and has an intensely bitter taste. It is used in medicine, in minute doses, a full one being about $\frac{1}{30}$th of a grain.

Brucine.—Brucine is contained in the *St. Ignatius bean*, and in the *Strichnos nux vomica*, along with strychnine. It is generally prepared from the latter plant, which is much cheaper. The powdered nuts are treated with very dilute, boiling sulphuric acid, and expressed. The acid is next saturated with excess of milk of lime, by which sulphates of lime, strychnine, and brucine are thrown down. The precipitate is collected on a filter, and dried, and then treated with boiling alcohol, which dissolves the two alkaloids. The liquid is filtered while hot, and in cooling deposits the greater part of the strychnine. The brucine remains in solution and may be obtained by evaporation. They are both purified by repeated crystallization in alcohol. Brucine is slightly soluble in water, freely soluble in alcohol, but insoluble in ether. It is alkaline, bitter, and very poisonous.

Cinchonine.—This alkaloid exists with quinine in most of the cinchona barks, and is obtained from them in the same way as quinine (see Quinine). The mother-liquors containing sulphate of cinchonine, are precipitate with carbonate of soda, and the precipitate is digested in ether, which dissolves the quinine. The cinchonine is dissolved in alcohol, and the solution is decolorized with animal black; it is next filtered and submitted to slow evaporation, when the cinchonine is deposited in quadrilateral crystals. Cinchonine is insoluble in cold water, but soluble in 2,500 parts of boiling water. It is alkaline and bitter, and like quinine, a febrifuge, though in a less degree.

Morphine.—Morphine, or Morphia, is the most important alkaloid obtained from opium. To obtain it, the opium is digested in tepid water, and strongly expressed several times. The solution is now evaporated down with powdered carbonate of lime. When about the consistence of a syrup, water is added, and the precipitated meconate of lime is filtered off. The liquid is again concentrated at a gentle heat. When concentrated and quite cold, a solution of chloride of calcium and a little hydrochloric acid are added, and the mixture is left to stand for fifteen days. During this time crystals of hydrochlorates of morphine and codeine are deposited. In order to separate these, the crystals are dissolved in water, and treated with dilute ammonia, which precipitates the morphine, leaving the codeine in solution. The morphine is purified by repeated crystallizations in alcohol. When prepared in this way, morphine is often contaminated with a little narcotine, which may be removed by treating with ether in which morphine is quite insoluble. Morphine is very slightly soluble in cold water, in boiling water it is more soluble, and still more so in boiling alcohol. It has no smell, but an intensely bitter taste, and has a powerfully narcotic action. It is used medicinally in very minute doses as a sedative. In larger doses it is extremely poisonous.

Quinine.—Quinine is, perhaps, on account of its tonic and febrifuge properties, the most important alkaloid known. It exists with cinchonine and other substances in the bark of the cinchonas. The bark is powdered, and boiled several times with sulphuric, or hydrochloric acid; after each boiling it is carefully expressed, and afterwards the liquors are mixed together. The quinine, cinchonine and some impurities are precipitated with carbonate of soda, and the precipitate is collected in a cloth, compressed, dried, and digested with alcohol. The solution is next treated with dilute sulphuric acid, in sufficient quantity to exactly saturate the alkaloids, after which the alcohol is removed by boiling. The liquid is now allowed to cool, when the quinine is deposited as sulphate in crystals. The cinchonine, which is more soluble, remains in the mother-liquors. The crystals of sulphate of quinine are dissolved in alcohol, and the solution is decolorized by the addition of a little animal black; they are subsequently purified by recrystallization. If the mother-liquors still contain quinine, they are precipitated by carbonate of soda, and the precipitate is re-dissolved in sulphuric acid. The sulphate of quinine is separated by repeated crystallizations. Pure quinine may be prepared from the sulphate by precipitating it with a mineral alkali.

Prepared in this way, quinine forms a white amorphous mass. It is inodorous, very bitter, soluble in about 350 parts of cold water, and 400 parts of boiling water, in 2 parts of cold alcohol, 60 parts of ether, and 6 parts of chloroform. Quinine is a powerful alkali; it alters vegetable colours, and forms a series of well-defined stable salts, among which is a soluble carbonate. Sulphate of quinine is much valued as a medicine, and as it is very expensive, it is much adulterated. The principal adulterations are crystallized sulphate of lime, boric acid, sugar, salicine, mannite, stearic acid, and the sulphates of cinchonine, and quinidine. Imperfect purification, however, will often account for the presence of the two latter.

Strychnine.—Strychnine is contained in the *Strychnos nux vomica* and in the *St. Ignatius* bean. The method of preparing it has been described under Brucine.

Strychnine is colourless and inodorous, but has an extremely bitter taste. It dissolves in 6667 parts of cold water, and in 2500 parts of boiling water. It is a most deadly poison, half a grain being sometimes sufficient to cause death, though its effects vary with different individuals. It is much valued as a medicine for paralytic disorders, but the utmost care should be taken in the use of it, for very many deaths have been caused through carelessness in administering too large doses of this dangerous remedy. It was formerly largely made use of for the purposes of the poisoner, but chemical science has rendered the detection of it so easy and so certain that it has happily been abandoned of late years. It is an ingredient in various poisons for vermin, beetles, &c., though it is not by any means to be recommended for this purpose.

Alkaline Earths.—The term "*alkali*" formerly comprehended only the four substances, potash, soda, ammonia, and lithia. It has now, however, come to be used in a much wider sense, comprising a very large number of bodies possessing similar properties to the four above-mentioned. Among these are the metallic oxides, baryta, lime, and strontia, to which were given the name of the "*alkaline earths*," probably to distinguish them from certain other earths, not possessing the properties of an alkali, such as alumina and magnesia. The distinguishing characteristics of the alkalies are their solubility in water; their power of neutralizing acid; the corrosive action exerted by their aqueous solutions all animal and vegetable matter; and the property of changing the colour of vegetable colouring matter, such as litmus and turmeric. All these conditions are fulfilled to a greater or less extent by the alkaline earths; the only point of difference seems to be that their carbonates are insoluble, or almost insoluble in water: whereas the carbonates of the alkalies proper are very freely soluble therein.

Baryta, BaO. This earth may be prepared by the ignition of the nitrate or carbonate of barium. When required in quantity the best method consists in heating in a porcelain retort a mixture of nitrate and sulphate of barium, the weight of the latter being slightly in excess. If the nitrate be heated alone, it fuses and is apt to attack the porcelain. A strong red heat is required. Baryta is also prepared by heating the carbonate with one-tenth of its weight of lamp-black; the mixture is made into a paste with oil, and subjected to a white heat, in a porcelain or earthenware crucible.

Baryta is extremely caustic, poisonous, and strongly alkaline. It is infusible, except in the oxyhydrogen blow-pipe flame. It unites readily with water, forming the hydrate $BaHO$. It is soluble in ten parts of boiling water; this solution is used in the laboratory as a test for sulphuric acid. Baryta is also used in sugar-refining (see Sugar).

Lime, CaO. When carbonate of lime is strongly heated, it decomposes, forming lime and carbonic acid gas. This process is conducted on a very large scale, and is called "lime-burning" (see Lime). Lime does not exist naturally, but, in combination with carbonic acid, it constitutes a considerable portion of the earth's crust. It is a hard, white powder. It is absolutely unaltered by the highest known temperatures. It absorbs water eagerly, giving out much heat and forming the hydrate or "slaked" lime, $CaHO$. The applications of this substance to the arts and manufactures are exceedingly numerous, and will be considered under the article on Lime.

Strontia, SrO.—Strontia does not occur naturally, but it may be prepared by igniting either the carbonate, strontianite, which is found in the lead mines of Strontian, in Argyllshire, or the sulphate, celestine. It is of a greyish-white colour, infusible except the oxyhydrogen blow pipe flame, and has a strongly alkaline reaction. It combines readily with water, giving out heat and passing to the hydrate, $SrHO$, a fine white powder. The salts of strontium are extensively used in pyrotechny for the preparation of "red fire" (see Pyrotechny).

Ammonia. (Fr., *Ammoniaque*; Ger., *Ammoniak.*) Formula, NH_3.

We are indebted, probably, to the Romans for the name of this substance, its source being a district near Libya called Ammon, Amun, an Egyptian god, being worshipped at this place. The Egyptians were in all probability acquainted with ammonia in some form, although by what name it would be idle to conjecture.

Under ordinary temperatures and pressures, ammonia has all the properties of a permanent gas; it can be liquefied and even solidified. Faraday succeeded in liquefying this gas under a pressure of six and a half atmospheres, at the temperature of 5°, into a colourless and nearly odourless liquid, which solidified into a white translucent crystalline mass at $-75°$. One volume of the liquid raised to 15° at the pressure of 30·2 inches, formed 1009·8 volumes of the gas. It is very soluble in water, from which it can be again expelled by boiling; it is, however, impossible to entirely remove all the ammonia when water has once become impregnated with it.

At 0°, water takes up 1050 times its volume of the gas, and at 25° it takes up 580 times its volume, and has then a sp. gr. of 0·880. This liquid is known in commerce under the name of "Liquor Ammonia Fortiss."; it possesses strongly alkaline properties; diluted with three times its volume of water it forms the spirit of hartshorn of pharmacy. It mixes with the fatty oils and acids, and forms salts corresponding to those of the alkalies; mixed with olive oil, it forms the "hartshorn and oil" of medicine, and is the basis of many stimulating embrocations; it dissolves resins, and other vegetable principles, forming ammoniated tinctures and varnishes. Hatter's varnish is made by dissolving shellac in a solution of ammonia. In some pharmacopœial preparations it is used mixed with alcohol, for extracting resinous or resinoidal matters; after the extraction of the vegetable principles by this mixed solvent, the alcohol is sometimes drawn off by distillation, as in the manufacture of a strong essence of ginger for making "ginger beer," &c.

The composition of ammonia is expressed by the formula NH_3, it is not extensively met with as a natural product, its chief commercial sources being the waste products obtained in the destructive distillation of animal and vegetable substances containing nitrogen, such are the "bone liquor" obtained in the preparation of animal charcoal used in sugar refining, &c., and the "gas liquor" obtained in the destructive distillation of coal for illuminating purposes.

The more important preparations of this substance are:—The strong aqueous solution of the gas, "Liquor Ammonia Fortiss." Sulphate of ammonia, used extensively as a manure, and for the production of other ammoniacal preparations. Chloride of ammonium, used for manufacturing other salts of ammonia, galvanizing, galvanic batteries, and as a flux. Carbonates of ammonia, for confectionery and medicinal uses. Sulphide, oxalate, nitrate, phosphate, and bromide of ammonium used in photography, chemistry, &c. Ammonia and its compounds enter into combination with many metallic substances, forming important series of double compounds, having special though limited applications to the industrial arts and manufactures.

The minor salts of ammonia are obtained by neutralizing an acid with the carbonate, for neutral salts, or by dividing a solution of a known weight of the carbonate into definite parts, neutralizing one portion first, then adding the remainder for basic salts, and *vice versâ* for acid salts. Nitrate of ammonia is employed for the production of nitrous oxide gas, which is at present largely used by dentists. This salt should be perfectly neutral in its solution; 4 ounces of the dry salt heated in a glass retort should yield one cubic foot of the gas at the ordinary temperature and pressure. As this gas is soluble in water, which takes up three-fourths its volume of the gas, it should be washed and collected over warm water. Phosphate of soda and ammonia, or sodium ammonium hydrogen phosphate is an important chemical reagent for separating magnesia. The dry and fused salt is employed as a flux; it is prepared by dissolving 6 parts of crystallized disodium hydrogen phosphate (ordinary phosphate of soda), and one part of ammonium chloride in two parts of boiling water, the double phosphate crystallizes out on cooling, and may be freed from the sodium chloride which is formed, by recrystallizations, from a small quantity of boiling water containing a little ammonia. Schweitzer's solution, which is employed for dissolving and separating cotton fibres from silk, wool, &c., is made by simply dissolving the recently precipitated oxide of copper in strong liquid ammonia.

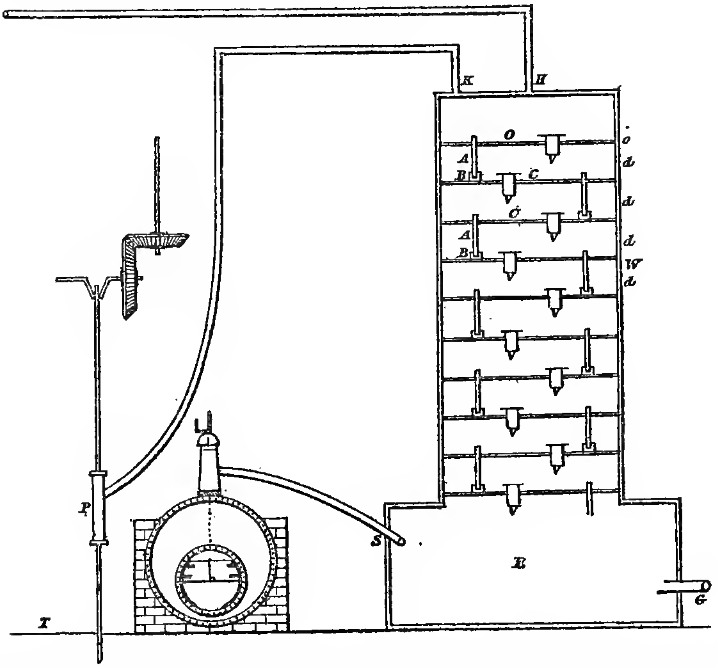
The sulphides of ammonium are formed by saturating the solution with well-washed sulphuretted hydrogen, or by distilling a mixture of the alkaline sulphides or iron pyrites with sal-ammoniac or the sulphate.

Ammonia exists, or rather is found after a short time, in animal excreta, the earliest source of this substance, as far as we know, being the excrement of the camel, in which the Egyptians at one time carried on an extensive trade. It exists ready formed in the excreta of certain serpents, as the boa, in the form of urate of ammonia, and which a few years ago was largely prescribed for consumptive patients by an eminent London physician. Human urine yields, when fermented, a large quantity of ammonia, which results from the oxidation of urea; this has been utilized as a source of ammonia. Schöenbein has shown that ammonia is formed when water is evaporated in atmospheric air, and that nitrate of ammonia is produced in many cases of combustion. He accounts for the presence of ammoniacal salts in volcanic vapours, &c., by evaporation only, since he considers it impossible that nitrogenized matters can be present in volcanoes.

In 1861, Mr. Manning patented an arrangement for collecting ammonia from the waste gases arising from combustion, as in factories. It is obvious that this is scarcely practicable where the conduction of the furnace smoke into chambers or other reservoirs is likely to interfere with the draught. On the other hand, the sooty matter from chimneys was for a long time an important source of sal-ammoniac. Ammonia exists in chimney soot, principally as carbonate, sulphate, and chloride; to the agriculturist it is an important fertilizer. The ammoniacal salts from soot are easily extracted by percolation with warm water, but better still by digestion with agitation. By sublimation, the ammoniacal salts are driven over, mixed with tarry matter, from which they are separated by conversion into sulphate, and crystallized. Although this substance is so rich in ammonia, it does not appear to be used for its production. The liquid obtained from the soot by boiling does not give rise to that objectionable frothing, when heated with milk of lime, which takes place with gas or bone liquor; it seems, therefore, eminently adapted for the production of liquor ammonia, especially on the small scale. The gas, after washing, may be passed into a suitable vessel or receiver containing acid, for the production of its salts. For the collection of ammoniacal salts from the waste gases given off during the combustion of coal in factories, it is necessary to avoid any obstruction to the draught. But still there is a very promising field open for the application of a well-devised method for condensing and collecting the ammoniacal salts given off when coal is consumed in a factory furnace.

In 1841, a patent was obtained for the application of a particular apparatus, which was hitherto used in this country for distilling alcohol, to the production of ammonia. It is shown in Fig. 194, and consists of an upright vessel W, divided into compartments *d*, by perforated diaphragms of sheet iron. Fitted to each diaphragm are several small valves, weighted so as to rise whenever the accumulated gas has attained a desirable amount of pressure; the valve being lifted or forced up allows the gas to enter the second compartment, and so on through each successive division. A pipe A is attached to each diaphragm, which projects about an inch above its upper surface, and reaches below nearly to the bottom of a small cup B, fitted on the upper side of the next diaphragm. This pipe allows the downward flow of the liquid, which enters for distillation at K, in the upper part of the apparatus. When these small cups are filled with liquid, the ends of the tubes reaching into them are closed, which prevents the upward passage of the gas through these tubes. The apparatus is connected to an air-tight receiver E, in which the descending liquid is accumulated. The receiver is supplied with an outlet G, and stopcock for drawing off the liquid, and near the top a pipe or inlet for steam S.

194.



The liquid undergoing distillation covers the upper surface of these perforated diaphragms, as the pressure of the steam being upwards prevents the liquid falling through the small perforations, and as the steam cannot ascend but through these small holes, the liquid lying on them becomes heated, and in consequence readily parts with its gaseous or volatile matters. The object of this arrangement is simply to expose a large surface of the liquid to the action of the heat; the liberated ammonia escapes by the weighted valves to the outlet H at the top. According to the inventor, the management of the apparatus varies in some measure with the form in which it is desired to obtain the ammonia. If the ammonia be required to leave the chamber as gas, the steam, which ascends, and the ammoniacal liquid, which descends, must be so adjusted that the ammoniacal liquid is only slightly heated during its passage through some of the upper compartments, becoming progressively hotter as it descends. If the ammonia is to be collected and condensed with the vapour of water, the supply of steam must be such that the ammoniacal liquid in the upper part of the apparatus is maintained at the boiling point. The advantages possessed by this arrangement are, that a large evaporating surface is obtained, and a continuous flow of the liquid to be distilled can be maintained. The apparatus is generally made of wood lined with lead. There is no particular limit to the number of compartments; but the distillation will be more complete by increasing the number of them. In the figure P is a pump for supplying from the tank T a steady flow of fresh liquid into the still. The gas may be passed through coolers, or direct into water or acid. The fluid collecting in E may be maintained at the boiling point for a short time before being allowed to run away, so as to make sure that all the ammonia is expelled.

Ammonia from Gas Liquor.—The ammoniacal fluid collected in the manufacture of gas from coal contains both free and fixed ammonia. Its value as a source of ammonia is generally regulated by its specific gravity. A liquid having a sp. gr. of 1·023 should yield about 1200 grains per gallon of ammonia by boiling alone, and on the addition of caustic lime should yield about 200 grains per gallon. Converted into sulphate, the total ammonia should amount to about 80 lb. per 100 gallons of the liquid.

The quantity of ammonia contained in gas liquor is subject to great variation, due partly to the coal itself and to the quantity of water which is produced during the distillation. All the nitrogen contained in coal is not converted into ammonia; cyanogen compounds are also produced, which are condensed as well. Probably the temperature of the retorts when the coal is thrown in, or the rapidity of the heating, may influence the changes which take place.

When coal is distilled a quantity of impure hydrocarbons are formed; these, together with the water and other volatile matters, pass from the retorts, and are separated from the gas as it leaves the hydraulic main, the gas being received in the holders, whilst the matters separated from it flow into large wells or underground tanks. On standing, a separation takes place, the watery portion which contains the ammonia and its salts falling to the bottom, and the hydrocarbons floating on the top. The watery portion is known as "gas liquor," and the black oily portion is called "gas tar."

One ton of good cannel coal will yield about 8 gallons of gas liquor. The gas liquor is pumped up from these tanks as required into suitable reservoirs for removal, such as boilers or tanks, which are fixed on railway trucks or waggons, for conveyance by rail or road, or barges where water transit is available. The latter is the most convenient and economical, the barges are of large capacity, and fitted with tanks capable of holding from 80 to 100 tons of liquor. The liquor, at its destination, is pumped into large tanks, usually constructed of masonry and wood, from which it is supplied either to the boilers or stills as required, or mixed with acid at once for the production of salts, the gases which are liberated in this latter case being conveyed to the furnace and burnt. As a large quantity of sulphur compounds are disengaged, it has been proposed to utilize the gases for the production of sulphuric acid.

The treatment of the crude liquor with acid does not appear to be so extensively practised as it was a few years ago, it seems more usual at present to bring the liquor into some more easily manageable bulk, which is effected by distilling with milk of lime when all the ammonia is to be recovered, or by driving off the free ammonia, by heat alone, when circumstances render the recovery of the combined ammonia unremunerative.

The best method for treating the gas liquor is evidently a matter to be determined by local conditions; for instance, the erection of a large plant in London, to work on the principle of saturating the liquor at once, could scarcely be so profitable an undertaking as the same arrangement carried out where land is so much cheaper. There are some localities where the lime refuse used in liberating the combined ammonia would either accumulate to become a serious nuisance, or would have to be carted away, and land purchased to discharge it upon. Such a thing could not be thought of in a city like our own metropolis. Where large quantities of acid and liquor can be easily and cheaply obtained, it is evidently more economical, especially where land is dear, to avoid the accumulation of useless refuse, and to work up the liquor in the quickest possible way; this at present necessitates the throwing away of a large quantity of the combined ammonia. The advantages of this latter method are the compact form which the plant may be made to take, and, the conditions of the raw supply being favourable, the rate at which the salts of ammonia may be obtained ready for the market.

Ammonia from Tar.—When the tar from gas works is distilled, a quantity of ammonia passes over at the commencement of the operation which is condensed in lead chambers with sulphuric acid; the sulphate thus obtained is supplied principally for agricultural manures. It is generally contaminated with all the impurities found in commercial sulphuric acid.

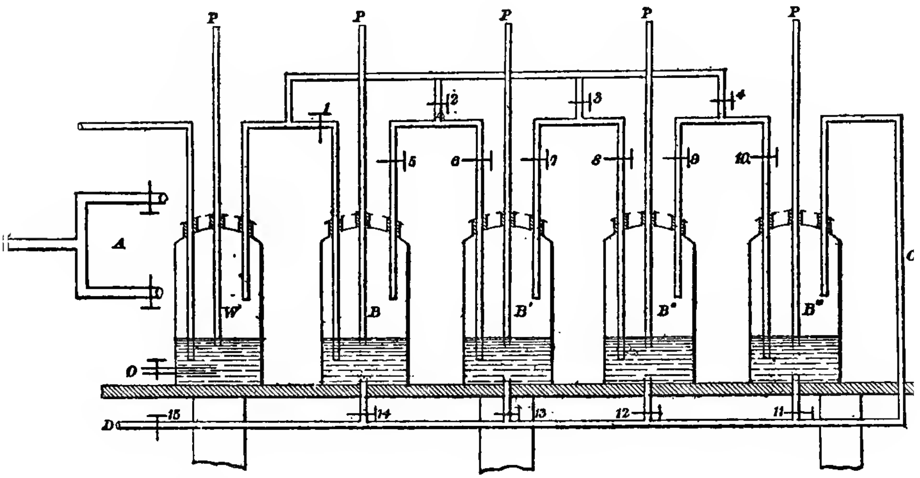
Frequently the tar as received from the gas works is run off into large tanks, and the ammonia liquid drawn off by decantation, neutralized with sulphuric acid and evaporated in iron pans.

The crude salt obtained from the tar fetches about 20*l.* per ton. Being impregnated with several volatile matters, it can scarcely be used for the manufacture of other ammoniacal preparations, and without considerable expense and trouble.

As commercial sulphuric acid contains more or less arsenious acid, it is easy to conceive that the continued use of large quantities of this salt as a fertilizer may become a subject of great interest to the toxicologist.

Aqueous Solution of Ammonia.—Water absorbs Ammonia with avidity. 1 volume of water at 0° dissolves 1050 times its own volume of the gas, and at 25° 580 times its volume. The Liquor Ammonia Fortiss. of commerce has a specific gravity of 0·880 and consequently contains 38·2 per cent. of ammonia. The absorption by water gives place to a rise of temperature; consequently in the manufacture of this article it is necessary to surround the vessels in which it is collected with ice; some manufacturers place ice in the condensers themselves, which rapidly takes up the gas and becomes liquid; on account of this, a small residuum will be found on evaporating a little of the solution to dryness in a platinum dish and igniting. When made in glass vessels it will be found to act slightly on the glass; earthenware allows the gas to escape though its pores, it is said, and consequently it is made on the large scale by condensing in vessels of iron. Copper or lead are not admissible, as their oxides are dissolved by ammonia. A quantity of sal-ammoniac (this is the salt usually employed, as a soluble salt of lime is formed, which can be easily removed from the retort) is placed in an iron retort, with 1¼ to 1½ times its weight of slaked lime, and the same quantity of water; the retort is connected with a series of Woulfe's bottles, made of cast iron, which are kept perfectly cool. The apparatus is shown in Fig. 195. A is a two-branch piece leading from the still, so as to connect with two series of bottles. W is a wash-bottle, with outlet O, so as to draw off the accumulating water; B B′ B″ and B‴ are bottles containing water or ice; C, a circulating pipe; P, a pressure-gauge or safety-tube; D, an outlet for the ammoniacal solution; and R, the connection for the still. In the first bottle, W, the water and the impurities which are mechanically carried over are condensed or arrested. The retort is gradually heated so as to give a slow current of gas and to ensure its absorption. The bottle nearest the retort will become strongly saturated, whilst those in succession will be more or less impregnated with the gas. As soon as the contents of the first bottle are fit for removal, they can be drawn off and the bottle filled either with fresh water, or the weaker solution from one of the next bottles. Since the solutions are lighter according to their degrees of saturation, a convenient method is to connect the bottles together at their lower tubulures, and to make the shorter limb of the leading tubes dip just under the liquid, so that the pressure of the gas will drive the lighter and more highly charged portion over into the next receiver and so on to the end of the series, the heavier portions are then driven towards the retort, which serves to create a circulation of the liquid and gives an equal degree of saturation. The retort may be heated in a water bath or by means of a steam jacket. W and B, &c., are Woulfe's bottles. W receives the impurities and steam coming from the retort. B B′, &c., are Woulfe's bottles in which the absorption takes place. A safety tube P, and outlet for drawing off the liquid should be supplied to each bottle. Lime being liable to great variation, it is necessary to use this article in excess. This method of preparation suggests a means of testing the lime which is convenient and simple. The lime is first sampled as carefully as possible, and a weighed quantity, say 100 grains, is taken and placed in a weighed filter; a warm solution of sal-ammoniac, rather strong, is poured over the lime and continued as the liquid filters away with any lime in it (which can be determined by means of oxalate of ammonia); the residue on the filter is well-washed, dried and weighed; the loss indicates the amount of caustic lime present. Good hard stone lime can be obtained which keeps better than the softer kinds, yielding 95 per cent. of caustic lime.

195.



In the manufacture of liquor ammonia, where the use of ordinary ice is inadmissible, and it is necessary to employ distilled water, the gas may be conveniently cooled by being passed through a long series of tubes surrounded with cold water, or a freezing mixture, before being conducted into the water.

In 1867, Mr. Reece obtained a patent for producing cold by the evaporation of liquid ammonia in a special form of apparatus, the same arrangement is claimed of nearly anhydrous ammonia. It consists essentially of a boiler, an analyzer, which, with slight modifications, resembles Coffey's ammonia still, a rectifier and a condenser. The other portions of the apparatus belong to its refrigerating functions and the collection of the volatilized ammonia. From the condenser the ammonia may be passed into water contained in Woulfe's bottles, or any suitable receiver. Mr. Reece works his apparatus for refrigerating to a pressure of eight atmospheres, but for producing liquor ammonia there is obviously no occasion to work beyond the ordinary pressure.

The boiler may be supplied with gas liquor, or an ammoniacal salt dissolved in water, to which milk of lime or a caustic alkaline solution may be added. On heating the contents of the boiler, the ammonia and steam together pass into the analyzer, thence into the rectifier, which is kept well cooled; the rectifier, which consists of a series of straight tubes, open at both ends, and, fitting into chambers, allows the condensed steam to fall back into the analyzer, from which it flows into the boiler again; the gas finally passes into the condenser almost free from water. The operation is continued until all the ammonia is expelled from the boiler and analyzer.

The ammonia accumulating in the condenser may be liquefied provided the pressure be sufficiently high, and the analyzer supplied with a solution of ammonia. The liquefied ammonia is allowed to flow into a suitable vessel containing tubes or coils through which the liquid to be cooled is made to traverse. By the abstraction of heat the ammonia becomes gaseous, and is led back again to the analyzer or rectifier.

For freezing purposes liquids of a non-congealable character are passed through the tubes until the temperature is sufficiently low; for this purpose a solution of chloride of calcium is preferred.

There are several methods in use for expelling ammonia from the raw gas liquor, or the mixture of the liquor and milk of lime, viz. by heating in large boilers fixed in masonry, so that the direct action of the furnace fire may be employed; by the injection of high pressure steam into the heated liquor, or the circulation of steam through tubes traversing the vessel containing the liquid, or by blowing a current of air through the liquid.

The method which has lately been most strongly advocated for expelling the ammonia, especially for the production of sulphate, is that known as the "steaming process," and which consists in injecting into the liquor high pressure steam through numerous small orifices, in a tube or series of tubes circulating through the liquor. To the manufacturer it is a matter of great importance not only to know that he is obtaining the maximum amount of ammonia, attainable by the process he adopts, but to get off the ammonia with the least possible consumption of fuel. In any case it is advisable to heat the liquor before passing into the stills or boilers; this is generally done by the waste steam from the evaporating pans or heat from the flues; preference however is given to the steam, which should circulate through the liquor, so as to avoid further dilution.

The injection of the steam as jets into the liquor does certainly not appear so economical a process as the testing with circular coils, for the waste steam and water from the coils may be made to heat the evaporators, or may be turned to account in other ways, or returned to the boilers themselves; on the other hand, the waste liquor itself may be utilized for some of these purposes, so long as there is no fear of fouling or stopping up the pipes, &c. From an economical point of view, as regards fuel, the expulsion of the ammonia by steam circulating in pipes may be the best, but if the injected steam facilitate the escape of the ammonia, even with an extra consumption of fuel, there may be circumstances under which it may be a more desirable process to adopt.

The following estimate of the cost of producing 1 ton of ammonium sulphate by the steam process is given by a manufacturer of large experience:—

	£	*s.*	*d.*
Gas liquor (average)	11	0	0
Coal (20 cwt. at 18*s.* 6*d.*)	0	18	6
Lime (5 cwt.)	0	4	0
Acid (20 cwt.)	2	5	0
Wages	0	6	8
Packages	0	5	0
Management, rent, &c.	0	5	0
	£15	4	2

The coal here estimated for is large and of good quality, such being found to pay best in the long run, except where slack is readily obtainable at a very low cost. The quantity of 20 cwt. may be considered excessive, many manufacturers being of opinion that it is possible to work with 15 cwt.

Fresenius has published the following method for preparing a solution of pure ammonia, which is very convenient for working on a small scale. Six and a half kilogrammes of ordinary commercial crystallized chloride of ammonium, and 3·5 kilogrammes of sulphate are mixed together and passed through a sieve so as to break up any large masses of the salts. The mixture is placed in the retort in layers, with intervening layers of hydrate of lime prepared by moistening 10 kilogrammes of lime with 4 of water. The whole mass is then moistened with 8 kilogrammes of water. The gas is first washed in an iron Woulfe's bottle, attached to which is a glass tube for showing the height of its contents; to one of the tubulures is fixed a glass balloon which the gas traverses before entering the refrigerator. The receiver, which may conveniently be a large carboy, contains 21 kilogrammes of distilled water. The wash bottle is supplied with a top so as to remove a portion of the liquid which passes over from the retort. The use of the chloride and sulphate possesses the advantage that the residuum is easily removed from the retort, the sulphate of lime which is formed prevents the chloride of calcium which is also formed from producing a mass, and less water is also required when operating with the mixture than with the sulphate only. After 5 or 6 hours the greater part of the ammonia is distilled, the gas which is still disengaged may be collected in another receiver with more water than is sufficient to dissolve it completely. At this period of the operation the upper part of the wash bottle is filled with white vapours. These vapours indicate the drying of the contents of the retort and the decomposition of organic matters. On the appearance of the vapours the receiver must be taken away and replaced by a smaller one. This product becomes milky and is reserved for a future operation. The great point in this is, that the residue is more easily managed in its removal from the retort. If it was necessary to recover the chloride of calcium from this waste, it could be easily dissolved out with warm water. Carbonate of ammonia, chlorine, lime, copper or lead, and a little organic matter, containing carbon, are its principal impurities. A sample when made may be free from carbonic acid, but contain carbonate of ammonia from absorption of carbonic acid from the air; the contamination with copper or lead may be avoided by using iron vessels and connecting pipes. The carbonaceous matter may arise from the salt employed, or the lutes used in making the joints. When pure, it is colourless and leaves no residuum on evaporation; by heat in open vessels it rapidly loses its gas, consequently it should be kept in well stoppered *green* glass bottles in a cool place. An alcoholic solution of ammonia may be prepared by passing the gas into alcohol containing 85 per cent. to 90 per cent. instead of water.

It is a common practice to determine the strength of an ammoniacal solution by reference to its specific gravity; it is obvious that if the solution contain any soluble matter other than the gas itself, its specific gravity cannot be taken as representing the strength or degree of saturation with the gas; it is therefore desirable to ascertain the absence of fixed impurities by evaporating a known quantity on the water-bath. Should no residuum be left, the quantity of gas present may be accurately found by reference to a table of specific gravities.

The following table given by Otto is regarded as being reliable, the determinations being made at 16°.

Specific Gravity.	Per cent. of Ammonia.	Specific Gravity.	Per cent. of Ammonia.	Specific Gravity.	Per cent. of Ammonia.	Specific Gravity.	Per cent. of Ammonia.
·9517	12·000	·9583	10·250	·9654	8·375	·9721	6·625
·9521	11·875	·9588	10·125	·9659	8·250	·9726	6·500
·9526	11·750	·9593	10·000	·9664	8·125	·9730	6·375
·9531	11·625	·9597	9·875	·9669	8·000	·9735	6·250
·9536	11·500	·9602	9·750	·9673	7·875	·9740	6·125
·9540	11·375	·9607	9·625	·9678	7·750	·9745	6·000
·9545	11·250	·9612	9·500	·9683	7·625	·9749	5·875
·9550	11·125	·9616	9·375	·9688	7·500	·9754	5·750
·9555	11·000	·9621	9·250	·9692	7·375	·9759	5·625
·9556	10·950	·9626	9·125	·9697	7·250	·9764	5·500
·9559	10·875	·9631	9·000	·9702	7·125	·9768	5·375
·9564	10·750	·9636	8·875	·9707	7·000	·9773	5·250
·9569	10·625	·9641	8·750	·9711	6·875	·9778	5·125
·9574	10·500	·9645	8·625	·9716	6·750	·9783	5·000
·9578	10·375	·9650	8·500				

This table is supplemented by that of Carius. Approximately, it will be found from these tables, that a difference of 1 per cent. ammonia gives a difference in specific gravity from 0·0022 to 0·0044, the differences in the specific gravity becoming less as the solution becomes more highly charged with ammonia.

Carius' table is given at a temperature of 14° F.

Specific Gravity.	Per cent. of Ammonia.	Specific Gravity.	Per cent. of Ammonia.	Specific Gravity.	Per cent. of Ammonia.	Specific Gravity.	Per cent. of Ammonia.
·8844	36·0	·9016	28·4	·9227	20·8	·9470	13·4
·8848	35·8	·9021	28·2	·9233	20·6	·9477	13·2
·8852	35·6	·9026	28·0	·9239	20·4	·9484	13·0
·8856	35·4	·9031	27·8	·9245	20·2	·9491	12·8
·8860	35·2	·9036	27·6	·9251	20·0	·9498	12·6
·8864	35·0	·9041	27·4	·9257	19·8	·9505	12·4
·8868	34·8	·9047	27·2	·9264	19·6	·9512	12·2
·8872	34·6	·9052	27·0	·9271	19·4	·9749	6·0
·8877	34·4	·9057	26·8	·9277	19·2	·9757	5·8
·8881	34·2	·9063	26·6	·9283	19·0	·9765	5·6
·8885	34·0	·9068	26·4	·9289	18·8	·9773	5·4
·8889	33·8	·9073	26·2	·9296	18·6	·9781	5·2
·8894	33·6	·9078	26·0	·9302	18·4	·9790	5·0
·8898	33·4	·9083	25·8	·9308	18·2	·9799	4·8
·8903	33·2	·9089	25·6	·9314	18·0	·9807	4·6
·8907	33·0	·9094	25·4	·9321	17·8	·9815	4·4
·8911	32·8	·9100	25·2	·9327	17·6	·9823	4·2
·8916	32·6	·9106	25·0	·9333	17·4	·9831	4·0
·8920	32·4	·9111	24·8	·9340	17·2	·9839	3·8
·8925	32·2	·9116	24·6	·9347	17·0	·9847	3·6
·8929	32·0	·9122	24·4	·9353	16·8	·9855	3·4
·8934	31·8	·9127	24·2	·9360	16·6	·9863	3·2
·8938	31·6	·9133	24·0	·9366	16·4	·9873	3·0
·8943	31·4	·9139	23·8	·9373	16·2	·9882	2·8
·8948	31·2	·9145	23·6	·9380	16·0	·9890	2·6
·8953	31·0	·9150	23·4	·9386	15·8	·9899	2·4
·8957	30·8	·9156	23·2	·9393	15·6	·9907	2·2
·8962	30·6	·9162	23·0	·9400	15·4	·9915	2·0
·8967	30·4	·9168	22·8	·9407	15·2	·9924	1·8
·8971	30·2	·9174	22·6	·9414	15·0	·9932	1·6
·8976	30·0	·9180	22·4	·9420	14·8	·9941	1·4
·8981	29·8	·9185	22·2	·9427	14·6	·9950	1·2
·8986	29·6	·9191	22·0	·9434	14·4	·9959	1·0
·8991	29·4	·9197	21·8	·9441	14·2	·9967	0·8
·8996	29·2	·9203	21·6	·9449	14·0	·9975	0·6
·9001	29·0	·9209	21·4	·9456	13·8	·9983	0·4
·9006	28·8	·9215	21·2	·9463	13·6	·9991	0·2
·9011	28·6	·9221	21·0				

Carbonate of Ammonia.—On the large scale, this salt is obtained by heating sal-ammoniac, or the sulphate of ammonia, with chalk (carbonate of lime, or carbonate of potash or soda); the carbonate sublimes and condenses on the sides of the receiver. The receivers are constructed of lead, iron or earthenware; the latter is used in the manufacture of the salt used in medicine and other purposes requiring a pure salt of ammonia; the inside of these receivers are sometimes lined with a coating of clay, or prepared canvas and clay, which prevents the metallic impregnation, and at the same time allows the sublimate to be more easily detached. The receivers are made in sections bolted together and luted at the junctions. It is easier to obtain the purified salt by employing a well prepared chloride or sulphate, than to attempt to resublime an impure carbonate, as the impurities are carried into the condensers mechanically.

The carbonates of ammonia of commerce have a variable composition, and consist principally of a sesqui-carbonate mixed with other carbonates. Carbonate of ammonia is met with in commerce in irregular pieces about three-fourths of an inch thick, with a slightly crystalline fracture when broken, which crumble and pass into an opaque mass on exposure to the air. The carelessly prepared salt may contain more or less of the impurities contained in the commercial muriatic or sulphuric acids, a matter of great importance, especially when used in pharmacy and chemical analyses.

The amount of carbonic acid in a sample of carbonate may be obtained from the loss when a weighed quantity is decomposed in a carbonic acid apparatus. The salt dissolved in hydrochloric acid in excess and evaporated to dryness will give the weight of ammonia as chloride. The difference, if any, will be due to water. It should dissolve completely in water, and the solution should undergo no change on the addition of a little sulphide of ammonium. A portion of the salt dissolved in nitric acid in excess should produce no change in a solution of nitrate of silver.

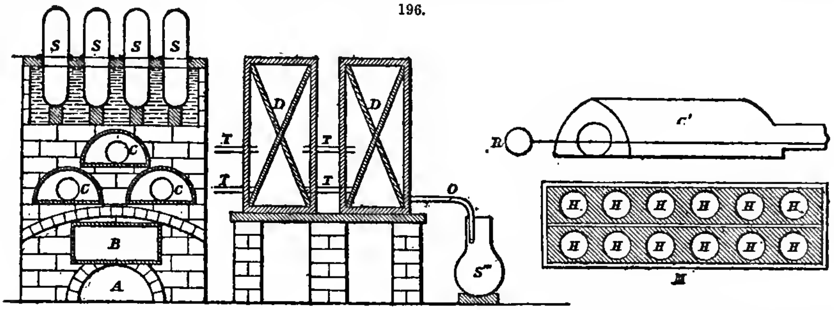
Several methods have been introduced for the production of this salt on a commercial scale. As far back as 1825, Mr. Holmes, of Liverpool, manufactured this salt from stale or fermented urine;

it is curious to note that in 1867 it was proposed to manufacture ammonia from the same article, at Bayeres. In 1844, Dr. Turner obtained a patent for distilling guano to obtain salts of ammonia, and in 1849, Mr. Hills secured a patent for distilling a mixture of charcoal or coke and guano for the same purpose, and in the same year the same inventor obtained carbonate of ammonia by the action of heat on peat.

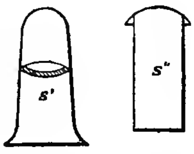
At the present time the crude carbonate is obtained from a mixture of the chloride or sulphate of ammonia and common chalk, which is heated in retorts and sublimed, the chloride or sulphate being first obtained from "gas liquor" as follows:—The free ammonia is first driven off and received in condensers with muriatic or sulphuric acid, the combined ammonia which remains in the retorts is drawn off with the liquids still remaining, and sufficient acid is added to convert the ammonia compounds into chloride, or sulphate. This solution, after allowing the impurities to subside, is decanted; taking care not to allow the floating film of oil and tarry matter to run off, and evaporated in large hemispherical iron pans set in brickwork, and which are generally heated by the waste heat from the furnaces. The crystals obtained are more or less black from tarry matter; when drained and slightly washed they are redissolved, a quantity of matter separates, which had been mechanically mixed with the crystals; the solution should be syphoned off, evaporated and set to crystallize in shallow iron or lead pans. This yields crystals of a dirty white colour, but are so far freed from volatile tarry matter, that they are now ready for conversion into carbonate.

For this purpose cast iron retorts, the shape of an elongated muffle, are used. They are shown in Fig. 196, in which A is the ashpit, and B the fireplace; C C C are the retorts, S S S S the subliming-pots, D D the condensing chambers, T T T T pipes leading from the retorts, and O an outlet for the steam and vapours. S''' is an earthenware subliming-pot; C' a retort, with a rod R for clearing the outlet to the condensing chambers; M is the top of the furnace, with spaces H for the subliming-pots. In Fig. 197, S' is a leaden subliming-pot in two halves, with an iron ring, and S'' another, made of bent sheet lead, with a top.

196.



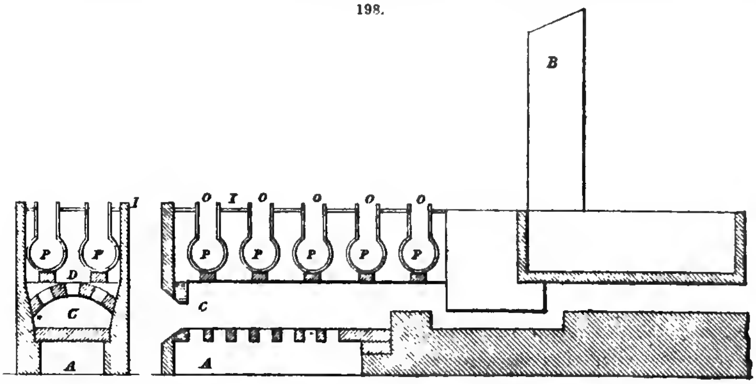
197.



The neck of the retort is round, and closed with an iron door, kept in its place by means of a screw. The retorts are about 7 ft. long and 1 ½ ft. deep. Three are set in brickwork in the form of a triangle, and heated by one fire. They communicate with a leaden chamber which is technically called a balloon. It is about 6 ft. high, 8 ft. long, and 2½ ft. wide. These balloons are supported upon scaffolding, so as to be on a line with the retorts, and are kept in their places by iron bands. At the end of each balloon is a small pipe, which is always kept open so as to allow the escape of steam and water, which is highly charged with carbonate; this is collected for resublimation. The retorts are heated cautiously. They are recharged every twenty-four hours with a fresh mixture of two parts carbonate of lime, and one part ammoniacal salt; the chalk is well dried on an iron plate, which is set over the flue, so that the waste heat of the fires economically desiccates it. All the retorts are not charged at the same time, for often there are five and six sets, and the times of charging are so arranged as to occupy as few hands as possible; the residue in the retort being withdrawn, the fresh supply is thrown in, the door luted on and, with the exception of an occasional stirring with an iron rod which passes through the door of the retort, it is left for the usual twenty-four hours. When the retorts have been in work for about fourteen days, the balloons are opened, and the impure carbonate is found as a thick crust, lining all the sides; it is more or less coloured from impurities. Each balloon has a small hole, closed with a plug, to enable the workmen to see how the sublimation is going on. The pipes leading from the retorts to the balloons are cleaned out after every charge, as they are liable to become choked up.

This crude carbonate is submitted to a second sublimation in iron tanks or pans, Fig. 198, about 16 ft. long and 2½ ft. deep, 2 ft. 7 in. wide at the bottom, and tapering to 2 ft. at the top. These tanks are closed with two plates of iron with holes in each about 1 ft. in diameter and 1 ft. apart from each other; to each of these openings is luted a receiver formed by simply bending a piece of sheet lead into the form of a cylinder, its ends being kept together by iron straps; the height of these receivers is about 2 ft., the top is closed either by soldering on a plate of lead or by luting. A small fire is first lighted at each end of the tank, and the heat gradually raised and regulated, preferably by inserting a thermometer through an opening into the pan. At the end of fourteen days the leaden receivers are lined with the carbonate which is carefully removed, the part next the lead being scraped off, when the salt is ready for the market. In the figure, I is an iron plate, P the subliming-pots, C the fire-place, A the ash-pit, B the chimney, D fire-bricks to support the pots P, S spaces filled in with clay or sand, and O open spaces or holes in the plate I. The receivers are reshaped, and after cleaning are ready for another operation; sometimes these receivers are made in two halves in the form of domes; 13 cwt. of the rough muriate yields about 9 cwt. of the rough carbonate. The heat in subliming the refined salt must not be too high, as the colour is injured thereby.

198.



The chloride of calcium obtained as a waste product in this manufacture may probably receive an important application. M. Knob has found that this salt is capable of absorbing its own weight of ammonia gas, and giving up the same again when it is heated; it has been proposed to utilize this as a means of easy transport. It is quite possible that in small gas works, where the production of ammoniacal liquor is too small to pay for its transport, an easy method of accumulating and stowing it away must have been for some time a great desideratum. Of course, it will be necessary to obtain the gas as dry as possible. The free ammonia in distilling could be more economically condensed with an acid, provided the acid could be cheaply procured, and obtained as a crude salt for transport, since it would be necessary to dehydrate the distillate; but where the dry salts can be acted upon with caustic (slaked) lime, the gas would be easily taken up by the chloride of calcium.

An important application of the ammoniacal liquor of the gas works is in its extraction of the sulphur from the gas, by the scrubbing process. As much as nine-tenths of the sulphur is said to be removed by this process, and the illuminating power of the gas itself is increased. Mr. Bowditch does not believe that the sulphur is removed by the ammonia liquor, but the experiments made a few years ago at Nottingham and Taunton, seem conclusively to prove that at least a very large proportion of the sulphur is removed. According to the same authority the ammoniacal liquor, diluted with at least three times its bulk of water, may be applied as manurial matter to land. This ought to be a useful hint to small gas companies who at present do not find it profitable to save the liquor.

Other methods have been proposed for reducing the bulk of the ammoniacal liquor from gas works, with the view of rendering its transport practicable in a financial sense. Mr. F. Braby, in a paper read before the British Association, in 1869, gives a very simple and interesting method for effecting this object. The cost of carriage is evidently a matter of the first consideration. Mr. Braby states that on the average one gallon of liquor contains only 2 oz. of real ammonia, so that if any plan could be devised by which a concentration could be made that one gallon should contain say 40 oz. of real ammonia, the cost of transit would be twenty times less, or in the one case the cost of carriage being 20*l.* for a given bulk of liquid containing a certain quantity of ammonia as produced at the gas works, the cost of carriage would be reduced to 20*s.* for the same quantity of ammonia by removing simply the greater bulk of the water. At present to carry 1 ton of ammonia, it is necessary to take with it no less than 80 tons of water. The result of this dilution is, that a very great deal of this liquor is thrown away, forming no doubt in most cases a great nuisance to many localities; by concentrating, the nuisance would be removed and converted into a source of profit.

The process is thus described:—"To the common ammoniacal liquor a certain quantity of slaked lime is added. The liquor thus treated is placed in a capacious boiler or still, capable of holding 5000 gallons. The whole is then heated and maintained at a temperature of from 38° to 94°, the liquor being slowly but constantly stirred by means of an internal agitator, the spindle of which passes through a stuffing box in the end of the boiler. A powerful blast of air from a double action force-pump, actuated by a small steam engine or otherwise, is blown continuously through the liquor. The air enters by two long perforated pipes placed near the bottom of the boiler, and in its upward passage it is compelled to pass through a horizontal diaphragm drilled with numerous small holes. The result of this arrangement being, that the air in its ascent is subdivided into innumerable small sheaves and bubbles, to which and all of which, in accordance with well-known and recognized laws, the ammonia attaches itself, and is carried away, with only a very small proportion of aqueous vapour. An exit pipe is fixed to the top of the boiler, so as to carry away the mixture of air and ammonia, and the extremity of this pipe dips into a supply of water contained in a cool and suitable receiver, where the ammonia is immediately absorbed, and the air, after thus affecting its removal in a separate state, escapes through the water and is permitted to pass off into the atmosphere. These receivers are almost three parts full of broken ice.

The following dimensions are given of a working plant which was erected at Deptford. A reservoir 35 ft. long, 7 ft. wide, and 6 ft. deep, was made to contain the liquor. The bottom was formed of 1 ft. of concrete, 2 courses of bricks, and 2 courses of red flat tiles; the sides were of 14 in. brickwork, 2 courses with tiles in conjunction with concrete. The wrought iron still is set in brickwork so that the flame may play more than half round its external surface; it is 30 ft. long by 6 ft. in diameter. About 4000 gallons of liquor are pumped into it for each operation. Two cast iron 3-in. air pipes, which are attached to the ammonia generator, extend along its whole length, and are situated one on either side, and nearly at the bottom. They are perforated with holes increasing in size as they extend from the inlet. Into these pipes, and from them into the gas liquor, is driven atmospheric air by means of a pair of cast iron force-pumps. These are 20 in. in diameter, 1 ft. 8 in. stroke, with rods and slings, wrought-iron connecting rod and crank, and a cast-iron beam 6 ft. long. On the entry of the streams of air they are caught and agitated by the twelve iron fans of a stirrer, making about 80 revolutions per minute. The air together with the lime and the various constituents of the gas liquor (viz. water, ammonia, carbonic dioxide, sulphuretted hydrogen, sulpho-cyanides, &c.,) are thus brought continuously into intimate contact. The air loaded with the volatile alkali, which has become eliminated from the solution, passes upwards into the steam chest and through a branch pipe into the purifier or washer. This is a small wooden vessel of the capacity of 350 gallons, containing lime and being about one-third full of water. It has a tight head and a stout perforated elm false bottom, the holes being concentric and increasing in number and dimension as they radiate from the inlet which is brought below the false bottom.

This purifying vessel is furnished with a small agitator having two blades, one revolving above and the other below the false bottom. There are two trial or test taps at appropriate heights, to test for gas or for water, and there is also a pipe sealed at one end, rather less than half way from the bottom, for the purpose of leading away any excess of liquid that may accumulate, owing to the condensation of aqueous vapour, which may pass over with the volatile alkali. There is a long straight tube or safety pipe from the washer, and the bent pipe from the ammonia generator is also provided with a safety valve and a vacuum valve. In the washer the ammonia is deprived of any remaining hydrosulphuric acid or other impurity that may have escaped being fixed in the generator. About half a bushel of finely sifted slaked chalk lime is found to be a suitable charge for the washer, and, when this becomes saturated or impure, it is renewed by means of a pipe and tap placed at the bottom of the vessel. The washer being a close vessel soon becomes full of air and gas, which are forced by the pressure through a pipe opening into the top, and leading to a coil or worm placed in a cold water cistern, and terminating in a deep close vessel about one-third full of pure cold water, which has been condensed from the waste steam from the engine. A portion of the ammonia becomes absorbed by the water, but the residue together with all the air, after bubbling up through the liquid, is conducted by a bent pipe to nearly the bottom of a second similar receiver, and thence in the same to a third, but which is open at the top.

The air, having fulfilled its function, is now permitted to escape into the atmosphere, the whole of the ammonia having, however, been arrested. This last receiver, instead of water, contains a strong solution of chloride of iron, which being denser and possessing a higher specific gravity than water offers a greater pressure and resistance to the passage of the gas. The iron salt is, of course, decomposed, with the formation of *muriate of ammonia* in solution, with deposition of a green mud containing sesquioxide of iron, which, after having been calcined, is found to constitute an excellent pigment for rough iron or wood-work.

After the whole of the ammonia has been extracted from the gas liquor, the contents of the still are run off into a draining pit, from which the clear solution finds its way into the sewers, and the solid inodorous lime compounds may be carted away. This draining pit is constructed of 1¼-in. deal boards together with sand and brickwork. It is 4 ft. 9 in. wide, 5 ft. 4 in. deep, and 10 ft. long. There are fillets on which are resting three perforated shelves or platforms. The bottom is formed of perforated deals with 6 in. of sand, also with gravel and cement. There are channels and small drain pipes leading into a large central earthenware pipe, and from thence into the sewer. The sharp sand, &c., under the perforated boards can be removed at will, and be replaced by fresh materials whenever required. Care must be taken that the large pipe from the boiler to the washer be sufficiently high to guard against any back pressure. The vacuum valve opens and admits air, when the fire of the still is withdrawn and the steam becomes condensed.

In order to ascertain the exact state of the contents of the boiler at any required height, and to avoid tapping the upper portion of the boiler at too many places, the following simple contrivance is adopted:—There is one tap at the lower end, to which is attached a short pipe inside the still, working easily on an elbow. To this is connected a copper wire having its outlet just above the external surface of the boiler, and by which wire the short pipe may have its orifice presented at any required height, to ascertain the state of the contents of the vessel. For instance, supposing the fire to be withdrawn and the agitators to be at rest, if the end of the tube were pulled up by the wire and the tap opened, a clear liquid would issue, which could be tested in order to ascertain whether the whole of the ammoniacal gas had been removed. On the other hand, if the short tube were allowed to lay along the bottom of the still the opened cock would allow the sulpho-calcareous mud to escape.

There are many gasworks where ammoniacal salts are now manufactured, but it is suggested that, in new works, or at those where the gas-liquor is not at present utilized, it would be preferable, in the event of the adoption of the principle herein advocated, that the ammonia, after concentration, should be sent to the sulphuric or muriatic acid works, rather than that the acids should be sent to the gas-works. In metallurgy, it is found more advantageous to transport the calcined or partly-prepared ores to the coal districts for smelting, rather than to take the fuel to the mines. Barges fitted with tanks ordinarily employed in the conveyance of gas-liquor, contain from 3000 to 8000 gallons. A land journey of 12 miles, with two horses for a load of 500 gallons in a tank-van, now costs 1*l.* By rail the cost of freight is 1*d.* per ton per mile.

The advantages of the above-described system may be summed up as affecting a considerable economy in labour, time, and occupation of plant, together with the facility of extracting the whole of the ammonia from the gas liquor in a pure condition. A manufactory, previously consuming 10,000 gallons of gas liquor per week, may now utilize 24,000 gallons, and at about half the expense of fuel of that formerly incurred.

According to Sir Robert Kane, the yield of ammonia from peat as sulphate was 24·8 lb. per ton. Dr. Hodges, of Belfast, obtained 22·75 lb. per ton. These results were obtained from the working of Irish peat, presumably on an experimental scale; for in Mr. Sullivan's report to the Directors of the Irish Peat Company, in 1855, the working results showed only 3 cwt. per 100 tons of peat = 3·36 lb. per ton. The production of ammonia from the peats occurring in the Highlands of Scotland is stated to be more satisfactory; and if peat can be profitably worked for the production of oils and paraffin, there can be no reason why it should not become an important source of ammonia. Bituminous schist, when distilled, yields ammonia, though generally in small quantities.

Ammonia from Bones.—The ammoniacal liquor from bones yields, according to Muspratt, from ¾ lb. to 1¼ lb. of ammonic chloride per gallon; but, as he has pointed out, this quantity is subject to much variation from many causes. Since the amount of ammonia obtained depends upon the nitrogenous substances present, such as gelatine and chondrin, it is evident that the extraction of these matters for the manufacture of glue or size must seriously impair the bones for the production of ammonia. As 100 parts of gelatine yield about 20 parts of ammonia, it is evidently more profitable to convert all the matter removable by boiling into glue than to turn it into ammonia. When gelatine is submitted to dry distillation, it yields carbonate, sulphide, and cyanide of ammonium, amines or ammonia-like substances, pyridene bases, pyrrol, and other compounds.

From whatever source the ammoniacal liquor is obtained, its conversion into liquor ammonia or salts is generally effected by the same processes.

Volcanic Ammonia.—In the neighbourhood of volcanoes, or coal mines which have been set on fire, ammonia, generally as chloride, is found. The principal source of volcanic ammonia is the crude boracic acid from the lagoons of Tuscany. It exists principally in the form of double sulphates, which is set free on the addition of soda-ash in the manufacture of borax. The carbonate of ammonia which escapes is collected in a suitable receiver, and after a second purification takes the form in which it is found in commerce. Messrs. Howard and Sons, Stratford, Essex, manufacture large quantities of ammoniacal compounds from this source, which are extensively used in pharmacy. The ammonia salts thus obtained are perfectly free from all traces of oily matter and other impurities which accompany its production from gas or bone liquor. Volcanic ammonia is free from pyrrol, and the corresponding substances met with in ammonia from gas or bone liquor. The salts obtained from this source, when pure, disappear when heated, without leaving any carbonaceous residue. Pyrrol is detected by the purple colour which it strikes when an excess of nitric or sulphuric acid is poured into a solution of an ammoniacal salt.

Chloride of Ammonium.—For the production of this salt on the commercial scale, several methods are in use for the treatment of the ammoniacal liquor, by substituting sulphuric acid for the hydrochloric acid and sulphates for chlorides; the same methods are applicable for the manufacture of the sulphate of ammonium.

By the addition of acid to the crude liquor:—The liquor when received at the works is pumped into large tanks, which are capable of holding two or three hundred thousand gallons each; it is pumped from these tanks into circular vats, or tuns, for working. These vats contain sufficient space to allow the working up of about 20,000 gallons of crude liquor at one operation.

Hydrochloric acid is then added, and the escaping gases, which are highly disagreeable and dangerous, are conducted to the furnace and burnt. The amount of acid required varies with the strength of the liquor; to determine the amount, a trial should be first made, and the quantity of acid required to give a distinctly acid reaction should be used. The whole is agitated whilst the acid is being added, and allowed to settle. The acid, combining with the ammonia, sets free a quantity of oily matter, which floats on the surface of the solution of the chloride, and by subsidence the heavier impurities from the tar settle to the bottom.

Means are provided for drawing off the solution at different heights in the vats, so that the disturbance may be as little as possible. It is conveyed by troughs to the evaporators, which are usually square or rectangular, and constructed of cast-iron plates bolted together. They are heated by the waste heat from the furnaces, or if a fire be used, the flues are constructed so as to heat the liquid upon the whole surface of the bottom, as well as the sides. The liquid, when sufficiently concentrated, is transferred to the crystallizing pans or tubs. Care is taken that the liquid during the concentration does not become too acid; this is avoided by the addition of ammonia liquor from time to time.

Large crystals are to be avoided, as they lead to embarrassment in the subsequent steps of the manufacture. As the crystallization proceeds, the crystals which form on the surface are broken up by frequent agitation. A fair crop of crystals being obtained, the mother liquor is drawn off, and conveyed again to the evaporators. The salt thus obtained contains a large quantity of tarry matter; a great deal of this can be removed by washing the crystals with a warm concentrated solution of the salt and draining, or by one or more recrystallizations. By cautiously heating the crude salt so that it does not sublime, the water and free acid are removed, and the tarry matter to which it owed its black colour is decomposed; this is more completely effected if the crude salt be somewhat acid. The dry salt, which is now of a dark greyish colour, is ready for the subliming pots.

The heat should be carefully regulated during this operation, as the colour of the salt may be spoilt by the evaporation of the tarry matter. The subliming pots vary in size, according to the extent of the other portions of the plant. They are constructed of cast-iron circular pots set in brickwork, the flues are arranged so that the heat from the furnace circulates around them. The pots are closed with a heavy dome, which is kept in its position either by its own weight or wedges. It is safe to have a small hole in these domes so as to allow the escape of any water or non-condensable matter; the hole is kept clear by thrusting through the salt, which accumulates over it, a short iron rod. These holes allow also the operation to be watched.

A sublimer holding a charge of 2 to 2½ tons may have a diameter and depth of about 8 or 9 ft. The domes fit air-tight, by being luted outside with clay and canvas. The above charge will require about seven to nine days to work off. If the temperature has been too low, the mass, instead of having a finely-grained structure, will present a somewhat cloudy or effloresced appearance, though still fibrous. If the whole of the water has not been removed before placing the crude crystals in the sublimers, the portions in contact with the covers will be contaminated with the iron, and stained a brown colour; this is cut away with axes before being packed for the market.

Another method of treating the crude ammonia liquor for the production of chloride is to convey the ammonia from a still or boiler direct into a vat containing strong hydrochloric acid. The noxious gases are conducted away to the furnace and burnt. The ammonia and a portion of the steam together entering the acid make the whole very warm, which helps to destroy any empyreumatic matters which may be carried over. The liquid is drawn off into shallow tanks, to allow the impurities to subside, and is then concentrated in the evaporators and set by to crystallize; the solution may be almost enough concentrated on the evaporators as to deposit the salt on cooling, but there would probably be more trouble in getting rid of the water before it could be sent to the sublimers, if in this state. Where, however, the salt is to be converted into liquid ammonia, this would be a matter of no consequence.

The manufacture of the chloride by this method would no doubt be far preferable to the former, even if we allow the salt to crystallize in both cases the same way.

By the first method, enormous quantities of water have to be got rid of by evaporation; four or five days have to be allowed for the impurities to subside after the acid is added, and the product itself is a very impure article, and requires care to prevent the tarry impurities passing into the sublimate.

By the second method, 20,000 gallons of crude liquor could be worked up with a comparatively small plant in a single day suitable for the crystallizers, and the salt so obtained would, when dry, be sufficiently pure for a great many purposes, in fact, for the more important uses to which it is applied.

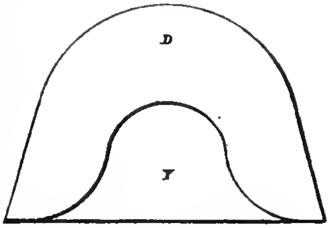
The addition of milk of lime to the crude liquor when placed in the stills or boilers will liberate the combined ammonia, and thus make the yield from the same gas liquor equal to that obtained by the first method.

The ammonia gas may be passed into a solution of chloride of iron or manganese instead of hydrochloric acid, and in manufacturing sulphate of ammonium, the sulphates of iron or manganese may be employed; the gases which are generated form insoluble compounds with these metals, which are deposited before the solution passes to the evaporators.

The manufacture of the salts of ammonia is best carried out on a large scale; the sublimation of the chloride is much more economically conducted by working on large quantities of the crude salt, from the fact that the cost of labour and fuel remains nearly the same for working off large or small charges.

The manufacture of the chloride of ammonium from the carbonate is carried out in Glasgow by utilizing the chlorine refuse from bleach-works and bleaching-powder manufactories. The carbonate of manganese, which settles down by standing, is regenerated into peroxide, and utilized again for chlorine. The mother liquor, or bittern, from sea-water is also employed. The chloride is obtained by evaporating, with occasional stirring so as to avoid the formation of large masses of crystals; it is well dried and mixed with a little animal or vegetable charcoal, which, by acting on the chloride of iron present, prevents the sublimate from being coloured. The Scotch chloride is white, contains but little iron, and is free in most cases from lead. It sometimes shows the presence of manganese. In Liverpool, the chloride is sublimed in iron domes; consequently, the salt is stained with the chloride of this metal, and in addition is generally contaminated with lead. In the sublimation of the chloride, it is found that a quantity of the salt collects in the centre of these domes in a conical heap, which is called the yoke. To avoid this, it is usual to build up in these domes a brickwork form of the yoke, Fig. 199, in which D is the iron dome and Y the yoke. The heat necessary to sublime this portion of the salt must be raised so high that it is decomposed; hence, in practice, it is used in the recharging of the subliming vessels.

199.



It is easy to see that no aqueous vapour, or as little as possible, must be incorporated with the salt for sublimation. The loss sustained by the crystallized salt on drying is about 20 to 25 per cent. and in subliming a further loss of 10 to 12 per cent. The chambers in which the salts of ammonia are sublimed being lined with iron or lead, various devices have been practised with a view to prevent the impregnation of the salt. Siliceous slabs, and a preparation known as Keat's alum plaster, are largely used for this purpose.

Messrs. Baggs and Braby proposed to treat the crude gas liquor with a solution of chloride of iron to obtain the chloride of ammonium.

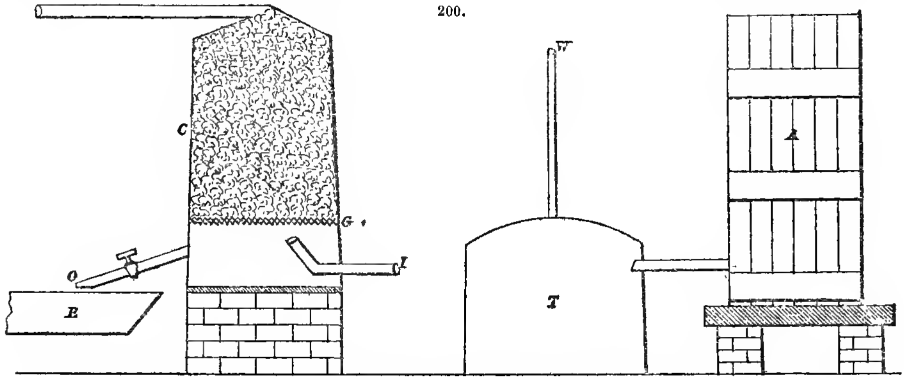
The double chloride of iron and ammonia, which is formed in the crude salt and sublimes with the chloride, is removed, as in Calvert's process, by adding 5 per cent. of biphosphate of lime, or 3 per cent. of the phosphate of ammonia.

Preparation of pure Chloride of Ammonium.—Professor Stas has shown that to obtain ammonic chloride absolutely free from compound ammonias (amines), and other organic matters, requires very complex manipulation. From the commercial sulphate he proceeds as follows. Two kilogrammes of sulphate is heated with 1½ kilogramme of concentrated sulphuric acid, the temperature being raised until the sulphate is decomposed with effervescence. At this stage, nitric acid is gradually added, until the liquid, which previously had a strong blackish colour, becomes quite colourless. The organic matters and compound ammonias are thus destroyed, with the liberation of carbonic acid gas. The acid sulphate, suitably cooled, is poured into about 10 times its volume of cold water, and the excess of acid nearly saturated by lime water. The sulphate of calcium having subsided, the supernatant liquor is mixed with an excess of slaked lime, contained in a very large globe and heated in a bath of a saturated solution of common salt. The liberated ammonia, after washing, is passed into pure water, and afterwards saturated with a current of pure hydrochloric acid gas. The solution is evaporated to dryness in a globe of hard glass, and the residue, sublimed in an atmosphere of ammonia obtained from a portion of the same chloride. The free ammonia is expelled by heating until a vapour appears. In obtaining the pure chloride from the ammonia contained in the commercial chloride, he proceeds by oxidizing the organic matter by the addition of nitric acid of sp. gr. 1·4, and boiling until all the chlorine is driven off. The solution of the ammoniacal salt is treated with hydrate of lime as before, and the gas, well washed, passed into distilled water, through which a current of pure hydrochloric acid is passed to saturation. The liquid is evaporated, and the residuum sublimed in an atmosphere of ammonia. The first process would certainly recommend itself over the other, if it were necessary to produce this salt on a commercial scale with this high degree of purity.

Sulphate of Ammonium.—As it is easier to obtain this salt in a certain degree of purity than the chloride under the same circumstances, it is usual to convert the crude preparations into sulphate, even if required afterwards to be converted into chloride. One or two recrystallizations being generally sufficient, this is due not so much to any peculiarity of the different salts, but to the carbonizing action of the sulphuric acid on the tarry matters carried over mechanically in the first distillation.

The conversion of the ammonia into sulphate, or the formation of any other salts by a simple substitution of the acid may be carried out in the same way, is to convey the gas, as generated in a Coffey's still or retort, into a receiver containing the acid. Formerly the gas entered a receiver packed with coke or charcoal, over which the acid was allowed to trickle gently, any ammonia which escapes the lower part of the apparatus will meet in its upward escape with sufficient acid to fix it. Sufficient vapour enters this receiver to keep the salt in solution, otherwise it would condense and clog the charcoal, and perhaps lead to an accident. If the acid be diluted, it will save the necessity of conveying the steam as the solvent, and will further help to keep the receiver cool. The solution of the sulphate condensed falls to the bottom of the receiver, and may be drawn off, as shown in Fig. 200.

200.



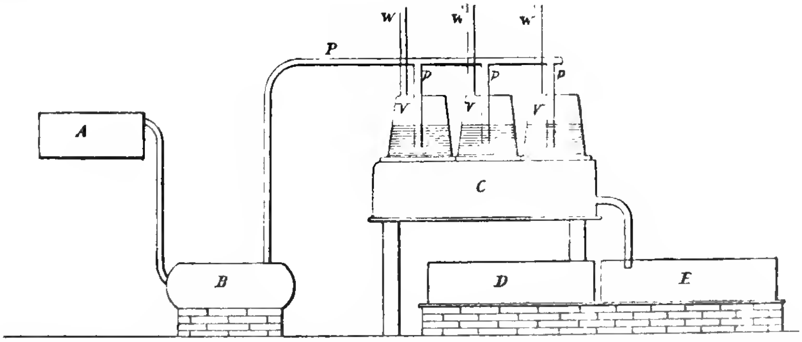
The sulphate is converted into chloride by mixing a concentrated hot solution of the salt with a warm saturated solution of chloride of sodium, and removing the crystals of sulphate of sodium, which deposit on the sides of the pans.

The impure carbonate of ammonia is converted into sulphate by heating with gypsum (sulphate of lime). By sublimation sulphate of ammonia passes over, leaving carbonate of lime in the retorts. The solution of the impure carbonate is sometimes converted into sulphate by percolation through gypsum, the lime salt being converted into carbonate by an exchange of acid.

The manufacture of this salt is much more economically carried out by conveying the ammonia gas direct into a vessel containing strong sulphuric acid. If precautions be taken to pass the ammonia into the acid, free from tarry contaminations, it is possible, by a recrystallization, to obtain the salt with a remarkable degree of purity. When the ammonia passes over into the acid it is accompanied with steam and certain volatile matters contained in the gas liquor, most of which, immediately coming in contact with the strong and hot acid, are carbonized, and so effectually prevented from contaminating the product.

Fig. 201 shows the arrangement for this method of production. A cylindrical boiler A is placed so that the liquid or vapours produced in it can be conveniently received in another boiler B, and which may be either above or below A. These boilers may be heated by the direct heat of a furnace or an inlet of steam. A better plan is to heat the contents of these boilers by passing steam through a series of circular tubes or pipes, which prevents the further dilution of the ammoniacal liquor, the waste steam from the evaporating pans may be used for this purpose. From B the ammonia is conveyed by a pipe P into vats or tuns V V′ V″, containing strong sulphuric acid. Branch pipes *p* reaching nearly to the bottom of the vats are supplied with taps so that the ammonia can be made to pass into either of them. When the acid in any one of the vats is saturated, the resulting solution of sulphate is drawn off into a large tank C, and allowed to stand until all the impurities have subsided. The clear liquid is then drawn off into shallow pans E, and evaporated. The sulphate which crystallizes out, accumulates on the bottom of these pans, and is removed into other pans D to drain. The salt is finally dried by being placed in wicker baskets, and is now ready for the market.

201.



The vats are lined with stout sheet lead, and are made perfectly air-tight, an outlet is made in the top, so that by means of a waste pipe W the noxious vapours arising from the decomposition in the vats can be led away to be burnt in the furnace.

So far we deal only with the uncombined or free ammonia; to obtain the ammonia which is not free, milk of lime is added to the contents of the retorts, and the process conducted in the same way. At one time the sulphate was obtained by adding sulphuric acid direct to the ammonia liquor, the gases which were evolved were burnt in the furnace.

In localities where the lime waste is likely to become troublesome, and large supplies of gas liquor can be easily obtained, it is questionable whether it is not more economical to run away the combined ammonia than to take the trouble of extracting it.

The sulphate of ammonium is employed extensively as a manure and for the production of ammonia alum.

The manufacture of ammoniacal salts is not at present confined to any particular locality. London, Liverpool, and Glasgow, are the principal seats of its manufacture. The conditions necessary for successfully carrying on this manufacture are, large supplies of ammoniacal liquor without much expense for conveying it to the factory, and the vicinity of large acid works. The demand for artificial manures has stimulated the development of this manufacture, and so keenly is the competition felt in the cost of production, that one of the most important considerations is to economize fuel by employing waste heat wherever practicable.

Estimation of Ammonia in Ammoniacal Preparations.—For manufacturing purposes, the volumetric methods are the simplest, and yield results sufficiently exact for any commercial purpose. For solutions of ammonia, liquor ammonia, &c.; an accurately marked pipette, holding, say 10 c.c., is dipped into the liquid, so as to take out a definite quantity without risking any loss of the gas, which could scarcely be avoided by pouring out. The 10 c.c. is poured into a narrow stoppered bottle, previously tared; from the weight of the 10 c.c. the sp. gr. may be obtained by simply shifting the decimal point one place nearer to the left, thus, if the 10 c.c. weigh 9·65 grammes the sp. gr. of the sample is ·965, as 1 c.c. of water weighs 1 gramme.

If the solution be pure, the percentage of ammonia present may be determined by reference to a table of specific gravities.

When neutralizing the solution with an acid, it is safest, if the solution be strong, to dilute with water, so as to avoid a loss of gas from the heating which takes place when an acid is added, the acid used in titrating should consequently be somewhat dilute; from the number of c.c. of standardized acid (sulphuric or hydrochloric) required to neutralize the solution, the amount of ammonia can be at once determined.

As a control, if the solution contained ammonia only, and hydrochloric acid has been used, the mixture should be evaporated to dryness on the water bath, and dried at 100°, until the weight is constant, or at least, until the loss becomes very slight. This will also furnish a test for the strength of the acid. The amount of the alkali contained in the carbonates and bicarbonates or their mixtures may be determined in the same way.

100 parts of ammonium chloride contain :—

Ammonium NH_4	33·72	or	Ammonia NH_3 . . .	31·85
Chlorine Cl.	66·28		Hydrochloric Acid HCl.	68·15
	100·00			100·00

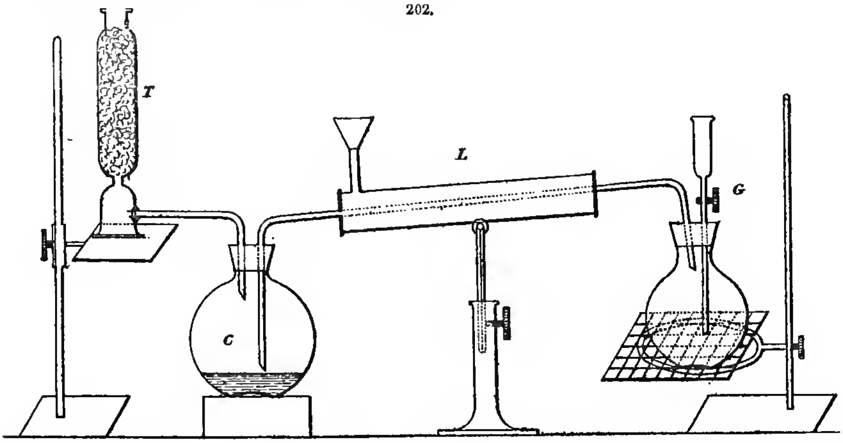
Sulphate of ammonia, not being so stable on drying as the chloride, indicates the non-suitability of sulphuric acid for the estimation of ammonia gravimetrically.

As the carbonates of ammonia when heated in solution are decomposed, the methods given for the volumetric determination of the carbonic acid contained in a sample of this salt require care in their application, and can scarcely be recommended.

A solution of chloride of barium is added to the hot solution of the ammonia carbonates, and the precipitated carbonate of baryta collected on a filter and well washed. The carbonate of baryta is then dissolved in a measured quantity of standard acid, which must be in excess, and the excess of acid carefully titrated with a solution of standard alkali. A much simpler method is to determine the loss direct of carbonic acid, when a weighed quantity is decomposed with hydrochloric acid in any of the ordinary forms of carbonic acid apparatus.

Combined ammonia requires a different treatment. When the ammonia can be expelled from its combinations by means of soda, potash, or lime, the salt is boiled in a flask with a solution, preferably, of caustic soda or potash; the liberated ammonia is collected in a receiver containing a measured quantity, in excess, of hydrochloric acid, and after the decomposition and absorption of the gas is completed, the excess of acid is titrated. As, however, the fumes of chloride may return to the evolution flask, and become again decomposed, it is evident that inaccuracies may occur. The apparatus is shown in Fig. 202, in which G is the generating flask, L a Liebig's condenser, C the condensing flask, and T a tower in which the vapours escaping through C are condensed. This method is suitable for estimating the ammonia in "gas liquor," which contains both free and combined ammonia, to ascertain how much exists in each of these conditions, the distillation is first carried on without the addition of potash or soda, until all the free ammonia has passed over; the contents of the retort are allowed to cool, and the receiver charged with acid as before. On the addition of caustic potash or soda to the contents of the retort and renewed heating, the combined ammonia is decomposed, the liberated ammonia passing over into the receiver. The results, which are only approximately correct, since many salts volatile at 100° may be present, will furnish a far better idea of the alkalimetrical value of a sample of gas liquor than can be obtained from its specific gravity. The determination of ammonia or ammonia salts in the juices, leaves, or stalks of plants is generally made in the same way. It is, however, important to bear in mind that the caustic alkalies may, by acting on other nitrogenized substances contained in the plant, generate ammonia; thus, in the case of tobacco or snuff, where the excise regulation fixes the percentage of alkaline salts which may be present, we must guard against the reduction of nitrates, and remove by means of ether, alcohol, &c., those principles which may generate ammonia when heated in a free state, such as nicotine. Hydrate of magnesia may be employed in such cases instead of the alkalies, since it does not act on the nitrogenous principles present, but liberates the ammonia only.

202.



The separation of ammonia from most other volatile substances may be best effected by means of the bichloride of platinum.

Small quantities of ammonia are determined by the "Nessler test." A standard solution of ammonium chloride is prepared, and a certain portion being measured into a suitable cylindrical vessel, in a similar glass is poured a portion of the ammoniacal fluid to be examined; equal portions (2 c.c.) of the Nessler reagent is added by means of a small pipette to the contents in the two tubes, when, if the same tint is struck in the two fluids, the amounts of ammonia present are equal; if the tints are not equal, the standard solution may be diluted, or made stronger if required, and again tested, until the tints exactly match each other. An important condition is that no precipitate must take place; if the ammonia present in the liquid to be tested be so large as to give a precipitate, it should be diluted to some equi-multiple of its original bulk. The matching of the tints being performed as before, the amount of ammonia present must be obtained by multiplying the quantity contained in the standard solution by the degree or number of times to which the dilution has been carried.

Dr. Wanklyn has proposed an ingenious method of determining the amount of organic contamination in water by the Nessler test, which commends itself more especially, as it can be performed by any person who can fairly conduct a delicate chemical test.

The increased consumption of ice cannot be regarded with indifference by our medical authorities, when we consider the immense amount of nitrogenized impurities which are sometimes met with in this article when used as an article of consumption.

A measured quantity of the water or dissolved ice is first distilled, and the distillate collected which will contain the free ammonia. Wanklyn uses 500 c.c., and collects the first 50 c.c. of distillate for Nesslerizing; the succeeding 150 c.c. are collected and thrown away. A mixture of caustic potash and permanganate of potash is then added to the residue in the retort, and the distillation again proceeded with, and each 50 c.c. of the distillate is collected until 150 c.c. have passed over; each of these is Nesslerized, and the quantities of standard ammonia-solution used to match the tints added together for the amount of "albuminoid" ammonia.

The mixture of caustic potash and permanganate is made by dissolving 200 grammes of potash and 8 grammes of crystallized permanganate of potash, so that the solution is equal to 1 litre. 50 c.c. of this solution is required for each analysis.

In this latter part of the process, the nitrogenized principles, whether animal or vegetable, which may be contained in the liquid is oxidized, and ammonia is obtained as a product of the decomposition.

A great deal of acrimony has unfortunately been introduced into the discussion of the merits of this process, and though perhaps it may not satisfy the requirements of a strictly scientific inquiry, it certainly may lay claim to this important and useful function, that a contaminated water could never be allowed to pass without condemnation. On the other hand, a water which may be quite harmless is made to take a suspicious character as regards its sanitative merits. To an individual of a highly nervous temperament, this may be as great a source of trouble as if the water were decidedly contaminated.

Preparation of the "Nessler Reagent" for Ammonia.—Dissolve 62·5 grm. of potassic iodide in about 250° c.c. of distilled water, and add gradually a cold saturated solution of corrosive sublimate until the mercuric iodide precipitated ceases to be re-dissolved on stirring; continue adding drop by drop until a slight precipitate remains undissolved. Dissolve 150 grm. of solid potassic hydrate in 150 c.c. of distilled water; allow the solution to cool, and add it gradually to the above solution, and make up with distilled water to one litre.

On standing a brown precipitate is deposited, and the solution becomes clear and of a pale greenish-yellow colour. It is ready for use as soon as it is perfectly clear, and should be decanted into a smaller bottle, as required.

Standard Solution of Ammonic Chloride.—Dissolve 1·5735 grm. of dry ammonic chloride (the ordinary commercial kind is generally sufficiently pure for the purpose) in 1 litre of water. It is convenient to have a strong and weak solution as well. 100 c.c. of this solution is taken and made up to 1 litre; 1 c.c. of this latter solution will contain ·00015735 grm. of the salt, which corresponds to ·00005 grm. of ammonia (NH_3).

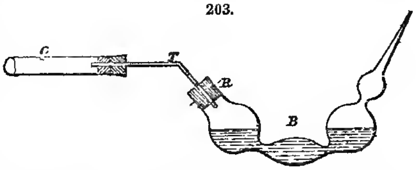
Distilled water, free from ammonia, and a solution of sodic carbonate, which must also be free from the slightest trace of ammonia, are also required for the application of the Nessler test.

Determination of Nitrogen as Ammonia.—Organic compounds containing nitrogen, which is convertible into ammonia, are heated in a combustion tube with soda lime; the ammonia which is formed is received in a suitable bulb apparatus containing a quantity of standardized hydrochloric acid. After complete condensation the excess is titrated with standard alkali. This method is used for the determination of nitrogen and ammonia in manurial substances. When it is desired to ascertain only the ammonia present, a small quantity of the substance—guano, for instance—is boiled in a flask with caustic magnesia, and the liberated ammonia received in a condenser containing standard acid as before. Soda or potash are not to be used in such cases, as they convert, in many instances, the nitrogeneous constituents present into ammonia.

In the estimation of nitrogen by combustion with soda-lime, E. Mulder points out the following sources of error. The cork may absorb some ammonia, to prevent which the cork is recommended to be covered with tinfoil. If the hydrochloric acid is not sufficiently dilute, a small quantity of chloride is liable to be carried away with the hot steam. He recommends that the substance to be burned should first be mixed with soda-lime in fine powder, and this mixture with a larger quantity of granulated soda-lime. An ammoniacal salt should be first mixed with carbonate of lime. For absorbing the ammonia he uses a U-tube, filled with fragments of glass moistened with hydrochloric acid. Dr. Knop has found that the column of soda-lime should not be too long, as the ammonia is likely, especially when strongly heated, to be decomposed.

An improved form of the Will and Varrentrapp apparatus has been recently devised by Mr. H. Shepherd, F.C.S., which has met with universal approval, for nitrogen determinations as ammonia. The bulb nearer the combustion tube, instead of being elongated into the ordinary form with a long bent tube, is supplied with a short neck, with a larger opening, so that the acid may be supplied more readily from a burette. This is fitted with an indiarubber cork, perforated so as to admit a short bent tube, for connecting with the combustion apparatus. The ordinary form of bulb, from the bent tube being fractured by the heat of the combustion furnace, rendered it necessary to use a fresh bulb apparatus for nearly every determination. Fig. 203 shows this bulb; C is the combustion tube, T the bent tube passing through, R an indiarubber cork, and B the absorption apparatus.

203.



Mr. H. Shepherd, chemist to Messrs. Ollendorff's Manure Works, Victoria Docks, recommends tincture of cochineal as indicator for these determinations, instead of litmus.

Small quantities of nitric acid, and nitrates or nitrites, are conveniently estimated by conversion into ammonia, which can be received in a condenser, when distilled, containing acid, or Nesslerized if the quantity be very small. Hydrate of soda and aluminium foil or filings (zinc answers as well), when dissolved in the presence of nitrates, give rise to the formation of ammonia, from the fact that nascent hydrogen decomposes the nitric acid, and combining directly with the nitrogen thus set free. When a large quantity of zinc is rapidly dissolved, ammonia is formed from the direct combination of the nascent hydrogen with atmospherical nitrogen. It has been proposed to utilize this synthetical formation of ammonia by means of electrolytical hydrogen from water. The decompositions which occur in our atmosphere by heavy electrical disturbances show that ammonia and nitric acid are both formed.

Lithia. (Fr., *Lithine*; Ger., *Lithion*).—Formula LiO_2; combining weight, 39.

This substance, the oxide of the metal *lithium*, is an alkaline or earthy salt, and was discovered in the minerals *petalite* (silicate of aluminium and lithium) and *triphane*, in the year 1817, by Arfvedson. It is a white, caustic salt, possessing alkaline properties to an intense degree; it has such a powerful affinity for water that it can only be obtained in the form of a hydrate. It has also the power of attacking or corroding platinum, so that, in its preparation, silver vessels should be employed in preference to those made of the former metal. The hydrate has much the same taste, causticity and alkalinity as those of potash and soda, but it is not nearly so readily soluble in water. When held in the colourless flame of the Bunsen lamp, it imparts to it a rich crimson tinge, by which the presence of the metal lithium is recognized in qualitative analysis.

By means of the spectrum analysis, lithia has been shown to exist in minute quantities in sea-water and in many mineral waters; in blood, milk, and the ashes of some plants; and that instead of being a very rare substance, as had always been supposed, it exists in a state of very wide diffusion. The principal source of lithia is a hot spring, lately discovered in the Huel Seton mine, Cornwall, which contains about 34 grains of chloride of lithia per gallon. The only application of lithia at present is as a medicine, in which the whole supply is consumed.

Potash.—Considerable confusion has always entered into the use of the terms *kali*, *alkali*, *potash* and *soda*, arising probably from the very familiarity with which from ancient times the substances have been regarded. The term "alkali," as is well-known, was applied by the Arabians to the various soda salts obtained from the ashes of marine plants. Afterwards the salts of potash, similarly found in the ashes of land plants, and the carbonate of ammonia were included in the term, the word "potash" signifying evidently a preparation of the ashes of plants in pots. Probably both potash and soda were known to the ancients, and some vague distinction between them recognized, as for instance, when in Jeremiah ii. 22, "nitre and much sope" are mentioned as possessing evidently different cleansing properties. Pliny speaks of a soap made from the ashes of plants and grease, and it is very likely, from the evidence of several of the old writers, that the causticizing effect of lime upon solutions of alkali was known. It may be noticed that the particular character of this reaction—the withdrawal of carbonic acid—was first explained by Black.

An exact line of demarcation between potash and soda was first drawn by Duhamel in 1736. Up to that time ammonia and various of its salts had been distinguished as "volatile" alkalies, and the potash and soda salts, indiscriminately, as "fixed" alkalies. Potash was forthwith styled "vegetable" alkali, because it was supposed to be produced solely from the ashes of plants, and soda, "mineral" alkali, from its existence in rock salt, &c. Klaproth proved that the salts of potassium also existed in various forms in minerals, and substituted the term "kali" for vegetable alkali.

The term "potash," too, is often employed in a very loose manner, to designate sometimes the hydrate of potassium, sometimes the carbonate, sometimes the oxide, and so on. As far as possible in the present work, the term will be confined to the hydrate—KHO.

The metal potassium, in combination, besides yielding four oxides—monoxide, K_2O; dioxide, K_2O_2; trioxide, K_2O_2; tetroxide, K_2O_4—at present, chiefly interesting to the student of chemistry, forms a series of salts of very great importance in the arts and manufactures. These will now be considered in order.

Hydrate of Potassium. (FR., *Hydrate de potasse*, or, simply, *Potasse*; GER., *Kali*).—Synonyms, potash; potash hydrate; potassium hydroxide; caustic potash. Formula, KHO. Combining weight, 48·1; specific gravity, 2·1.

This substance, usually termed caustic potash, was formerly supposed to be simply an oxide of potassium. Darcet, however, showed in 1808 (ann. Chim. lxviii., 175), that some other body was present besides oxygen and potassium—or soda, and it was then commonly believed that the oxide was combined with water. It was not until comparatively recent times that caustic potash was in reality a *hydroxide*, a compound derived from water by substituting potassium for a portion of the hydrogen.

The hydrate of potassium, or caustic potash, is a hard, white solid, with occasionally a fibrous structure, soluble in about half its weight of water (1 part dissolving 2·13 parts of KHO), freely soluble in naphtha, glycerine, and alcohol, and to some slight extent in ether. For water it has a very strong affinity, absorbing it greedily from the air upon exposure, and passing, first into a carbonate, and finally into a bicarbonate, through combination with carbon dioxide. Its combination with water is accompanied by a considerable evolution of heat. When the concentrated solution is cooled the hydrate $KHO + 2H_2O$ crystallizes out in clear colourless acute rhombohedra. Two distinct hydrates are formed with water, the one having a formula $KHO + H_2O$, and the other $KHO + 2\,H_2O$. The following tables drawn up by Dalton and Tunnermann give somewhat varying percentages of hydrate and monoxide contained in aqueous solutions at 15° temperature, and different densities:—

DALTON.

Specific Gravity.	KHO per cent.	K_2O per cent.	Specific Gravity.	KHO per cent.	K_2O per cent.
2·4	..	100·0	1·42	40·97	34·4
2·2	100·05	84·0	1·39	38·59	32·4
2·0	86·22	72·4	1·36	35·01	29·4
1·88	75·74	63·6	1·33	31·32	26 3
1·78	67·65	56·8	1·28	27·87	23·4
1·68	60·98	51·2	1·23	23·22	19·5
1·60	55·62	46·7	1·19	19·29	16·2
1·52	51·09	42·9	1·15	15·48	13·0
1·47	47·16	39·6	1·11	11·31	9·5
1·44	43·83	36·8	1·06	5·59	4·7

TUNNERMANN.

Specific Gravity.	KHO per cent.	K_2O per cent.	Specific Gravity.	KHO per cent.	K_2O per cent.
1·3300	33·693	28·290	1·1437	16 846	14·145
1·3131	32·345	27·158	1·1308	15·498	13·013
1·2966	30·998	26·027	1·1182	14·151	11·882
1·2805	29·650	24·895	1·1059	12·803	10·750
1·2648	28·303	23·764	1·0938	11·456	9·619
1·2493	26·954	22·632	1·0819	10·108	8·487
1·2342	24·606	21·500	1·0703	8·760	7·355
1·2268	24·933	20·935	1·0589	7·412	6·224
1·2122	23·585	19·803	1·0478	5·957	5·002
1·1979	22·237	18·671	1·0369	4·717	3·961
1·1839	20·890	17·540	1·0260	3·369	2·829
1·1702	19·542	16·408	1·0153	2·021	1·697
1·1568	18·195	15·277	1·0050	·6738	0·5658

In either a liquid or solid state, caustic potash is a most powerful alkali, neutralizing acids, decomposing metallic salts, possessing a vigorous corrosive action upon animal and vegetable tissues, turning reddened litmus solution blue, turmeric brown, and producing a purple colour with an infinitely dilute solution of alizarin, or an acidified solution in alcohol of cochineal, or logwood. It destroys many of the silicates—and hence, should not be kept in glass or porcelain vessels—forming silicate of potassium, and separating the bases. Especially is it destructive to a lead-glass, dissolving out the lead oxide. Its action upon most organic bodies is to take from them the carbon and oxygen necessary for its conversion into carbonate. At a temperature somewhat below redness caustic potash melts to a thick colourless liquid, possessing the most powerful caustic properties. At a full red heat it volatilizes in white feathery fumes, being decomposed into potassium, hydrogen and oxygen. It forms soaps with various fats, oils and resins, and dissolves sulphur, the sulphides of antimony, arsenic, &c., also many bases—alumina, silica, &c.

Caustic potash is usually prepared by dissolving one part of commercial carbonate in 12 parts of water, boiling the solution and gradually adding one part of thoroughly burnt lime—preferably made into milk of lime. The boiling is continued for about twenty minutes after the whole of the lime is added, when a dense carbonate of lime is formed, and falls to the bottom as a heavy powder. Caustic potash remains in solution together with an admixture of various other salts of potassium, the sulphate and chloride, &c. The clear liquor is run off and evaporated to dryness in an iron—or, if required of particularly good quality, a silver, vessel. It is then fused at a strong heat, whereby the water is as far as possible expelled, and run into moulds. The lime must be added until a small portion of the filtered liquid gives no effervescence when treated with an acid. The moulds are of iron usually, and are in two halves, screwed together to make a tight joint. The fused caustic potash is poured in at the top, and, when cool, the halves are unscrewed and the solid product, in the form of sticks removed. This is the ordinary "stick," or "lump" potash of commerce. A still better article may be made by treating the stick potash with methylated spirit, or alcohol, evaporating the solution to dryness, and fusing in an iron or silver vessel. It is never, however, free from a certain admixture with other salts of potassium. The "*liquor potassæ*" is usually prepared in this way, the process being carefully conducted so as to leave only the smallest possible quantity of carbonate. The quantity of water must not be less than that stated, and it is well to have a slight excess of lime. Liquor potassæ and lump potash have usually about the following composition:—

	Liquor Potassæ.	Lump Potash.
Hydrate of potassium	5·40	68·75
Carbonate "	·21	4·90
Sulphate "	trace	·07
Chloride "	·10	·75
Nitrate "	trace	trace
Caustic soda	·25	13·57
Soluble silica and alumina	·03	·40
Water	94·00	11·50
	99·99	99·94

Liquor potassæ should stand about 1·05 specific gravity.

The well known "potash" and "pearl ash" of America and Russia are very extensively used in this manufacture. It will be noted that the process is similar to the ordinary production of caustic soda, and may be carried out from the commencement, employing chloride of potassium in place of the corresponding chloride of sodium. This substance heated with sulphuric acid, gives a sulphate of potash with the evolution of hydrochloric acid. The potash salt furnaced with chalk and small coal in a reverberatory furnace gives an impure carbonate, which is drawn out of the furnace in large lumps answering to the "black ash" of the Le Blanc soda process. These lumps are broken up and lixiviated in tanks, the dissolved pure carbonate run off into pans, boiled down to dryness and furnaced.

The best carbonate to use in this process, is that obtained by igniting cream of tartar. The crude potash, or pearl ash, gives only an impure product, and requires further purification by the treatment with alcohol as above mentioned. This is Berthollet's plan. The first caustic solution should be concentrated until it attains a thick consistency, and well agitated with one-third its volume of alcohol. The mixture is then allowed to settle, the impurities—chloride, carbonate, and sulphate of potash, &c.—subside with whatever lime or oxide of iron may be present, and the lighter caustic potash solution remains clear upon the top. This is decanted off, freed by distillation from the alcohol, and evaporated to dryness in a silver vessel. Whatever impurities are left float on the surface during concentration, and are removed. The pure hydrate is then run into moulds, or poured out on plates to cool.

Other methods of preparation are the following:— (*a*) by the action of the metal potassium upon water; hydrogen gas is evolved, and hydrate of potash formed. The liquid is evaporated and fused in silver apparatus as already described. In this way the purest caustic potash is prepared. (*b*) By the action of the monoxide upon water, thus:—

$$K_2O + H_2O = 2\ (KHO).$$

(c) By decomposing nitrate of potassium with metallic copper at a red heat, thus :—

$$2\ KNO_3 + 3\ Cu_2 = 6\ CuO + N_2 + K_2O.$$

One part of the potassium salt, and 2 or 3 parts of copper clippings are arranged in layers in a crucible and exposed to a dull red heat for half an hour. The mass is then allowed to cool, lixiviated with water and settled. Oxide of copper separates out, and the clear caustic potash in solution is decanted off, evaporated and fused. (d) By decomposing sulphate of potash by hydrate of barium, thus :—

$$K_2SO_4 + BaH_2O_2 = BaSO_4 + 2\ KHO.$$

The baryta water is added in slight excess, and the sulphate of barium settled out, leaving caustic potash to be treated in the manner already described.

The uses of caustic potash are many and varied. Its chief application, of course, is in the manufacture of soap. It is also used in the refining of saltpetre, in the manufacture of oxalic acid, and is a chemical reagent, absorbing carbon dioxide in organic and inorganic analyses, drying gases, &c. It is a powerful poison, and is used to some considerable extent in medicinal preparations as an antacid.

The chief impurities are carbonate of lime, oxide of iron, peroxide of potassium, carbonate of potassium, sulphate of potassium, and nitrate of potassium. The presence of most of these bodies depends upon the care with which the preparation is conducted.

The following analyses by Tatlock represent the composition of various kinds of commercial potash.

	White.	Brown or Cream.	
	1.	2.	3.
Hydrate of potassium	77·64	75·64	71·05
Carbonate ,,	4·62	2·54	3·14
Sulphate ,,	·38	·21	·69
Chloride ,,	2·29	·93	2·26
Nitrite ,,	·87	..	..
Hydrate of sodium	4·67	2·59	3·20
Soluble silica and alumina	·30	·20	·55
Insoluble matter	·02	·22	·69
Water	8·84	17·80	15·80
	99·68	100·13	100·38
Potassium in hydrate	54·11	52·72	51·60
Equal to potash (K_2O)	65·19	63·51	62·17
Potassium in carbonate	2·61	1·44	1·78
Equal to potash	3·14	1·73	2·11
Potassium in sulphate	·17	·09	·31
Equal to potash	·20	·11	·37
Potassium in chloride	1·20	·49	1·18
Equal to potash	1·44	·59	1·12
Potassium in nitrite	·40	..	..
Equal to potash	·48	..	..
Total potassium	58·49	54·74	54·87
Equal to potash	70·45	65·94	66·10
Total available potassium	56·72	54·16	53·38
Equal to potash	68·33	65·24	64·31
Or carbonate of potassium	100·24	95·71	94·34
Total alkali calculated as potash	73·83	68·28	68·08
Ratio of sodium to available potassium—potassium, 100	4·73	2·74	3·35
Ratio of soda (Na_2O) to available potash (K_2O)—potash, 100	5·29	3·07	3·85

The manufacture of potash is carried on to a large extent in France and Germany. In England very excellent qualities are made upon a considerable scale in Lancashire and at Glasgow, the Greenbank Alkali Company and the North British Chemical Company being the largest manufacturers.

Carbonate of Potassium. (Fr., *Carbonate de Potasse*; Ger., *Kohlensäures Kali*).—Synonyms, carbonate of potash, potashes, pearl ash, salt of tartar. Formula K_2CO_3. Combining proportion 138·2. Specific gravity 2·2.

The terms "potash," "potashes" are very commonly given to this substance, from one of the methods of its preparation, i. e. *pot ashes.* Formerly its only source was the ashes of plants, and about one-third of the total potashes now imported into this country are still the product of the old processes. The treatment of the ashes of plants to obtain carbonate of potassium is a time-honoured institution, and the industry is still an important one in districts where wood is plentiful—in Canada, North America, Russia, Hungary, &c. As the old forests became extinct, other sources of an article of every day use had to be found, and, as will be noted hereafter, the methods of preparation are now exceedingly various.

Carbonate of potash is a hard white solid—sometimes a white granular powder—with a strong alkaline reaction and taste. At a temperature somewhat over 800° it melts, losing a portion of its carbonic acid. At a still higher temperature it slowly volatilizes. All the acids, even in a dilute state, decompose it with evolution of carbon dioxide, leaving a salt of the acid employed. It is exceedingly deliquescent, absorbing moisture from the air, and forming a thick oily liquid, sometimes kown as "*oleum tartari per deliquium.*" It is soluble in about its own weight of water at the ordinary temperature, the solubility increasing with the heat applied:— thus,

At 0° 100 parts of water dissolve 89·4 parts of carbonate.
20° " " 112 " "
40° " " 117 " "
60° " " 140 " "
135° " " 205 " "

These solutions are always accompanied by the evolution of heat. The following table gives the densities and corresponding percentage composition of various carbonate solutions at 15°.

Specific Gravity.	K_2CO_3.	Specific Gravity.	K_2CO_3.	Specific Gravity.	K_2CO_3.
	per cent.		per cent.		per cent.
1·00914	1	1·18265	19	1·38279	37
1·01829	2	1·19286	20	1·39476	38
1·02743	3	1·20344	21	1·40673	39
1·03658	4	1·21402	22	1·41870	40
1·04572	5	1·22459	23	1·43104	41
1·05513	6	1·23517	24	1·44388	42
1·06454	7	1·24575	25	1·45573	43
1·07396	8	1·25681	26	1·46807	44
1·08337	9	1·26787	27	1·48041	45
1·09278	10	1·27893	28	1·49314	46
1·00258	11	1·28999	29	1·50588	47
1·11238	12	1·30105	30	1·51861	48
1·12219	13	1·31261	31	1·53135	49
1·13199	14	1·32417	32	1·54408	50
1·14179	15	1·33573	33	1·55728	51
1·15200	16	1·34729	34	1·57048	52
1·16222	17	1·35885	35	1·57079	52·024
1·17243	18	1·37082	36		

When a concentrated solution is cooled, crystals of carbonate, having the composition $2K_2CO_3 + 3H_2O$, and belonging to the monoclinic system, separate out. When these are heated to 100° they fall into a powder, losing two-thirds of their water of crystallization. At 130°, the whole of the water is driven off, and an anhydrous carbonate, in the form of a white powder, left.

It has been stated already that there are many methods of preparing carbonate of potash. For laboratory purposes, or where a particularly pure article is required, the crystals of cream of tartar (bitartrate of potassium) may be calcined, the residue treated with water, evaporated and dried at a low red heat. Or a stream of carbon dioxide may be passed into a solution of pure hydrate of potassium, and the resulting carbonate evaporated to dryness, and ignited. Or one part of saltpetre may be heated with two parts of oxalic acid and a little water, evaporated to dryness, and ignited. Or pure saltpetre may be fused in a porcelain or earthenware crucible, and small pieces of charcoal dropped in till all deflagration ceases.

Upon a manufacturing scale, the following are the principal sources of carbonate of potassium:—About one half of the total produce is still made from the ashes of land and marine plants; one-fourth from sulphate of potassium, produced by the decomposition of the chloride by sulphuric acid, and from various potassium compounds; the remainder from "Suint," or the wool of sheep impregnated with the sweat exuded from the skin, felspar and other silicates. Although the last named source is as yet comparatively untried ground, it should be noted that in reality felspar and the other silicates yield, in the first instance, their potash salts to all the other sources. Many powerful agencies—the oxidizing action of the air, the wearing and disintegrating force of water, and especially water containing carbonic acid, the very carbon dioxide in constant expiration by animals—are continually at work breaking up the hardest rocks, and dissolving and carrying away the alkalies contained therein. One Table will suffice to show the changes induced by this process of decomposition—felspar being the example.

	Per cent. in Original Mineral.	Per cent. in Mineral after Decomposition.
Silica	65·21	32·50
Alumina	18·13	18·13
Potash salts	16·66	2·80
Soda	..	0·25
Lime	..	0·35
Magnesia	..	0·27
Oxide of iron	..	0·73
Water	..	5·11
	100·00	60·14

Manufacture from Wood-ashes.—Potassium salts abound in many land and marine plants, the ashes obtained by calcination showing great diversities in quantity and composition. The carbonates are found usually in the largest proportion, also the chlorides, sulphates, phosphates, and silicates. The following Table will sufficiently exhibit the remarkable diversity in composition; the proportions given are of 1000 parts.

	Ash.	Potash, K_2O.
Pine wood	3·40	0·45
Beech	5·80	1·27
Ash	12·20	0·74
Oak	13·50	1·50
Elm	25·50	3·90
Willow	28·00	2·85
Vines	34·00	5·50
Ferns	36·40	4·25
Wormwood	97·40	73·00
Funitory	219·00	79·90
Dahlia, with blossoms and leaves ..	79·92	19·98
,, stems after flowering	44·57	3·60
,, bulbs	99·16	13·44
,, branches	23·05	2·56
Acacia ,, ...	21·59	2·56
Grape stems	88·88	41·66
Vines	46·66	12·73
Skins of grapes	72·91	14·88
Stems of a cluster of grapes	..	39·81
Grape stones	..	9·50

A great deal of this diversity is of course due to the soil in which the plants have been grown. The vegetable salts are contained in the juice, therefore the more succulent the plant the greater the yield of these substances. As a rule, the twigs and leaves yield more potash than the larger growths. Potatoes, chestnuts, heather, broom, furze, sorrel, beet leaves, and tobacco stalks may be mentioned as yielding upon incineration large quantities of potassium salts. As a sample of the composition of timber, the following analysis (Berthier) of the ash of pine wood may be given:—

Soluble in Water.	
Carbonate of potassium	1·86
Sulphate of potassium	3·63
Chloride of potassium	1·88
Carbonate of sodium	6·03
Silica	·18
Insoluble in Water.	
Lime	38·51
Magnesia	9·56
Oxide of iron	·09
Oxide of manganese	·36
Carbonic acid	32·77
Phosphoric acid	·91
Silicic acid	4·19
	99·97

It will be seen what an enormous amount of material has to be treated to obtain, say, one ton of commercial carbonate of potassium. The wood of the pine yields about 1·25 per cent. of ash, and of this not one-fifth consists of carbonate. Large timber is usually selected in preference to the smaller growths or herbaceous plants, although these are far richer in potash salts, because the soils in which the trees are grown is not impoverished by a too rapid utilization of their potassium compounds. Without an altogether unremunerative system of artificial preparation of the land, it would be impossible to keep up a supply of the woods which are richest in potash.

The method of manufacture, as usually carried on, is of the simplest possible description. The plants, or timber, are arranged in pits some 3 or 4 feet deep, or piled upon the ground and burned, fresh material being added from time to time until a sufficiently large heap of ashes is obtained. During this process whatever organic salts of potassium and sodium are present are converted into carbonates and hydrates, and remain behind with the other potash, &c., salts when the combustion is completed. The ash obtained is sifted carefully from half-burnt wood or charcoal, and placed in a series of wooden vessels for lixiviation. This part of the process is conducted in a variety of ways. Commonly the tanks are ranged in three rows one above another. Each is provided with a false perforated bottom loosely covered with cinders or straw. Below the false bottom a pipe communicates with the tank placed immediately below it. The ashes are filled in upon the false bottoms of the uppermost row of tanks, and water at a temperature of about 110° run upon them. A small quantity of slaked lime should be added to render the dissolving out of the carbonate and hydrate of potassium more certain and complete. The strong liquors are run off, as soon as each tank fills, to the evaporating pans, fresh water being run on meanwhile. When the liquors begin to come over weak, the lye is run upon the second set of tanks placed below, in which fresh ashes have been placed, and again, when sufficiently strengthened, run off to the pans. This operation is continued at will, the fresh water and weak lye always coming upon unexhausted ash. The final weak liquor from each tank may be run to waste if a particularly good product is required. It will be seen that this method of lixiviation corresponds almost exactly with the tank operations of the Le Blanc soda process.

The lye, of a light-brown colour if good, is evaporated in the iron pans mentioned, until it assumes a thick consistency. Sometimes the operation is continued until the mass is almost solid—being in the state of the "black salts" of the corresponding soda process—sometimes the thick liquors are boiled down in a separate vessel to dryness. A pretty constant agitation should be kept up during evaporation. This crude product consists chiefly of carbonate and sulphate of potassium, with about 12 per cent. of water, also various impurities and empyreumatic bodies. From the drainers into which it is raked, or the pots, it is spread upon the sole of a reverberatory furnace and thoroughly calcined, the heat being kept under until the salts are thoroughly dried, but finally urged to redness. During calcination the mass of salt is carefully paddled and turned over, so that every portion is exposed to the action of the heat. The loss of weight amounts usually to about 20 per cent., all carbonaceous matters being burned out, potassium hydrate converted into carbonate, and the various lower sulphur salts oxidized into sulphate. The product is then known as "pearl-ash." Commercial "pot-ash" is the crude product of the pans or pots—the evaporated lye, before the impurities have been removed in the carbonator, as described. The "pot-ashes," known as "firsts," "seconds," "thirds," and "unbrandables," according to quality, are usually of a grey colour. If the carbonating process has been carefully conducted, the "pearl-ashes" are white, or very nearly so. The latter may be subjected to a second refining process, being redissolved, concentrated, evaporated, and furnaced in similar apparatus to that used in the first process. The product then corresponds to the "refined alkali" of the soda manufacture. It is sometimes called "salt of tartar." The very finest quality is made by washing out the soluble carbonate from the calcined pearl-ash, and evaporating the solution in iron pans, keeping the mass well stirred. It then assumes a granular form, and a beautifully white colour.

There is a considerable variety of both pot-ashes and pearl-ashes, the products of the different localities where they are manufactured having their own distinctive characteristics. The American pot-ashes are usually grey, or reddish grey, and of three qualities, containing respectively 35 to 40 per cent. of potash, 48 to 52 per cent., and 54 to 58 per cent. They are usually packed in oak barrels, weighing from 3 to 10 cwt. each. The American pearl-ash is of good quality, very fairly white, and ranging up to 58 per cent. In Russia and Poland the carbonate is often manufactured from the ash of straw, the product being inferior, and going by the name of "potasse de paille." The best Russian pot-ashes, often called Kasan, contain from 48 to 52 per cent. of potash. French pot and pearl-ashes are of superior quality, and are often manufactured from the lees of wine and vine stalks. The Tuscan are of three qualities—60 per cent.; 50 to 55 per cent., white; 50 to 55 per cent., blue. The following Tables show the composition of average samples of the various kinds of pot-ashes:—

	Tuscany.	Russia.	Vosges.
Carbonate of potassium	78·24	60·22	39·43
„ sodium	3·67	7·61	4·17
Sulphate of potassium	11·66	15·77	38·74
Chloride „	1·00	3·99	8·46
Insoluble	·65	2·40	2·66
Moisture	4·59	9·50	5·34
Phosphoric acid, lime, silica, &c. ..	·27	·53	1·20
	100·08	100·02	100·00

Large quantities of American pot-ashes are still imported into this country, chiefly from the ports of Montreal, Quebec, and New York, and are consumed in the manufacture of soft-soap. The quantity is becoming smaller year by year, less timber being felled now than formerly for this purpose, and also because the demand for potash is now almost entirely supplied by the carbonate made from the sulphate by Le Blanc's method, and by that obtained from the French beet-root vinasses. The amount of potash obtained from timber is exceedingly small, as compared with the quantity of the latter consumed. Pine-wood contains about 1·25 per cent. of ash, of which about 0·12 per cent. is potash; hence, in order to produce 1 ton of commercial pot-ashes, containing 65 per cent. of total potash, about 520 tons of timber would have to be burned. In the course of a few years, it is probable that timber, as a source of commercial potash, will be entirely superseded by the newer European methods. The following table represents average samples of Montreal pot-ashes of different qualities:—

	Firsts.	Seconds.	Thirds.
Carbonate of potassium	35·01	30·12	38·47
Hydrate „	43·26	36·53	..
Sulphate „	12·86	14·05	53·34
Chloride of sodium	2·90	9·47	0·62
Carbonate „	2·23	5·88	6·03
Insoluble	·96	2·67	1·54
Water	2·80	·90	..
	100·02	99·62	100·00

An average sample of good Canadian pearl-ash is given in the following table:—

Carbonate of potassium	74·44
Sulphate „	13·01
Chloride „	3·14
Carbonate of sodium	2·58
Soluble silica, &c.	1·76
Insoluble „	·35
Water	4·72

American pot-ashes contain, as a rule, more caustic potash than other qualities. This is owing to the use of lime in the lixiviating tanks; and, for many purposes, as, for example, soap-making, where the pot-ash has ultimately to be causticized, it is a positive advantage, saving lime in the after process.

New and better methods of manufacture have to a large extent supplanted the wood process; but the industry is still a very large one. It is carried on chiefly in America, Canada, Russia, France, Italy, Poland, Belgium, and Austria; America alone supplies about one-half of the total amount manufactured. The prices range from 20*s.* to 24*s.* per cwt. for pot-ashes, and from 28*s.* to 32*s.* for best pearl-ashes.

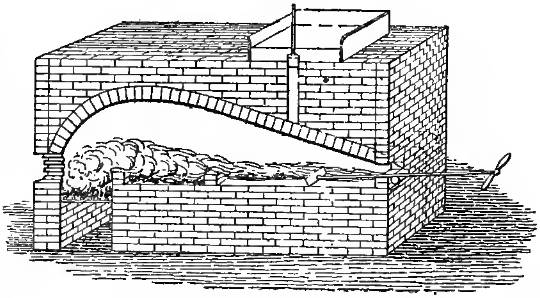
Carbonate of Potash from Beet-root Molasses.—The existence of considerable quantities of potassium salts in the juice of beet-root has been for long a recognized fact, and many processes have been set on foot for their extraction. These salts are for the most part left in the mother liquors or " molasses " of the ordinary sugar-refining process, after crystallization.

The following table represents the ordinary composition of the molasses salts:—

	1.	2.	3.
Potash	51·05	49·69	49·50
Soda	8·14	9·71	9·86
Lime	4·08	4·30	3·36
Magnesia	·18	·14	·14
Carbonic acid	28·80	28·42	28·32
Sulphuric acid	7·74	7·71	9·29
Phosphoric acid			
Silicic acid			
Chlorine			
Oxide of iron			
	99·99	99·97	100·47

The potash salts are extracted from the molasses in the following manner:—The liquors are diluted down to about 1·05 and slightly acidified with sulphuric acid. A small quantity of the yeast of beer (2 to 2½ per cent.) is added, and the whole is then allowed to ferment for a period of about five days. The spirit is then distilled off, leaving a liquor, usually called "vinasse," which contains all the original potash salts. To this an excess of chalk is added, and the resultant sulphate of lime, &c., allowed to settle. To facilitate this process, it is usual to concentrate the liquors slightly in an iron pan and then run them into tanks to settle. The clear supernatant liquor is siphoned off into wrought-iron pans, boiled down to dryness, and finally calcined in a reverberatory furnace. The crude product is called "salin," and contains from 35 to 45 per cent. of carbonate of potash. The effect of the lime is to notably increase the proportion of the potash salt. The composition, of course, varies very considerably with the different soils, and state of the soils, upon which the beet-root has been grown.

204.



A very excellent furnace for calcining the vinasses is shown in Fig. 204, the construction of which will be at once apparent. The sole of the furnace is divided into two compartments. The liquors are kept in a small bath placed upon the arch, and a portion is run down, as may be required, into a suitable vessel placed upon the bed of the compartment farthest from the fire, to which vessel is attached a long handle to move it forward. As soon as the contents of this ladle assume a thick, pasty consistency, they are removed to the compartment next the fire, where calcination is completed. In the meantime the ladle is drawn back and refilled with another charge of liquors.

A refined product has of late years come into favour. This is produced either by washing the crude "salin" with water, and boiling down and calcining the resultant liquors, or by crystallizing out as far as possible all impurities.

Or, to obtain a still better carbonate, the "salin" is washed, and the lixivium concentrated up to 1·5. During concentration, sulphate of potassium and chloride of potassium crystallize out and are skimmed off. The mother liquors are further concentrated and run into shallow cooling pans. Here a mass of crystals—a mixture of various salts, but chiefly a double salt of carbonate of potassium and sodium—separates out. The residual liquors are then removed, boiled down to dryness, and calcined. The crystals are dissolved and recrystallized, the mother liquor again yielding a quantity of pure potassium carbonate.

Two other processes for obtaining carbonate of potassium from molasses may be mentioned. Billet distils the "vinasses" in an ordinary gas retort, passing the products of distillation first into a small vessel where the greater part of the tar condenses, then through a worm placed in water, the products of condensation falling into a reservoir. The uncondensable gases pass off into a purifier, and may be burnt. In the retort is left a product answering to the "salin" already described. This is raked out, lixiviated, evaporated, and calcined. Seymour treats the saccharine juices with solution of caustic baryta, or sulphide of barium, obtaining saccharate of baryta as a precipitate. This is washed with a weak solution of caustic baryta. The liquors are evaporated or subjected to a stream of carbon dioxide, to remove the baryta as hydrate or carbonate, and the residual liquors boiled down to obtain the alkaline salts.

The extraction of carbonate of potash from beet-root molasses is a rapidly increasing trade. It is carried on chiefly in France, Germany, Belgium, and Austria, and yields something like 12,000 tons per annum.

Carbonate of Potash from the Lees of Wine and Tartars.—After fermentation, the lees or "yeast" is placed in bags and pressed into hard cakes. These are then dried and burnt over a slow fire, yielding a light porous product called "*cendres gravelées*," which consists of a mixture of salts, chiefly carbonate of potash; lixiviated and calcined in the manner already described, the *cendres gravelées* give a remarkably pure carbonate. The refuse from the manufacture of brandy is treated in similar fashion.

The well-known cream of tartar, or acid tartrate of potash, crystallized out from a solution of the crust which forms upon the casks during fermentation, is incinerated, and yields a black mass, called "black flux," which consists of various potash salts—chiefly carbonate—mixed with charcoal. This "black flux," deflagrated with nitre, yields a fairly good potassium carbonate, sometimes called "white flux." These processes are carried on only to a small extent, and chiefly in France and Spain.

Carbonate of Potash from the Sulphate, Brine Springs, &c.—Next to the ashes of plants, the greatest amount of carbonate of potassium is obtained from the sulphate. The process is almost identical with the Le Blanc soda process, the raw material (sulphate) being obtained either from chloride of potash and sulphuric acid by the ordinary sulphate process, or by decomposing the former with sulphate of magnesium, or "kieserit." Equal weights of sulphate, and finely divided limestone, or chalk, together with varying quantities of small coal, are furnaced together in a reverberatory furnace, the product being an exceedingly impure carbonate of potassium. When the decomposition is complete, the molten mass is raked out, broken up when cool, and lixiviated in tanks. The soluble salts of potash and soda are thereby dissolved out, evaporated, and calcined in a small reverberatory furnace. Further details of this process will be given when treating of the soda compounds.

A carbonate of better quality is produced by following more closely the carbonating operation of the soda process. The liquors from the tanks are evaporated, the chloride and sulphate of potassium which separate out during the concentration being skimmed off, and sawdust is thrown in. The dried salts are then removed to the carbonator and exposed to a heat at first gentle, but finally urged to dull redness. By this process, the sulphur compounds are oxidized into sulphate and the caustic potash converted into carbonate. The chief object of the sawdust is to keep the mass of salt open. A carbonate carefully made in this manner should give about the following composition:—

Carbonate of potash	89·59
Sulphate „	3·98
Chloride „	2·49
Carbonate of soda	2·33
Soluble silica and alumina	·19
Insoluble matter	·13
Water	1·27
	99·98

Upon a small scale, a hydrated carbonate is manufactured containing about 15 per cent. of water and having the formula $K_2CO_3 + 2H_2O$.

This is made by dissolving the crude carbonate, boiling down not quite to dryness, and allowing the mass to cool, stirring it vigorously in the meantime. The product is a fine white granular salt.

The manufacture of potassium carbonate from the sulphate by the methods described is a rapidly increasing industry. Something like 16,000 tons per annum are now produced, and, all things considered, it seems likely to supersede the other processes. It is much more amenable to the altered conditions of the labour market; a pure article is more readily obtained; and the soil is not impoverished by a too rapid withdrawal of the potash compounds, which must be the case where beet-root and other plants are the material operated upon.

It is of great importance to free the potassium carbonate as much as possible from soda compounds, as these considerably destroy the fine character which the potash salts give to the articles manufactured from them. In the preparation of bichrome, ferrocyanide of potassium and soft soaps, for example, the potash compound should not contain above 3 per cent. of soda.

Preparation from "Suint."—From this remarkable source about 100,000 kilos. of carbonate of potash of very good quality are annually obtained. Suint is the term given to the sweat exuded from the skin of the sheep, and retained in the wool. The residue left after lixiviation of the skins in water contains earthy matter mixed with charcoal so very finely divided that it may be used as black paint. According to MM. Maumené and Rogelet, a fleece weighing 4 kilos. contains 600 grm. of suint, capable of yielding 198 grm. of pure carbonate of potash. According to Fuchs, however, the quantity of suint amounts to only about 300 grm., made up as follows :—

Sulphate of potash	7·5	grm. =	2·5	per cent.
Carbonate „	133·5	„ =	44·5	„
Chloride „	9·0	„ =	3·0	„
Organic matter	150·0	„ =	50·0	„
	300·0	„ =	100·0	„

The potash salts, of course, are derived in the first instance from the soil upon which the food of the sheep is grown, and upon the nature of this soil depends the composition of the "suint." Other things being equal, it has been found that the merino wool contains the greatest amount of potassium salts, ranging as high as 30 per cent.

The process usually employed for the extraction of the potassium salts is that of MM. Maumené and Rogelet, and depends upon the ready solubility of the suint in water. The wool is pressed into casks and thoroughly washed with cold water. The grease of the wool forms, with a certain amount of lime, &c., always present, an insoluble soap, and the suint comes off remarkably freely, in the shape of a light brown solution, of about 1·15 specific gravity. This is boiled down to dryness, and treated as an ordinary potash liquor, calcined, lixiviated, and again furnaced in a reverberatory furnace. By this method, and by fishing out the chloride and sulphate of potash during evaporation, a very good carbonate is made. This process is carried to a considerable extent in France and Germany; Rheims, Elbœuf, and Verviers being the chief seats of the trade.

Carbonate of Potash from Felspar, &c.—It has already been noted that the silicates as a source of potassium carbonate form a comparatively untried ground. Many processes have been set on foot for the treatment of these minerals, but very little has yet been done with them on a manufacturing scale. The reader is referred for further information to the patents of Fuchs, Lawrence, Meyer, Ward, Tilghmann, and Sprengel. Most of these processes go upon the same lines—a calcination of the mineral with lime, and lixiviation of the product. Ward adds fluor-spar to the lime to assist in the decomposition of the silicate at the lowest possible temperature, thereby effecting a great saving in time and fuel. This seems to be the best process yet brought forward.

Carbonate of potash is used largely in the manufacture of soft soaps, being first converted into caustic potash. It is, for all purposes, the principal source whence the hydrate is obtained; and from it, too, are made the bichromate and yellow prussiate of potash, and various kinds of potash glass. In medicine, it furnishes an antacid and diuretic. It is also largely used for cleansing purposes; in Turkey red dyeing, for the emulsion of oil, and in printing, as a solvent of annatto, &c.

The only true means of determining the composition of any given sample is to make a complete analysis. The certain presence of soda compounds renders the ordinary alkalimetrical test of no use, inasmuch as the soda neutralizes the acid along with the potash.

Bicarbonate of Potassium. (Fr., *Bicarbonate de Potasse;* Ger., *Zweifach Kohlensaures Kali.*) Synonyms, acid carbonate of potash; potassium hydrocarbonate. Formula, $KHCO_3$.—This salt is of comparatively small importance to the manufacturing world. It is, however, used in certain medicinal preparations as a diuretic and antacid. It is usually met with in the form of large crystals derived from a right rhombic prism. Soluble in four parts of cold water, the aqueous solution has a slightly alkaline reaction and taste. Upon boiling, carbon dioxide is given off, and the monocarbonate left. The following table shows the solubility of the salt in water of different temperatures :—

At 0°,	100 parts of water dissolve	19·61	parts.
„ 10	„ „	23·33	„
„ 20	„ „	26·91	„
„ 50	„ „	37·92	„
„ 60	„ „	41·35	„
„ 70	„ „	45·24	„

The crystals, like the solution, are decomposable by heat into carbon dioxide and simple carbonate.

Bicarbonate of potash is usually prepared by passing a stream of carbon dioxide into a cold saturated solution of the carbonate. The gas is rapidly absorbed, forming a white crystalline precipitate of bicarbonate, which is redissolved in hot water, or by passing in steam, and leaving the solution to cool. The bicarbonate separates out in large crystals, which are drained and dried at a low heat. Another method of producing a very pure salt is to pass a stream of carbon dioxide, prepared from marble and a pure acid, into an alcoholic solution of pure caustic potash. The crystals of bicarbonate should be washed with fresh alcohol.

Chlorate of Potassium. (Fr., *Chlorate de Potasse;* Ger., *Chlorsaures Kali.*) Formula, $KClO_3$.—This salt has become of considerable importance from a manufacturing point of view. It forms anhydrous, tabular crystals, in taste resembling saltpetre, which melt and decompose at a low red heat, oxygen being disengaged from both acid and base, and chloride of potassium left. Heated with any combustible matter, chlorate of potash deflagrates violently, explosion often occurring with friction, or blows. It is slightly soluble in cold water, the rate of solubility increasing very rapidly as the temperature is raised. Thus:—

At 0°,	100 parts of water dissolve	3·33	parts of chlorate.
„ 13·32	„ „	5·60	„
„ 15·37	„ „	6·03	„
„ 24·43	„ „ ..	8·44	„
„ 35·02	„ „	12·05	„
„ 49·08	„ „	18·96	„
„ 74·89	„ „	35·40	„
„ 104·78	„ „	60·24	„

Formerly chlorate of potash was obtained only by passing a stream of chlorine gas into a solution of caustic potash, or the carbonate. The liquors were concentrated and cooled, when colourless crystals of chlorate separated out. The process adopted now is to pass chlorine gas into a mixture of milk of lime and chloride of potassium, contained in strong iron vessels fitted with agitating gear. Usually, these vessels are about 7 ft. in diameter by 7 ft. deep. A considerable degree of heat is generated, and chlorate of potassium and chloride of calcium are formed. The liquors are run off and crystallized in iron vessels, when the chlorate separates out and chloride of calcium remains in solution. The first crop of crystals is removed and placed in lead-lined tanks, where it is redissolved in boiling water, the necessary temperature being obtained by passing in steam. The solution is then run into shallow vessels and recrystallized. A very pure article may be made by this process, although, since great care is needed, there is a good deal of difference between the various brands. It should consist of nearly pure chlorate, the only impurity being about 0·25 per cent. of chloride and moisture.

This process is usually worked in connection with the "decomposing" section of the Le Blanc soda manufacture, and takes the place of, or is carried on concurrently with, the bleaching powder process. The chlorine is generated by the action of hydrochloric acid upon binoxide of manganese. The latter, in weight varying from two to five cwt., is placed in stills of greatly varying shapes, but always constructed of stone, preferably Yorkshire flags, carefully dressed and bound up with strong iron girders. Hydrochloric acid is run in, at a specific gravity of about 28° Twa., and steam introduced through a pipe passing through the cover of the still, and reaching below the level of the liquor. Chlorine gas is generated, and conducted away through earthenware pipes fixed in the cover, a mixture of chloride of manganese and iron being left in solution. A more detailed description of this part of the process will be given under the head of Bleaching Powder. It is usual now to recover the manganese from the "still liquors" by Weldon's patent process, for a full description of which the reader is also referred to the same article.

A third method of preparation is by heating chlorate of calcium with chloride of potassium, thus:—

$$Ca2ClO_3 + 2KCl = CaCl_2 + 2KClO_3.$$

Chlorate of potash forms a well-known source of oxygen gas, and this property of readily yielding up its oxygen makes it valuable for many purposes. It is largely used in calico printing, as an oxidizer; calico prepared with a solution of it saves time in ageing; a mixture of it with arsenite of soda is used to facilitate the fixing of iron mordants: it is also employed in some steam colours in low-class reds from Japan wood, in steam chocolates and blacks. Together with phosphorus this salt enters largely into the manufacture of matches, and especially "safety" matches; it is used in the production of fireworks and detonators for exploding dynamite. Finally, it enters into certain medicinal preparations.

About 3500 tons of chlorate are produced annually, the chief seats of the industry being in Lancashire, on the Tyne, and at Glasgow. The average price is about 10*d.* per lb.

Chloride of Potassium. (Fr., *Chlorure de Potasse;* Ger., *Chlorkalium.*) Synonyms, muriate of potash, digestive salts, *sal febrifugum Sylvii.* Formula, KCl.—This salt closely resembles ordinary chloride of sodium. It forms colourless, anhydrous crystals of a cubic form, and a saline and slightly bitter taste, which decrepitate when heated, fuse at a high temperature, and completely volatilize at a strong heat. Chloride of potassium is soluble in three parts of cold water, the solubility increasing with an increase of temperature; thus at 11·8° it dissolves in 2·89 parts of water; at 13·8°, in 2·87 parts; at 15·6°, 2·85 parts. The following table exhibits the percentage of the salt in aqueous solutions of different densities, and at 15°:—

Per Cent.	Specific Gravity.	Per Cent.	Specific Gravity.	Per Cent.	Specific Gravity.
1	1·00651	9	1·05914	17	1·11465
2	1·01300	10	1·06580	18	1·12179
3	1·01950	11	1·07271	19	1·12894
4	1·02600	12	1·07962	20	1·13608
5	1·03250	13	1·08654	21	1·14348
6	1·03916	14	1·09345	22	1·15088
7	1·04582	15	1·10036	23	1·15828
8	1·05248	16	1·10750	24	1·16568

Chloride of potash occurs native, sometimes pure, but more usually in combination with other metallic chlorides, and forming double salts; e. g. chloride of potassium and magnesium. Pure native chloride is called "*sylvine*," and occurs in the well-known beds of Stassfurth, near Magdeburg; also in Vesuvius, accompanied by deposits of "*kremersite*," a mixture of various chlorides of sodium, ammonium, and iron. The chloride of potassium and magnesium is called carnallite, and is perhaps the best known of all these potassic minerals. They have about the following composition:—

Carnallite.

Chloride of potassium	24·27
„ magnesium	30·98
„ sodium	4·82
„ calcium	2·82
Sulphate of calcium	1·05
„ magnesium	trace
Oxide of iron	0·14
Water	35·92

Chloride of potash may be obtained by burning the metal potassium in dry chlorine gas; by heating it in hydrochloric acid gas; by dissolving caustic potash, or the carbonate, in aqueous hydrochloric acid, or by the action of potassium upon various metallic chlorides. Usually, however, it is prepared by one of four principal methods:—(1) from the potassic minerals of which mention has been already made; (2) from the ashes of marine plants; (3) from sea-water and brine-springs; (4) as a bye-product in the treatment of beet-root molasses.

(1) Chloride of Potash from Potassic Minerals.—The head-quarters of the chloride of potash extraction are at the Stassfurth, Leopoldshall, and Douglcshall works in Saxony and the Duchy of Anhalt. A mixture of carnallite and other potassic minerals is here found in extensive deposits, varying from 150 to 400 ft. in thickness, and at depths of from 400 to 800 ft. from surface. Shafts have been sunk upon these deposits, supplying to some thirty-five works upwards of 500,000 tons of the crude minerals—technically called "potash salts," or "Abraum salts"—per annum. An analysis of these "potash salts" is given in the following table, and may be compared with the analysis of pure carnallite already set forth:—

Chloride of potassium	16·50
„ sodium	20·83
„ magnesium	21·99
Sulphate of magnesium	11·21
„ calcium	1·08
Insoluble	1·83
Water	26·54

The mineral is first broken up and lixiviated with water, heated by steam to about 110°, the proportions being so arranged that the solution shall stand at least at 53° Tw. (32° B.). After settling, the clear liquor is run off from all insoluble residue to shallow vessels, in which, upon cooling, crystals of chloride of potassium separate out, the double salt (carnallite) only forming in the presence of an excess of chloride of magnesium. These crystals are removed and thoroughly washed with cold water to remove all mother liquor and chloride of potassium. The purifying effect of these washings is shown by the following table by G. Krause:—

	Before Washing.	After First Washing.	After Second Washing.
Chloride of potassium	58·24	62·82	80·61
„ sodium	21·80	18·42	9·97
„ magnesium	4·75	1·10	·04
Sulphate of „	1·46	·70	·66
Water	13·75	16·96	8·72
	100·00	100·00	100·00

The water is then driven off by drying the crystals at a gentle heat. Sometimes the crude carnallite is dissolved in a hot strong solution of chloride of magnesium and recrystallized. These crystals are then subjected to the ordinary process described. The mother liquors, and the strongest of the wash waters, are evaporated to 36° B., when chloride of sodium separates out, and the chlorides of potassium and magnesium remain in solution. The latter being in excess, crystals of carnallite separate out when the solution is cooled, and are treated like the fresh potash-salt. The weaker wash waters are used to dissolve further quantities of the raw material. Various other processes are carried on at the Stassfurth works, more particularly the preparation of saltpetre, by decomposing the chloride with nitrate of sodium. The residue that is left from the first solution of the potash salts contains up to 75 per cent. of chloride of sodium, and is occasionally used in the manufacture of sulphate of soda. The presence, however, of 10 or 12 per cent. of insoluble matter, and the absence of the usual crystalline form of chloride of sodium as used in the decomposing process, render it somewhat unsuitable. Its only virtue is an extremely low cost.

The Stassfurth deposits were first worked on in the year 1861. At the present time about 70,000 tons of chloride of potassium are produced in the district. In 1868, the Kalutz (Gallicia) deposit was discovered, and a chloride of potassium of very great purity is now turned out from the works established in the district. The raw material here is somewhat richer than that at Stassfurth, containing from 22 to 24 per cent. of chloride, without the admixture of magnesium salts, and often in the state of pure sylvine. The process followed is an exceedingly simple one. The potash salt is broken up and digested with a hot saturated solution of chloride of potassium. The chloride is thereby completely dissolved, the chloride of sodium and the rest of the impurities being deposited. The strong solution is run into shallow crystallizing vessels and allowed to cool. A remarkably pure chloride separates out, the crystals, after draining and drying, giving the following composition:—

Chloride of potassium	98·83
„ sodium	·82
Insoluble	·10
Water	·19
	99·94

The mother liquors are returned to dissolve a fresh box of mineral. The Kalutz chloride is held in high esteem on account of its excellent quality, an absence of magnesia salts being especially desired.

(2) Preparation from the Ashes of Marine Plants.—Since the year 1730, when the industry was first introduced into Scotland, the treatment of kelp to obtain potash salts has become of considerable importance. Before this time, it had been a recognized source of profit in France and the Channel Isles, and also in Ireland, and the terms "vraic" and "varec" have an equivalent in our word "wreck," applied to various forms of sea-weed. For a long period, the manufacture was carried on chiefly for the sake of obtaining carbonate of soda, reaching its greatest prosperity at the commencement of the present century, when there were about fifteen works in the United Kingdom, Scotland alone producing 20,000 tons of finished products per annum. Since that time, owing to the discovery of new and better sources of potash salts, the kelp trade has dwindled into comparatively small compass. The British turn-out of kelp salts is now probably not more than 6000 to 7000 tons per annum.

Two kinds of weed are recognized: that which clings to the foot of the rocks and has to be detached at low spring tides, technically termed "cut-weed," and the loose plants that float upon the surface of the water, or are thrown upon the shore, to which the name of "drift-weed" is given. As a rule the latter is the richer in potassium salts.

The different varieties of sea-weed, too, *inter se*, give widely differing products when burned, and the selection and proper admixture of the material is a matter requiring considerable care and experience.

The burning is conducted in kilns of various forms and of rude description, built upon the level ground, with sides and ends of rough stone or brickwork. Sometimes pits in the ground form the kilns, 3 ft. in diameter and 18 to 20 in. deep. More commonly, however, the kiln is rectangular in shape, built with stonework sides and ends about 12 in. high, and varying in length from 6 ft. to 16 ft., and in width from 2 to 3 ft. The object in keeping the kiln narrow is to allow of the ends of the weed overlapping the sides, and so to admit the air freely throughout the mass. The weed is carefully arranged upon a bedding of dried heather or straw, and the whole mass set on fire. After burning for six or eight hours the ash begins to show signs of melting. It is then well stirred about to produce an equal flux, and finally allowed to harden into a rough cake, varying in thickness from 3 to 6 in., which is broken up by throwing water upon it, and removed. The operation is then recommenced with a fresh lot of weed. The fragments of cake are broken down somewhat further by hand labour, occasionally in a mill of edge stones or fluted rollers, and thrown into tanks arranged after the manner of the black ash vats of the Le Blanc soda process, to which the reader is referred. Here the kelp is lixiviated with water at 43° (110° F.), the first and strongest liquors run off to the settlers, and the subsequent weaker lye run upon the second tank, now filled with fresh kelp. This operation is continued without intermission over a round of four tanks, the fresh water being always run upon the "weakest" tank and the second liquor, after the best has been removed to the settlers, being turned upon fresh kelp. The strong lye is drawn off as soon as a freshly filled tank is covered with it. It then stands at about 50° to 55° Tw., and is drawn away till it falls to 35°. It is then turned upon the next tank. Sometimes a tank is considered finally exhausted when the lye standing upon it registers 5° Tw., but more usually lixiviation is continued down to 2°. After being allowed to settle, the liquors are pumped into an evaporating pan and concentrated, by waste heat where practicable, up to 60° or 65°, *hot*. During this concentration, various impurities, sulphate of potassium, &c., separate, and are fished out, the drainings being allowed to run back. The purified lye is drawn off and run into settlers, where chloride of potassium crystallizes out. These crystals are removed and drained. The mother liquor is again concentrated, and the operation of crystallizing and separating impure salts repeated. In this way, three crops of chloride crystals are obtained, the second being usually the best. The first test up to 90 per cent. of pure potassium chloride, the second to 98 per cent., whilst the third does not average 82 or 83 per cent. The salts that are separated from the lyes during concentration consist of chloride of sodium, sulphate of sodium, sulphate of potassium, and carbonate of sodium, and command a somewhat slow sale to glass manufacturers and to alkali makers, the latter using them for the purpose of manipulating their soda ash and refined alkali so as to produce the strengths required by their various contracts. The use of "kelp-salt," as it is called, for "reducing" purposes is, however, on the wane, a readier and cheaper material being found in common salt.

Kelp-salt contains, too, as a rule, appreciable quantities of insoluble matter, and the greatest objection to its use as a reducing agent is that it is apt to "fleck" the alkali, from its containing a certain amount of carbonaceous impurity.

In France, the kelp is roughly ground, and the tanks are usually built of wood, of much smaller dimensions than those in use in this country. The chlorides of potassium and sodium are extracted together by running fresh water, or weak liquor, upon the unexhausted tank, concentrating the lye and separating the chloride of sodium by fishing it from the evaporating pans in the manner already described. This deposit, carefully washed and drained, yields a very fair salt for many manufacturing and agricultural purposes. To purify it from an admixture of sulphate of potassium, it is sometimes washed in weak lye, in boxes fitted with false bottoms. A jet of steam is introduced, the mass thoroughly agitated, and, after settling, the supernatant liquor is run off, and the residue drained and dried. The lye from the evaporating pans, after the chloride of sodium is removed, is concentrated further and run into coolers, where the chloride of potassium crystallizes out in the manner already described.

It will be readily apparent that these methods are all of them exceedingly laborious, an enormous mass of material having to be treated to obtain even a small result. The process of incineration in the open, too, is manifestly faulty, as a great loss of volatile products and heat must ensue. Moreover, both waste and injury result from the inevitable admixture of the ash with sand and dirt, and the whole process is liable to be seriously interfered with by bad weather, &c.

Many methods have been devised with a view to remedy these defects; those of Lamont and Kemp may be mentioned. Stanford's suggestions, however, are more deserving of notice. He has proposed to submit the marine plants to destructive distillation in an iron retort, obtaining various inflammable gases, water, naphthas, and tar as volatile products of distillation, and a light porous charcoal left in the retort, which may be lixiviated and otherwise treated as ordinary kelp.

By this method, an exceedingly pure product has been obtained. It will be noted that this process is analogous to that of Billet for the treatment of "vinasses," already described. It is claimed for the method that, in addition to the usual products, there are obtained, from one ton of kelp, the following valuable substances:—

Volatile oil	6½ gals.	Colouring matter	6½ lb.
Paraffin oil	9 gals.	Pure charcoal	13 cwt. 39 lb.
Naphtha	3½ gals.	Gas (approximative)	4456 cubic feet.
Sulphate of ammonia	2 cwt. 48 lb.	Iodine	5 lb.
Acetate of lime	37 lb.		

These figures of course represent something like an *average* possible addition to the results usually obtained.

Another method of treating sea-weed has been devised by Schmidt, of the chemical works at Aalborg, in Jutland, Denmark, where the new ammonia-soda process is in operation. When this process is carried out completely, the ammonia is recovered, by boiling the waste liquors with lime or magnesia. The sea-weed, which abounds in the neighbourhood, is carefully stacked under cover and dried. It is then burnt in any convenient way, and a strong solution of the ash or "cake" is made. This is added to the waste liquor from the ammonia-recovery process, which contains chlorides of calcium and sodium. The potassium, magnesium, and sodium sulphates contained in the kelp are thereby decomposed, and hydrated sulphate of lime and magnesia precipitated, the operation being facilitated by the addition of a small quantity of chloride of barium. These precipitates are utilized in the manufacture of "pearl-hardening." The clear liquor is drawn off and the iodine precipitated with nitrate of lead as iodide of lead, which is separated by filtration and utilized for the production of iodine, &c. The liquor is then concentrated, and nitrate of soda added, to convert the potassium chloride into nitrate. Run into coolers, this salt crystallizes out of the mixture, leaving, as mother liquor, a solution of chloride of sodium, containing traces of ammonia and chloride of potassium, which is used again in the first process of the soda production—the decomposition with ammonia and carbon dioxide. It may be mentioned that, so far at least, the ammonia-recovery process has not been a great success, and in fact has been abandoned in the English works which manufacture soda by the Solvay method.

The sulphate and chloride of potassium obtained from the kelp lye may be converted into nitrate by decomposition with nitrate of sodium. Sometimes, instead of fishing the chloride of sodium from the pans, a shallow kind of scoop is lowered into the liquor, the top just reaching to the surface of the lye. By the force of ebullition, the salt is projected into these scoops, which are hoisted up when filled, the liquor draining back into the pan through a series of holes pierced just below the rim of the vessel.

The chief seats of the manufacture are, the west coasts of Scotland and Ireland; Jersey, Guernsey, and Sark; and, in France, Normandy, Brittany, and La Manche.

(3) Chloride of Potassium from Sea or Brine-Springs.—In sea-water, the salt occurs to an average amount of about 0·25 parts in 1000. The process of extraction has been an industry of considerable extent for many years in the South of France, and upon low-lying coasts where a hot sun may be depended on. The water is conducted into large shallow ponds, or "salt-gardens," and allowed to evaporate. Chloride of sodium separates out, mixed with a certain amount of sulphate of magnesium. The mother liquors contain considerable quantities of chloride of potassium, chloride of sodium, sulphate of magnesium, and chloride of magnesium. Two processes are adopted to obtain the products from these liquors. By the old method, they are allowed to concentrate to 31° B., and are then run off into shallow ponds, where, during the day, a second crop of chloride of potassium is deposited, and during the night a mixture of salts—chiefly sulphate of magnesium and a double sulphate of magnesium and potassium. The mother liquors are once more run off into a third series of ponds, where a further crop of crystals are deposited—chiefly a double chloride of potassium and magnesium. This is treated after the manner of the "potash salts" from Stassfurth, dissolved in water by the aid of steam at 120°, solution being facilitated by agitation. In place then of the double salt the chloride of magnesium remains in solution, and the chloride of potassium crystallizes out. From the mixed magnesium and potassium salts, by redissolving and recrystallizing, a double salt, $K_2Mg''S_2O_8.6HO$, is obtained, which is utilized in the production of carbonate of potassium by decomposition with chalk and small coal. Great loss of liquor, and injury to the salts, result from the slow process of natural evaporation and crystallization. A newer and better method is that of Merle, termed the "*méthode à vingt-huit degrés*." The mother liquors, after the first separation of chloride of sodium, are evaporated to 28° B., and then diluted with about 8 per cent. of pure water, to prevent a too rapid accumulation of chloride of potassium in the after processes. They are then passed through refrigerators, and reduced in temperature to 18°, when a double decomposition takes place between the chloride of

sodium and sulphate of magnesium. Chloride of magnesium remains in solution, and sulphate of sodium (Glauber's salts) crystallizes out. Thus:—

$$MgSO_4 + 2NaCl = MgCl_2 + Na_2SO_4.$$

The crystals are removed, and the mother liquor is evaporated to 36° B. (62° Tw.). During evaporation, the chloride of sodium, hitherto held in solution, and various other salts, separate out, and are removed. The liquor is then run into crystallizing cones, where the double salt of chloride of potassium and magnesium is deposited, and is treated as the "potash salt," carnallite, already described.

Chloride of potassium has hitherto been extracted from the waste of brine-springs upon only an experimental scale. Various methods have been proposed, other than those already set forth in treating of the manipulation of sea-water; but as yet they are only interesting to the chemist.

(4) Chloride of Potash from Beet-root Molasses.—The treatment of "vinasses," or beet-root molasses, to obtain carbonate of potassium has already been described. The charcoal, or *schlempe-kohle*, obtained on calcination, contains about 16 per cent. of chloride of potassium, and upon lixiviating the mass, concentrating the solution, and cooling, the chloride crystallizes out, and may be washed and dried. The salt thus obtained rarely tests beyond 75 per cent., and the production is carried on upon a very limited scale.

Chloride of potassium enters largely into the manufacture of saltpetre, alum, and chlorate of potash. From it is made, by decomposition with sulphuric acid, the greater part of commercial sulphate of potash, and it is used to a considerable extent as an ingredient of artificial manures.

Chromate of Potassium. (Fr., *Chromate de Potasse;* Ger., *Chromsaures Kali.*) Formula, K_2CrO_4.—This salt is a source of chromium preparations. It crystallizes in yellow, six-sided pyramids, isomorphous with sulphate of potassium. The solution in water—2 parts—is also yellow, with an alkaline reaction and a bitter saline taste. It is efflorescent, and exceedingly poisonous in all forms.

Chromate of potassium is prepared direct from native chrome-iron ore by calcination with saltpetre, or carbonate of potassium, or caustic lime, the ore being powdered and carefully heated with the alkali in a reverberatory furnace; or the bichromate may be subjected to a strong heat, and split up into oxide of chromium and chromate.

Chrome-iron ore is a compound of the sesquioxide of chromium and protoxide of iron, with certain admixtures of alumina, magnesia, and silica. It is found in considerable quantities in Russia, Greece, North America, and Turkey.

Bichromate of Potassium. (Fr., *Bichromate de Potasse;* Ger., *Zweifach Chromsaures Kali.*) Synonym, bichrome. Formula, $K_2O, 2CrO_3$, or $K_2Cr_2O_7$.—By slow evaporation, this salt crystallizes in fine, red, tabular crystals, derived from an oblique rhombic prism, which are anhydrous, and melt at a low red heat. At an ordinary temperature, it is soluble in about 10 parts of water, the solubility increasing rapidly with an increase of temperature. Thus, 1 part is soluble in—

20·14 parts of water at	0°
11·81 " "	10
7·65 " "	20
3·43 " "	40
1·98 " "	60
1·37 " "	80
·98 " "	100

At a high temperature, it is split up into the neutral chromate, oxygen, and oxide of chromium.

Bichrome is manufactured from the chromate by adding sulphuric acid, which unites with one half of the base to form sulphate of potassium. The process is usually carried out direct from the chrome ore, and is as follows:—The ore is carefully ground and sieved through a very fine mesh. It is then mixed with potash lime, prepared from the purest obtainable limestone and a solution of carbonate of potassium, as free from chloride as possible. The proportions are 7 cwt. of lime to 2¼ of carbonate. After being thoroughly mixed by any convenient apparatus, the whole mass is thrown into a reverberatory furnace constructed in similar fashion to a double-bedded sulpha of soda furnace, with a bed about 10 ft. long by 7 ft. wide, a fireplace 2 ft. 6 in. wide, and a crop of arch 2 ft. 6 in., narrowing down to 18 in. at the end farthest from the fire. The charge is spread over one of the beds and paddled carefully, under a bright flame. After about two hours, it is transferred to the bed nearest the fire, and a fresh charge introduced upon the back bed. Each charge is worked for about four hours, by which time nearly the whole of the oxide of chromium is completely oxidized. It is then withdrawn, and should have a greenish-yellow appearance, with hard lumps dispersed through the whole mass. With the chromate of potassium are now mixed chromate of calcium, free lime, silicate of potassium, and oxide of iron. The lumps are roughly broken up, and the whole is thrown into lixiviating tanks, and digested with a hot saturated solution of sulphate of potassium. The chromate of calcium is thereby converted into chromate of potassium, with the formation of sulphate of lime. The tanks are arranged in fashion somewhat resembling black ash vats, the liquors running from tank to tank until they are sufficiently strong. They are then drawn off and allowed to settle. Sulphate of lime is deposited, and the clear chromate of potassium run into cisterns lined with lead. Here it is treated with sulphuric acid, which abstracts a portion of the base, converting the chromate into bichromate. And inasmuch as the latter salt is not nearly as soluble in water as the chromate, a precipitation of the greater part of the bichrome takes place, leaving sulphate of potassium and a portion of bichrome in the mother liquors. This precipitate is removed, redissolved, and recrystallized in iron cones. The mother liquors are returned to the lixiviating tanks.

Bichrome is also occasionally made by heating the chrome ore with saltpetre in the manner described when treating of the chromate.

The manufacture of bichrome is a rapidly increasing one; as much as 11,000 tons per annum being now turned out in this country. The chief seats of the industry are in Lancashire and Glasgow.

Bichromate is largely used in calico printing and dyeing, for the raising of chrome oranges and other chrome shades, the fixing of catechu, and the raising of steam blues and greens. Its chief virtue lies in the readiness with which it parts with oxygen. Care must be taken not to employ bichrome too freely, as the chromic acid seems capable of forming some new compound with the oxide which fixes itself upon the cloth. If applied in too large a quantity, the cloth is liable to be injured by chromic acid.

The quality of this salt may be judged of to a certain extent by its appearance. If it is in good crystals of a uniform red colour, without any admixture of soft yellow crystals, it is good. A somewhat rough test consists in dissolving a known weight of pure metallic tin and ascertaining how much chromate is necessary to peroxidize it. A more accurate method is to reduce the chromic acid present in the sample into a salt of sesquioxide, by alcohol and hydrochloric acid, precipitate by ammonia, and determine the amount of chromic acid from the weight of oxide of chromium obtained. A good sample of bichrome should show 61 per cent. of chromic acid.

Cyanide of Potassium. (Fr., *Cyanure de Potassium;* Ger., *Cyankalium.*) Formula KCN.—This salt takes the form of a white, opaque solid, with crystalline fracture, or of cubic crystals. The crystals are deliquescent, exceedingly soluble in water, and intensely poisonous Soluble in *boiling* alcohol, the cyanide separates out again from the cooled solution. The aqueous preparation has an alkaline reaction, and is decomposed when boiled into ammonia and formiate of potassium. It is decomposed also by the feeblest acid—even by the carbonic acid of the air—exhaling an odour of hydrocyanic acid. It is readily fusible at a low red heat, and forms a series of double salts with certain metals, which are exceedingly useful in the arts.

Cyanide of potassium may be prepared in many ways; (1) by heating potassium in cyanogen gas, or vapour of hydrocyanic acid; (2) by transmitting pure nitrogen gas through a white-hot tube containing a mixture of carbonate of baryta or potassium, and charcoal; (3) by heating to redness nitrogenous organic matter—horn-shavings, hide-parings, &c.—with carbonate of potassium; (4) by passing the vapour of hydrocyanic acid into a cold alcoholic solution of hydrate of potassium, and pressing and drying the deposited crystalline salt; (5) by heating to whiteness carefully-dried ferrocyanide of potassium in a nearly-closed iron retort; nitrogen and other gases are evolved and a mixture of carbon, carbide of iron, and cyanide of potassium left; thus:—

$$K_4FeC_6N_6 = 4KCN + FeC_2 + N_2 .$$

The best process of manufacture upon a large scale, and that usually adopted, is as follows:— Eight parts of ferrocyanide of potassium are gently dried and mixed with three parts of dry carbonate of potassium of good quality. The mixture is fused at a low red heat in an iron or earthenware pot, the heat being kept up, and the mass well agitated, until all evolution of gas ceases, and a sample taken out upon an iron rod solidifies to a colourless, opaque solid. The pot is left to settle for a short time until all the sediment, consisting principally of finely divided metallic iron, is deposited, and then the clear salt is decanted off and poured into moulds to solidify. In this process, 2 equivalents of ferrocyanide and an equal amount of carbonate of potassium yield 5 equivalents of cyanide, 1 equivalent of cyanate of potassium, 2 equivalents of iron, and 2 equivalents of carbon dioxide. Carbonate of soda may be substituted for carbonate of potassium.

Cyanide of potassium is extensively used for photographic purposes, also in electro-gilding and plating; very occasionally it forms a potent reducing agent.

Ferricyanide of Potassium. (Fr., *Prussiate rouge de Potasse;* Ger., *Ferridcyankalium,* or *Rothesblutlaugensalz.*) Formula, $K_3FeC_6N_6$. Synonym, red prussiate of potash.—This salt forms fine anhydrous crystals belonging to the monoclinic system, of a deep-red colour. They have a specific gravity of 1·8, and a strong saline taste. The following table gives the percentage composition of aqueous solutions of varying densities:—

Specific Gravity.	$K_3FeC_6N_6$, Per Cent.	Specific Gravity.	$K_3FeC_6N_6$, Per Cent.	Specific Gravity.	$K_3FeC_6N_6$, Per Cent.
1·0051	1	1·0595	11	1·1202	21
1·0103	2	1·0653	12	1·1266	22
1·0155	3	1·0712	13	1·1331	23
1·0208	4	1·0771	14	1·1396	24
1·0261	5	1·0831	15	1·1462	25
1·0315	6	1·0891	16	1·1529	26
1·0370	7	1·0952	17	1·1596	27
1·0426	8	1·1014	18	1·1664	28
1·0482	9	1·1076	19	1·1732	29
1·0538	10	1·1139	20	1·1802	30

The solubility of the salt increases rapidly with an increase of temperature. Thus 100 parts of water dissolve—

At 4·4° .. 33·0 parts of ferricyanide.
„ 10·0 .. 36·6 „ „
„ 15·6 .. 40·8 „ „
At 37·8 .. 58·8 parts of ferricyanide.
„ 100·0 .. 77·5 „ „
„ 100·4 .. 82·6 „ „

The usual method of preparation is to pass chlorine gas through a solution of the ferrocyanide, or the same salt in a powdered state, until it no longer gives a precipitate of prussian blue with a persalt of iron.

The process is similar to that employed for the production of bicarbonate of soda, chlorine gas being generated in leaden vessels, or in the ordinary stone stills, by the action of hydrochloric acid upon peroxide of manganese, and passed through powdered ferrocyanide spread upon wooden shelves or trays in a close chamber. The ferrocyanide should be dried before use. The result of this first part of the operation is a deep orange-coloured powder, which is dissolved in hot water, and run into coolers to crystallize. Ferricyanide separates out from the chloride of potassium, crystallization being assisted by small rods or pieces of string. The mother liquors are evaporated and dissolved, and a second crop of inferior ferricyanide is obtained. Occasionally the first, powdered, product, without crystallization, is sold as a commercial article.

Ferricyanide of potassium, or red prussiate, as it is more frequently called, is largely used in dyeing and printing operations, to produce peculiar shades of blue, and as a "discharge" of indigo colour—chiefly for the former purpose. Its discharging powers depend upon the process of rapid oxidation already alluded to. If a piece of "dip" blue be soaked in red prussiate and dried, and then passed through a bath of caustic potash, the colour is immediately oxidized and destroyed. The process is, however, expensive, and certain difficulties arise in "thickening" the cloth. It has been proposed to use calcined magnesia in place of caustic potash, but the element of expense still forms a serious obstacle.

The best rough test for red prussiate is the appearance and size of the crystals. They should lose no weight when dried, and dissolve readily and *completely* in water.

Ferrocyanide of Potassium. (FR., *Prussiate jaune de Potasse;* GER., *Ferrocyankalium*). Synonym, yellow prussiate of potash. Formula, $K_4FeC_6N_6$.—This useful salt, when pure, occurs in the form of large, transparent, amber-coloured crystals—$K_4FeC_6N_6 + 3H_2O$—derived from an octahedron with a square base. They have a strong saline taste and are permanent in the air. At 100°, the three equivalents of water are driven off, leaving the anhydrous salt, and this at a little over red heat splits up into cyanide of potassium, carbide of iron, and various gaseous products. Heated, with free admission of air, the cyanide is converted into cyanate. Ferrocyanide is soluble in about four parts of cold, and two and a half parts of hot water. The following table gives the composition of the aqueous solution at different densities:—

Specific Gravity.	Percentage of Ferrocyanide.	Specific Gravity.	Percentage of Ferrocyanide.	Specific Gravity.	Percentage of Ferrocyanide.
1·0058	1	1·0479	8	1 0932	15
1·0116	2	1·0542	9	1·0999	16
1·0175	3	1·0605	10	1·1067	17
1·0234	4	1·0669	11	1·1136	18
1·0295	5	1·0734	12	1·1205	19
1·0356	6	1·0800	13	1·1275	20
1·0417	7	1·0866	14		

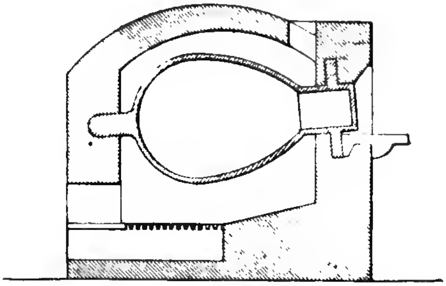
100 parts of water dissolve of ferrocyanide, at 12·2°, 27·8 parts
" " 37·7°, 65·8 "
" " 65·5°, 87·6 "
" " 96·3°, 90·6 "

The crystals become gradually decomposed in a strong light, giving off hydrocyanic acid and becoming very slightly alkaline.

Crystallized ferrocyanide was first manufactured by Macquer, about one hundred years ago, by dissolving prussian blue in caustic potash and concentrating the solution. Prussian blue and allied salts had been known for fifty years before Macquer's time. Since then endless patents have been taken out for its manufacture and improvement, of which may be mentioned those of Baumé, Gentèle, Naumann, Kuhlmann, Spence, Laming, Krafft, Swindell, and Bramwell. Nearly all these have been abandoned or not carried at all to a successful issue. For full details, the reader is referred to books of scientific research and the patent records.

The process of manufacture, as usually carried on, consists in the mutual decomposition of nitrogenous animal matter, an alkali, usually carbonate of potassium, and iron. The first part of the process is devoted to the fusion, or calcining, of the raw materials. Many forms of apparatus have been devised for the purpose. That set forth in Fig. 205 is perhaps the one in commonest use. A cast-iron vessel, shaped like an egg, with a narrow neck, is built into a brickwork furnace, resting upon the neck at the one end and a strong projecting knob at the other. It is also secured by a pair of cross-wise arms near the mouth, which run up into the brickwork. Heat is applied from underneath, only a small passage round the pot being left. The products of combustion finally pass off to the chimney through a hole just above the neck, at the end *opposite* to the fireplace. Another form of pot is cylindrical in shape, about 2 ft. in diameter and 2 ft. 6 in. deep. A series of such pots is arranged over suitable furnaces and through the cover of each passes a vertical shaft with revolving arms or blades upon it to agitate the contents of the pot and assist in the decomposition. In France, the apparatus employed resembles an ordinary gas retort. On the Continent, it is usual to carbonize the nitrogenous matter before mixing it with the potassium salt, for which purpose a variety of stills are used. In this way, a great part of the nuisance arising from the evil odours which escape when the raw materials are mixed and stirred up with the potash, is prevented. The animal matter is exposed to a low red heat, until the escape pipe from the still or retort begins to cool down. The gases which escape are ignited. The products of such previous distillation are about as follows:—

205



Animal charcoal	75 parts
Liquid, containing carbonate of ammonia	125 "
Animal oil	40 "
Loss	10 "

the original charge being 250 parts.

The process adopted in this country is somewhat rougher, no previous carbonization of the animal matter being effected. A charge of good commercial potassium carbonate, usually about 80 lb., is fused in a pot of the description set forth above. A varying quantity of animal matter, dependent upon the quality and constitution, is then introduced, together with a certain amount of iron clippings or borings, and the whole thoroughly stirred up, the heat being kept at low redness. It is not absolutely necessary to add the metal, as the iron of the pot will yield a sufficient quantity, but it is preferable to do so. The animal matter should be carefully introduced in small quantities at a time, so as to effect thorough decomposition, the stirring going on the whole time. Something like 100 lb. of nitrogenous material will be required by 80 lb. of potassium carbonate, but the charge, of course, varies with the percentage of nitrogen, and requires careful judgment. Dried blood, feathers, hoofs and horns are about the best material, containing from 14 to 17 per cent. of nitrogen. Wool and hair form a very fair material, with about 12 per cent. of nitrogen. Leather parings are often used, but only contain about 8 per cent. An excess of animal matter has to be added, because an enormous loss of nitrogen is sustained by evolution in the free state and by the formation of ammonia. In this part of the process, the organic matter is decomposed. The carbonate of potassium is reduced by the carbon to potassium, while another portion of carbon seizes upon the nitrogen to form cyanogen (CN) which promptly constitutes cyanide of potassium with the alkaline metal. Towards the end of the process, when a smell of ammonia is perceived, the pot should be tightly closed up and the fire urged away. After about two hours the mouth, or lid, is opened and the mixture, now of a thick pasty consistence, stirred up. If no tongues of flame make their appearance, the calcination is complete. The contents of the pot are then shovelled out and allowed to cool and harden into what is technically called "metal" or "prussiate cake." In place of potassium carbonate in this calcining operation, it has been proposed to use sulphate of potassium with small coal, or sulphide of potassium in an already reduced state. Besides protecting the pot from too rapid corrosion the addition of a little metallic iron greatly facilitates the process. The following are some recipes for charging:—

	100	parts	dried blood,
	30	„	potassium carbonate,
	3	„	iron scales, or borings;
or,	100	„	horn,
	34	„	potassium carbonate,
	3	„	iron;

or,	100	parts	leather,
	47	„	potassium carbonate,
	3	„	iron;
or,	130	„	fresh mixed animal matter,
	70	„	fresh potassium carbonate,
	130	„	"return," or recovered, alkali,
	40	„	animal charcoal,
	12	„	iron.

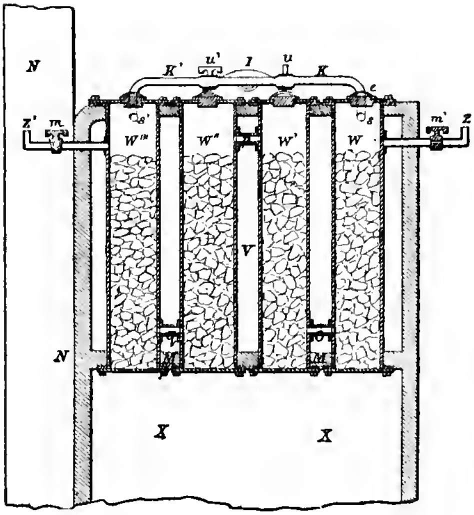
Prussiate cake of good quality will contain about 10 per cent. of cyanide of potassium, 4 per cent. of sulphocyanide, 3 per cent. of cyanate, 3 per cent. of sulphate, 57 per cent. of carbonate, 22 per cent. of silica and insoluble matter, together with traces of charcoal, lime salts, &c.

The "metal" or "prussiate cake" is broken up when cooled into small pieces, thrown into vats, and lixiviated with water, or weak liquor from previous operations. Sometimes the pieces are digested with cold water first, and the heat is gradually raised; sometimes the water, or liquor, is run on at once, hot. After lixiviation, the whole is allowed to settle, and the clear supernatant liquor drawn off by a leaden pipe, run into an evaporating pan, concentrated about 10°, and run into crystallizing cones. Here a first crop of impure crystals, a mixture of prussiate and chloride of potassium, separates out. These are removed, drained, redissolved in hot water, concentrated up to 1·27, and again crystallized. Prussiate of potash now separates in large and nearly pure crystals.

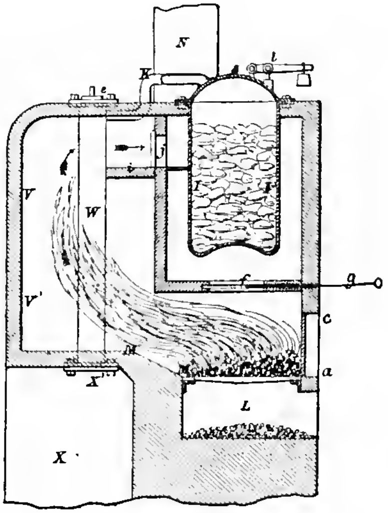
To make the best crystals, the solution of the first crop should be filtered through cloth after concentration. The crystallizing vessels should be set in not too cold a place, or surrounded with mats, &c., to prevent too rapid deposit of the crystals. The mother liquors are either used to lixiviate fresh cake or, when not too full of impurities, are concentrated to 1·35 specific gravity, and crystallized. A somewhat impure ferrocyanide is thereby obtained which may be purified by recrystallization. The mother liquors, when they are too impure to yield these secondary crystals, are evaporated and calcined, yielding a product termed "blue salts," or "return alkali." This contains up to 70 per cent. of carbonate of potassium, with various other salts and insoluble matter, and is used in the melting and calcining operation, along with fresh salt.

It is unnecessary to enter into details of the great variety of patents that have been from time to time taken out in connection with the manufacture of ferrocyanide. A great number of materials have been proposed as subjects of treatment—gas-lime, guano, coal, &c. Two patents, or improvements of the process just described, deserve mention. The first is Berry's, for the formation of cyanogen from animal matter, and is set forth in Figs. 206 to 209. He proposed to break coke or charcoal into pieces about the size of a walnut and to dissolve the potash salt in water, or, preferably, urine, and the iron in nitric or acetic acid. The whole of these materials are thoroughly mixed together until they form a thick paste, dried, and pulverized. They are then put into a series of iron pipes or retorts, similar to those used in the manufacture of coal gas, only placed vertically. The animal matter—dried blood, &c.—is placed in a separate compartment, but connected with the retorts mentioned. In Fig. 208, A B C D is a horizontal section of the whole furnace, in which are placed four elliptical pipes, about 6 ft. long and 18 in. in diameter. The arch given to the furnace serves to drive the heat back upon the pipes W, W, W, W. The fire-bars, or grates, are shown at *a b c d*, Fig. 208. I I, Fig. 207, is the retort, placed in a separate compartment. K K′ is a pipe connecting the retort with the elliptical pipes. In Fig. 206 is shown the pipe K K′, connecting the retort with the elliptical pipes. This connecting tube enters (Fig. 206) at S into the pipe W, and at S′ into the pipe W‴. In Fig. 209, the tube K K′, with its cocks *u* and *u′*, is shown in detail, C being a safety valve to prevent any accident arising from a possible obstruction of gases in the pipes. S is the cover of the retort, L the ash-pit, *a* and *c* the door of the furnace. The arrows indicate the direction of the current of heat, which passes off from the pipes through *j*. The pipes must be thoroughly heated before any fire is introduced to the retort, then the decomposition of the gases may be readily accomplished. The smoke finally escapes to the chimney *f*, *g* being an opening to expose the retort to the direct action of the heat. In Fig. 206 are shown the junctions connecting the four pipes with their gas burners Z Z through the cocks *m m*. *r r′ r″ r‴* are covers closing the pipes with holes in them, and stoppers *c c′ c″ c‴*. In this way, the current of the gases can be changed, and the otherwise necessary stirring up of the contents of the pipes avoided. About half through the process the cocks *u m′* should be closed, and *u′ m* opened. The gases then pass into the branch K′ and enter W‴, then through *g* into W, through *p* into *u*, O and W, finally escaping by the burner Z. By this regulation of the cocks *u m′* and *u′ m* the current can be reversed at will. It is advisable, however, to have holes in the pipes so arranged that the contents can be loosened if any obstruction occurs. The inflammable gases evolved by the decomposition show by the colour of the flame at the burners how the operation is progressing. When the jet becomes small and clear, with a pinkish colour, the reaction is complete. The animal matter is thoroughly carbonized, and the nitrogen, ammonia and other gases acting upon the mixture in the pipes have formed ferrocyanide of potassium of the quality known as prussiate cake, which is lixiviated and treated in the usual way.

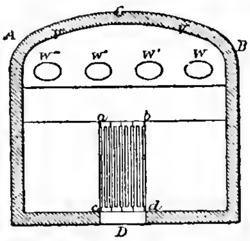
206.



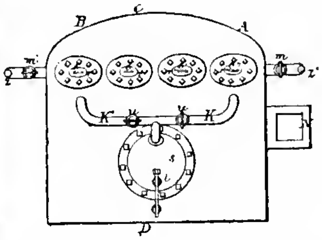
207.



208.

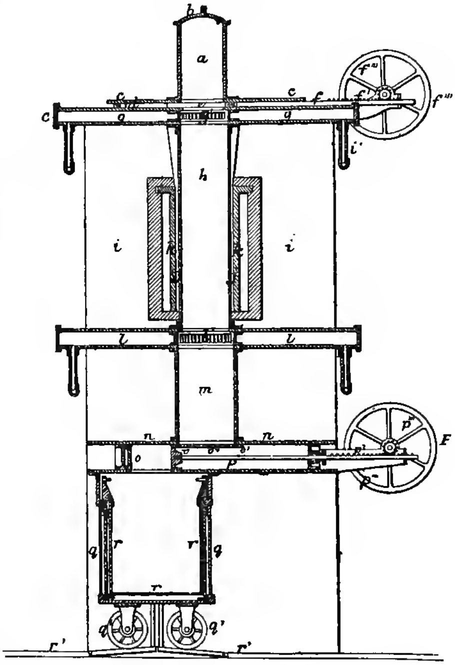


209.



Schinz's improved apparatus for effecting the decomposition of the materials and formation of ferrocyanide, without contact with the air, is shown in Figs. 210 to 213. At the upper part is a feeding cylinder *a*, of iron, fitted with a close cover *b*, and supported on an iron base-plate *c*. This plate has a circular hole in it corresponding with the interior of the cylinder. Beneath is placed an iron frame *d*, in which moves a slide *e*, Fig. 211. This slide also has a circular opening *e′*, which may be brought under, or withdrawn from the hole in the base-plate by means of a rod *f*, worked by a rack *f′*, a pinion *f″*, and wheel *f‴*. Beneath the iron frame is a flue *g*, which communicates, by means of a circular grate g', with a vertical retort h, placed immediately below. This grate g' is movable, in order that it may be cleaned when requisite. The furnace is placed below the flue g, from whence issue two gas-pipes i' i', beyond the walls i i of the furnace. The retort h is a sheet-iron tube, and it is surrounded by sand, &c., placed in the space j, to allow of contraction and expansion. The fireplace, at the lower part of the retort, has a cylinder of fire-clay k interposed between it and the sand. The retort has a second flue l, with a circular grate l', also furnished with two gas-pipes. This flue communicates, through the grate l', with a vertical cylinder m, placed immediately beneath the retort h, but larger in diameter. Into this descend the materials when cooled, and as it is air-tight they are preserved from the action of the atmosphere. The cylinder is supported by a rectangular box n, in which moves a flanged cylindrical slide o, furnished with a plate o', and so worked by a rod, rack, pinion and handwheel, p, p', p'', p''', that it can open or close a passage into the receiver q. This receiver runs upon wheels q' q'', and has a flanged top which fits tightly against the slide-box n. In it is a sieve of iron wire r, which can be removed when full and replaced when empty.

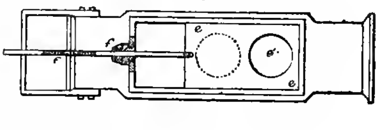
210.



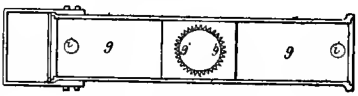
The feeder is filled with small pieces of coke, or charcoal, mixed with dry pearl-ash and iron borings or nails. The cover being replaced, the first slide e is removed, and the contents of the feeder drop into the retort h. Here they meet with the nitrogenous gases which are introduced by the gas-pipes, and steady decomposition takes place. After passing through and acting upon the alkaline materials, the waste gases issue through the lower grate and flue into any suitable exit. When the operation has proceeded long enough to saturate the volatilized potassium with cyanogen, the slide o is moved under the retort, and a portion of the produce falls into it. The slide is then forced forward and the contents fall into the receiver q, and an equal quantity of fresh material is introduced from the feeder. The process is thus continuous.

These methods present many advantages. A considerable saving of fuel and manual labour is effected; volatilization of potassium and potash compounds is prevented, thereby largely increasing the yield, and economizing the nitrogenous material. Finally, by cooling in an air-tight compartment the combustion of cyanogen into cyanic acid is rendered impossible. A modified form of Schinz's apparatus may be used for distilling or carbonizing the animal matter.

211.



212.



213.

Commercial prussiate may be rendered chemically pure by causing the crystals to effloresce in a stove, fusing them at a gentle heat in a glass retort, dissolving the fused mass in water, adding a little acetic acid, then precipitating the ferro-prussiate with alcohol, and twice crystallizing.

Ferrocyanide of potassium is used to a considerable extent in the production of the ferricyanide ("red prussiate") and cyanide. It also enters into the manufacture of Berlin blue and other pigments. Its principal uses are, however, in dyeing and calico printing, in the production of various shades of blue and to form prussiate of tin ("tin pulp") for steam blues. It is the production of the ferrocyanide that is chiefly valuable in these dyeing and printing processes; the salt is decomposed by an acid and the iron turned into prussian blue by combination with another portion of the same salt. Tin pulp, used largely in steam blueing, is made by mixing muriate of tin and yellow prussiate together and allowing the "pulp" to settle out. The evolution of prussic acid in manipulation of all steam blues should be guarded against.

Iodide of Potassium. Formula, KI.—Beyond some use as a drug, this substance is of slight importance, though exceedingly interesting in its reactions and characteristics. It is prepared (1) by adding iodine to a strong solution of caustic potash, free from all traces of carbonate. The iodine dissolves freely, the solution containing both iodide and iodate of potassium. Upon evaporation and ignition at a low red heat, the iodate is decomposed, yielding iodide and free oxygen. The mass is then dissolved in water, filtered, and crystallized. (2) Iodine (2 parts), water (10 parts), iron filings (1 part), or scraps of zinc, are digested together in a warm place. The resulting iodide of iron or zinc is filtered or decanted off, and boiled. A solution of pure carbonate of potash is added until all effervescence ceases, and a slight precipitate makes its appearance, iodide of potassium and carbonate of protoxide of iron being formed. The iodide is separated by filtration and evaporated. Upon cooling, the iodide crystallizes out. (3) Iodide of lime or barium is decomposed by sulphate of potassium, yielding insoluble sulphate of baryta and iodide of potassium in solution. To prepare the iodide of barium, 1 part of amorphous phosphorus is added to 40 parts of warm water, and 20 parts of dry iodine are gradually stirred in. If the mixture be coloured, it is heated upon a water-bath until perfectly clear, and allowed to settle. The clear supernatant liquid is then decanted off, and neutralized with a slight excess, first, of carbonate of barium, and then with baryta water. Insoluble phosphate of barium forms, and is filtered off, the filtrate consisting of pure iodide of barium.

This substance usually occurs in cubic crystals, occasionally in octahedra. The crystals are often opaque; they are anhydrous, melt at a low red heat, and volatilize completely at a higher temperature. Iodide of potassium, while not deliquescent, is very soluble in water, and in dissolving produces a considerable fall of temperature. It dissolves in 0·735 parts of water at 12·5°, 0·709 parts at 16°, 0·7 parts at 18°, and 0·5 parts at 120°. It is also soluble in alcohol; in 5·5 parts of specific gravity 0·85 at 12·5°, and in 40 parts of absolute alcohol at 13·5°. When heated, the alcohol dissolves a larger amount, the iodide separating again in needle-shaped crystals upon cooling. A saturated water solution boils at 120°. The deep-brown colour of an ordinary solution, owing to the presence of free iodine, is well known.

Nitrate of Potassium. (Fr., *Nitrate de Potasse;* Ger., *Salpetersaüres Kali*, or *Kalisalpeter.*) Formula, KNO_3.—The knowledge of this important salt has in all probability been a theory of gradual growth from very ancient times. The old alchemists named it "*sal nitre*" to distinguish it from "*nitrum*," the name by which soda was known before the term "*natron*" was introduced. Geber speaks of it as "*sal petræ*," this designation evidently having its origin in the fact that the salt was obtained by grinding and lixiviating certain rocks. "*Sal petrosum*" is mentioned in a Latin work of the seventh or eighth century. Agricola in his 'De Re Metallica' describes the refining of saltpetre by boiling the crude product of the washing of certain earths with quicklime and wood-ashes, lixiviating the liquors, concentrating, and crystallizing.

Nitrate of potassium occurs in considerable quantities in nature, in spring and river water, in the juices of certain plants—the sunflower, common borage, tobacco, &c.—but more widely as a constituent of the soil, in many porous rocks, and as a product of the continual process known as "nitrification." Lemery first discovered the salt as a constituent of the juice of plants in 1717, and it has since then been established that many species—especially the amaranthus—contain considerable proportions of it.

The process of nitrification is even yet but imperfectly understood. The simplest explanation seems to be that wherever organic substances containing nitrogen are exposed to the action of air ammonia is formed, and when an alkali—soda, potash, or lime—is present, a nitrate of the particular metal is produced by slow oxidation. Any circumstance that favours putrefaction assists nitrification; hence a warm damp atmosphere—15° to 20°. Hence, too, the productiveness of tropical climates, where decaying organic matters yield a constant supply of ammonia. The best known natural deposits, or "beds," of saltpetre are those of South America, India, Persia, Spain, and Hungary. Here the salts, formed in the natural manner described, carried down into the soil by the agency of rain, dew, &c., and rising again to the surface in the form of solution, are evaporated by the sun and air, and spread over the surface of the ground as a dirty white efflorescence. "Saltpetre earth" of this description will test about as follows:—

Nitrate of potassium ..	8·3 per cent.	Carbonate of calcium ..	35·0 per cent.
" calcium	3·7 "	Water	12·0 "
Sulphate of lime	0·8 "	Insoluble matter	40·0 "
Chloride of sodium	0·2 "		

Other saltpetre deposits, with a somewhat different origin, are found in caverns and places where animals and birds congregate, and in the shape of excrement provide an unfailing supply of organic matter. The caves of Ceylon, Kentucky, Teneriffe, upon the coast of the Adriatic and on the Missouri river are well known. A remarkable instance of rock deposit is found in the cave of Memoora, where the nitrate occurs in veins. The rock has been analysed as follows:—

Nitrate of potassium ..	2·4 per cent.	Carbonate of calcium ..	26·5 per cent.
„ magnesia	0·7 „	Water	9·4 „
Sulphate of magnesia ..	0·2 „	Residue (quartz, mica, talc)	60·8 „

Nitrate of potash is dimorphous. It crystallizes in long hexagonal prisms and in rhombohedra. The crystals are anhydrous. They are white and inodorous, with a strong saline taste, and are neither deliquescent nor hygroscopic. Below a red heat, at 339°, nitrate of potassium melts to a colourless liquid with a specific gravity of 2·1. Upon cooling, the fused salt forms an opaque white mass, usually known as "*sal prunelle.*" At a red heat, the salt is decomposed, yielding up oxygen, and finally nitrogen, and passing first into nitrite and then into protoxide and peroxide of potassium. Fused with carbon, sulphur, phosphorus, and other combustible substances, saltpetre deflagrates, liberating oxygen. In this way gold, silver, and even platinum undergo oxidation. Its use as a constituent of gunpowder and other explosives is due to this potency as an oxidizing agent. It is very soluble in hot, but only slightly soluble in cold, water, as the following table shows:—

Temperature.	Nitrate Dissolved per 100 parts Water.	Temperature.	Nitrate Dissolved per 100 parts Water.
°		°	
0	13·32	45·10	74·66
5·01	16·72	54·72	97·05
11·67	22·23	65·45	125·42
17·91	29·31	79·72	169·27
24·94	38·40	97·66	236·45
35·13	54·82	114·0	327·4

The proportions of nitrate contained in solutions of various densities are as follows:—

Specific Gravity.	Nitrate.	Specific Gravity.	Nitrate.	Specific Gravity.	Nitrate.
	per cent.		per cent.		per cent.
1·0058	1	1·0555	9	1·1097	17
1·0118	2	1·0621	10	1·1169	18
1·0178	3	1·0686	11	1·1242	19
1·0239	4	1·0752	12	1·1316	20
1·0299	5	1·0819	13	1·1390	21
1·0362	6	1·0889	14	1·1464	22
1·0425	7	1·0956	15	1·1538	23
1·0490	8	1·1026	16	1·1613	24

Nitrate of potash may be obtained by adding nitric acid to a solution of pure carbonate or hydrate of potassium in very slight excess and crystallizing from the concentrated liquor. Or by crystallization from a concentrated solution of chloride or carbonate of potassium with nitrate of sodium. Upon a large scale, two processes are followed:—(1) Saltpetre earths are lixiviated, and the solutions concentrated and crystallized. These saltpetre earths are (*a*) of natural formation; (*b*) artificially prepared. (2) By mixing chloride of potassium and nitrate of sodium, thus:—

$$KCl + NaCO_3 = KNO_3 + NaCl.$$

The nitrate crystallizes out from the concentrated solution, chloride of sodium being left. Very often carbonate of potassium is substituted for the chloride in this latter process.

The best known and esteemed crude saltpetre is of Indian manufacture. In many parts of the country the gathering and treatment of the saltpetre earths by "sora wallahs" (sora = nitre) is a considerable industry. From all possible sources—natural beds, or the products of drains, stables, walls, &c., wherever the process of nitrification has gone on—the earth is gathered up and piled in wooden boxes, or "kieves." Here it is lixiviated with successive washings of water, the resulting liquors being drawn off into rude earthenware or stoneware vessels, and allowed to concentrate by the action of the sun and air, or, after a more civilized fashion, run into iron pans, concentrated by an underneath fire and drawn off into crystallizing cones. During washing, the mass is kept as open as possible. The liquors usually contain about 14 per cent. of nitrate of potassium. The "sora wallah" has his regular round, visiting the same deposits year after year. The first crop of crystals that is obtained is exceedingly impure, containing sulphate of potassium and chlorides of potassium and sodium. They are dissolved in the smallest possible amount of hot water, and the solution is cooled and allowed to crystallize. The well-known "Indian" or "Bengal" saltpetre then separates out, an article of very fair purity.

The Indian saltpetre earth is, as a rule, rich in nitrate of potassium. When this is not the case, or when the solution after lixiviation contains large quantities of the nitrates of calcium, magnesium, sodium, and alkaline chlorides, treatment with carbonate of potassium is adopted, in order to convert all the nitrates present into nitrate of potassium. By this operation, the earthy nitrates yield their nitric acid to the potash of the wood-ashes; carbonates are precipitated, and the clear lye, now rich in nitrate of potassium, is drawn off, evaporated, and crystallized. Treatment with wood-ashes has always to be resorted to when manipulating the rocky nitrate deposits from caves.

It has been noted that "saltpetre earth" may be produced by artificial means—*grown* in fact. Owing its origin to the abnormal demand for saltpetre consequent upon the discovery of gunpowder, this industry has now become, in several countries of Europe, an important one, more particularly in France, Germany, Switzerland, and Sweden. In the last-named country, saltpetre forms one of the revenue taxes, and its preparation is therefore all but obligatory. A mass of earthy matter, with certain bases, lime, &c., is heaped up and exposed to the action of the air, being kept as open as possible by loose twigs or stones, &c. The heaps are moistened from time to time, all descriptions of animal matter and organic refuse being added (urine is especially rich in nitrogen), and a periodical turning over of the whole is carefully practised. This process usually goes on for about three years, long before which time a white efflorescence makes its appearance. It is usually arranged that certain portions of the heaps become "ripe" every year, so that the process may be continuous. The saltpetre earth is considered ready for lixiviation when 1000 cubic inches yield about 5 oz. of salt. To bring the nitrate to the surface as much as possible before removing it, the heaps that are considered ripe are left to themselves for some time before it is intended to lixiviate. In this way, the nitrate formation, undisturbed by fresh additions of liquid matter, rise and form a coat two or three inches thick. This is removed and treated in the same manner as the natural saltpetre earths already described. Sometimes the earth is massed in the form of walls, with nearly perpendicular sides, the liquid manure being poured down one side, and the saltpetre drawn by capillarity to the other, whence it is readily removed from time to time. By this means a certain amount of labour is saved, the walls being left almost intact, but a smaller result is obtained as the liquors have to be constantly reapplied. The heaps are generally formed about 6 ft. in height and 15 ft. in length. Upon the best "plantations," rude sheds are erected over them, that the amount of moisture may be carefully regulated. The sides of the sheds should be open, but protected from the wind and weather by rough palisading, or hurdles.

Although the treatment of artificial saltpetre earths is similar to the Indian process, the former is of course carried on in Europe with much more care and judgment as a rule. The most important point is to separate the nitrate of potash as promptly as possible from the chloride of sodium and other salts. For this purpose, the amount of water should be carefully regulated. In concentrating the lye, the different degrees of solubility of the various salts contained must be taken in consideration.

In its crude state, saltpetre is unfit for the manufacture of gunpowder and nitric acid, the presence of the chlorides of potassium and sodium being particularly objectionable. It has therefore to be subjected to a further refining process, which depends partly upon the different rates of solubility of the various salts at different temperatures, partly upon the mechanical action of animal gelatin upon the extractive matters contained, and partly upon the fact that crystals of saltpetre being homogeneous (that is, consisting of one salt alone), separate out without contamination from the solution containing the chlorides of potassium and sodium. The crude article is dissolved in boiling water, the salt being added to saturation and the heat gradually increased. A density of 1·5 or 1·6 should be attained. Small quantities of dissolved glue are introduced into the boiling solution, which separate out the various extractive matters. These partly rise to the surface, and form a scum which is removed from time to time, and possibly sink to the bottom of the pan. Sometimes the hot solution is further diluted with water to prevent the depositing of crystals of saltpetre, and allow time for the insoluble matters to separate out. The liquors are then run off into flat copper crystallizing pans, and while cooling are kept thoroughly stirred up with wooden rakes to prevent the formation of large crystals, which are apt to contain appreciable quantities of the mother liquors in their interstices, and yield when pulverized a damp powder. The fine needles which are obtained, having the appearance of a white powder, are termed "*saltpetre flour*." This is fished out and thrown upon a wire-gauze strainer placed across the crystallizing pan, to drain, the mother liquor falling back into the pan. The saltpetre flour is almost pure, the mother liquors containing the chlorides and returning them into the pan. The flour is then removed to the wash-pans and treated with cold water, or a saturated solution of pure saltpetre. The wash-pans are usually about 10 ft. long, 4 ft. wide, and 3 ft. deep, fitted with a false bottom upon which the flour is placed. When thoroughly washed, and freed from all adhering mother liquor, it is dried at a gentle heat and sifted to separate out the lumps. The mother liquors are evaporated, a sufficient quantity of potash salt is added to decompose the nitrates of the earths contained, and worked over again as crude lye from the saltpetre earths.

A very large proportion of the commercial saltpetre which is refined in this country is made artificially, by the mutual decomposition of nitrate of sodium ("chili saltpetre") and chloride of potassium. The process originated with F. C. Hills about the year 1846, and has since been improved by Anthon, Kuhlmann, and others. The reaction is exceedingly simple and direct:—

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

Chloride of potassium usually contains about 8 per cent. of chloride of sodium, but, as will be apparent from the above equation, the presence of this substance is of very slight importance, as one of the products is chloride of sodium. The exact composition of the materials, however, must be ascertained beforehand, that the proper proportions may be used. The nitrate usually contains from 95 to 97 per cent. of nitrate of sodium; therefore quantities of both materials in slight excess of the equivalent proportions must be taken. The chloride of potassium is dissolved in water with the aid of steam, the solution standing at about 1·25. The nitrate of soda is then added, and the whole well agitated. The heat is kept up to boiling point by an underneath fire, or coil of pipes; and as the decomposition proceeds, the chloride of sodium that forms and settles is fished out and placed upon iron drainers ranged alongside of the pans, that the mother liquors may run back into the solution. Evaporation is continued until a density of about 1·7 is attained. The liquors are then run off into a series of settlers, and left for a short time. When perfectly clear, they are transferred to crystallizing pans, where large crystals of nitrate separate out. These are somewhat impure, containing varying quantities of chlorides and other salts. They are accordingly taken off, dissolved in hot water, the solution concentrated up to 1·6, and recrystallized. The product is now of very fair purity—about equal to East Indian "petre"—and is refined by the process already described. The chloride of sodium left upon the drainers is removed to washing-pans, and digested with successive portions of hot water. The chloride being only slightly soluble, the saltpetre is thus entirely removed—or as nearly so as possible. The washed salt is then gently dried. Though not well suited for decomposition with sulphuric acid in the Le Blanc soda process on account of its irregular and non-crystalline form, this article is sufficiently good for all agricultural, fish-curing, and other purposes of a similar character.

The washings from the chloride and the mother liquors are mixed together, concentrated, and used, so long as they are fairly pure, in the place of water for dissolving purposes. The constitution of these liquors varies of course very much with the material used, the chloride of potassium especially being of uncertain character. Often a considerable amount of iodine is contained in them, which may be recovered. If the potassium chloride contains an appreciable amount of chloride of magnesium, it is cleared by adding a small quantity of soda ash to the solution. Sometimes crude carbonate of potassium is employed in place of the chloride, but the latter forms the cheaper material.

The saltpetre industry is a very important one, about 35,000 tons per annum being manufactured in this country and imported from other quarters. Of this quantity about 16,000 tons are produced artificially. The plant, as a rule, is of comparatively rough description, although new and better mechanical contrivances are now superseding the old methods. One of these consists of a complete apparatus for dissolving and agitating the first solutions, and forcing the liquors through a strainer, which retains the chloride of sodium and other impurities, and allows the cleared liquor to pass to the crystallizers. By agitating the cooling solution, too, and thereby preventing the formation of large crystals, the nitrate may be obtained in a condition approaching the "saltpetre flour" of the refining process, and in a sufficiently good state for most purposes without any after-purification.

The chief use of saltpetre is in the manufacture of explosives, fully five-sixths of the total consumption being applied to this purpose (see Explosive Agents). Minor uses are found in the curing of meat and fish, and in the preparation of certain diuretic medicines.

A detailed statement of the various methods of estimation belongs rather to scientific research than to a work like the present. For the guidance of manufacturers, however, it may be stated that the best method is that of Abel and Bloxam, a modification of Gay-Lussac's charcoal process. Twenty grains of the sample to be valued are weighed off and mixed with 30 grains of powdered resin in a platinum crucible. Eighty grains of chloride of sodium are added and the whole ignited gently until no more vapour comes off. After cooling a little, 25 grains of chlorate of potassium are added, heat is again applied, and gradually increased to redness, so as thoroughly to decompose the chlorate and fuse the whole mixture. It is then removed, dissolved in hot water, filtered, and washed. A drop or two of litmus solution is added to the solution and the amount of alkali, the carbonate of potassium formed in presence of an excess of carbonaceous matter, determined in the ordinary way with a standard solution of sulphuric acid. The original amount of nitrate is then readily calculated.

A rough method depends upon the observation of the temperature at which crystals are deposited from the solution of a sample. Forty parts of the saltpetre are dissolved in 100 parts of water at 55°, and the exact point when nitrate crystallizes out is noted. The determination of nitrate present is then read off by the following table:—

Crystallizing Points of various Solutions.

Degrees Centigrade.	Percentage of pure Saltpetre in Solution.	Percentage of pure Saltpetre in Sample.	Degrees Centigrade.	Percentage of pure Saltpetre in Solution.	Percentage of pure Saltpetre in Sample.
10·0	22·23	55·7	17·8	30·00	75·0
10·3	22·53	56·3	18·1	30·36	75·9
10·6	22·80	57·0	18·4	30·73	76·8
10·9	23·08	57·7	18·7	31·09	77·7
11·2	23·36	58·4	19·1	31·46	78·6
11·6	23·64	59·1	19·4	31·83	79·6
11·9	23·92	59·8	19·7	32·21	80·5
12·2	24·21	60·5	20·0	32·59	81·5
12·5	24·51	61·3	20·3	32·97	82·1
12·8	24·81	62·0	20·6	33·36	83·4
13·1	25·12	62·8	20·9	33·75	84·1
13·4	25·41	63·5	21·2	34·15	85·4
13·7	25·71	64·3	21·6	34·55	86·4
14·1	26·02	65·0	21·9	34·90	87·4
14·4	26·32	65·8	22·2	35·38	88·4
14·7	26·64	66·6	22·5	35·81	89·5
15·0	26·96	67·4	22·8	36·25	90·6
15·3	27·28	68·2	23·1	36·70	91·7
15·6	27·61	69·0	23·4	37·15	92·9
15·9	27·94	69·8	23·7	37·61	94·0
16·2	28·27	70·7	24·1	38·01	95·2
16·6	28·61	71·5	24·4	38·55	96·4
16·9	28·95	72·4	24·7	39·03	97·6
17·2	29·30	73·2	25·0	39·51	98·8
17·5	29·65	74·1	25·3	40·0	100·0

It is usual to apply to all methods of estimation the term "refraction." Conveying an entirely incorrect description of the ordinary analysis, the name is founded upon an old method proposed by Schwartz, based upon the appearance of the surface of the fused salt when fractured. Pure nitrate is coarsely radiate; when chloride of sodium is present the structure becomes less distinct, and with 3½ per cent. of the impurity disappears altogether, except at the edges.

Oxalates of Potassium. Formula, $K_2C_2O_4$.—The neutral salt crystallizes in transparent rhombic prisms containing one atom of water of crystallization, which become opaque and anhydrous at 150°. It is obtained by dissolving carbonate of potassium in oxalic acid to saturation, concentrating and finally evaporating the solution.

Potassium oxalate is used to some considerable extent in dyeing and printing, as a mild form of oxalic acid. It serves as a discharge, is employed in some steam colours to form oxalate of alumina, and occasionally as a mordant.

The *binoxalate*, KHC_2O_4, H_2O, forms colourless rhombic prisms, of a sour taste. This substance is often called "salt of sorrel," from its entering into the constitution of the plant. It also occurs in the *Rumex* and *Oxalis acetosella* and in garden rhubarb. It is soluble in about 40 parts of cold and 6 parts of boiling water. Under the name of "salts of lemon" it is largely sold to remove ink and iron stains.

The binoxalate is produced by dissolving oxalic acid in hot water, dividing the solution in two parts, saturating the one half with potassium carbonate and pouring in the other.

Silicate of Potassium. (Fr., *Silicate de Potasse;* Ger., *Kieselsaures Kali.*) Formula, K_2O, $4SiO_2$.—This salt forms a peculiar, transparent glass, with a slight green tinge due to the presence of iron. It is slowly soluble in water, forming an alkaline liquid possessed of cleansing properties, and decomposable by nearly all acids with liberation of silicic acid. It is usually manufactured by fusing 45 parts of sand, 3 of charcoal, and 30 of potassium carbonate in an ordinary reverberatory furnace. The carbon dioxide of the carbonate is reduced to oxide by the charcoal and finally driven off. A liquid silicate is made by heating the solid "glass" in powder with superheated steam in a close vessel. A thick fluid, specific gravity about 1·3, is formed, to which is often added silicate of soda solution.

On account of their cleansing properties, the silicates are used for mixing with soaps. For this purpose the mixed silicates of sodium and potassium are, however, chiefly employed.

Sulphate of Potassium. (Fr., *Sulfate de Potasse;* Ger., *Schwefelsaures Kali.*) Formula, K_2SO_4.—This salt occurs in nature in considerable quantities, in various minerals, and in the ashes of both marine and land plants. In the Stassfurth and Kalutz mines it is found in combination with sulphate and chloride of magnesium, forming the mineral *kainit.*

Sulphate of potassium forms hard, colourless, anhydrous crystals, insoluble altogether in alcohol and soluble in about 10 parts of water. The solubility increases slightly with an increase of temperature. Thus 100 parts of water dissolve:—

At	12·5° ..	10	parts of sulphate.	At	56·25°	22	parts of sulphate.
„	15 ..	10·38	„ „	„	68·75	22	„ „
„	31·25 ..	14	„ „	„	87·50	25	„ „
„	37·5 ..	17	„ „	„	100	26	„ „
„	50 ..	25	„ „				

The following table (Gerlach) gives the percentage of sulphate in aqueous solutions of different densities at 15°:—

Per Cent.	Specific Gravity.	Per Cent.	Specific Gravity.
1	1·00820	6	1·04947
2	1·01635	7	1·05790
3	1·02450	8	1·06644
4	1·03277	9	1·07499
5	1·04105		

Sulphate of potassium has a bitter, saline taste, and is neutral to test paper. The crystals decrepitate when suddenly heated, owing to the presence of a small quantity of mother liquor.

The usual method of manufacture is to decompose chloride of potassium with sulphuric acid, the process being almost exactly similar to the Le Blanc sulphate of soda process, to which further and detailed reference will be made hereafter. It may be mentioned that the decomposition of the potassium chloride, on account of the smallness and irregularity of the grain, requires the aid of mechanical contrivances even more than common salt. Large quantities of sulphate of potassium are also made from kelp, and as a bye-product in the treatment of beet-root molasses for carbonate of potash. The product of the kelp liquors is a peculiar, pasty substance which has to be dissolved in hot water, concentrated to about 48° Tw., and crystallized in order to get a useful article.

Plate sulphate is a term often applied to this article. The sulphate manufactured from molasses and "suint" is a much purer salt; so also is the product of the decomposition of chloride of potassium by sulphuric acid. The following table gives the composition of average samples:—

	Sulphate from Chloride.	Sulphate from Molasses, &c.
Sulphate of potassium	92·00	93·00
Chloride „	1·00	5·00
Sulphate of sodium	2·00	..
Chloride „	0·05	..
Sulphate of calcium	0·75	trace
„ magnesium	0·50	trace
„ iron	1·00	..
Sulphuric acid	1·50	..
Insoluble	0·50	1·00
Water	0·50	·50
	99·80	99·50

The beet-root sulphate usually contains also traces of the carbonates of potassium and sodium. It is, however, a very good article as a rule; about 2000 tons per annum are produced by this method upon the Continent.

Sulphate of potassium is employed in the production of carbonate by a process analogous to the

Le Blanc soda process, and enters into the manufacture of certain kinds of glass and alum. It is also used to a considerable extent as a manure.

Bisulphate of Potassium. (Fr., *Bisulfate de Potasse ;* Ger., *Zweifach Schwefelsaures Kali.*) Formula, $KHSO_4$.—This salt when pure crystallizes in flattened rhombic prisms, soluble in twice their weight of water at 15°, and less than half that amount at 100°. The solution has a strong acid reaction and taste. The crystals fuse at 197°, and at about 600° lose half their sulphuric acid.

Bisulphate of potassium is usually prepared by heating the neutral sulphate with sulphuric acid, in the proportions of about 87 parts of the salt with 49 parts of acid. It is necessary, however, as a rule, to have the acid in excess. It is also prepared largely as a bye-product in the decomposition of nitre by sulphuric acid—in the preparation of nitric acid, &c. It is used for cleansing metals, as a chemical reagent, and in calico printing and dyeing. For the latter purposes, it is only used for lower styles of work, as a substitute for tartaric acid. Its application requires care, as the fibre of the cloth is apt to be damaged by freed sulphuric acid.

Tartrate of Potassium.—The neutral salt is of slight importance. It crystallizes in right rhombic prisms, which are permanent in the air and have a strong saline taste. Tartrate of potassium is obtained by neutralizing cream of tartar with chalk or potassium carbonate. It is very soluble in water.

The bitartrate, or acid tartrate (Fr., *Tartrate acide de Potasse ;* Ger., *Saures Weinsaures Kali*, or *Weinstein*), is a substance of very considerable importance. It is commonly known as cream of tartar, or, in the crude state, "argol," and exists in the juice of the grape, tamarind, pine-apple, and many other fruits (see Argol). It forms small, hard, colourless, prismatic crystals of irregular grouping, with a strong acid taste and reaction, especially in solution. Exposed to heat in a close vessel it is decomposed with evolution of inflammable gas, leaving a mixture of finely divided charcoal and potassium carbonate. This residue has already been mentioned when speaking of the preparation of potassium carbonate. It is known as "black flux."

To refine the crude article and produce the commercial cream of tartar, the argol is dissolved in hot water and crystallized, the operation being repeated until a pure product is obtained. It is usual to employ a little pipeclay and animal charcoal or albumen to remove the colouring matter.

Cream of tartar and the crude tartar are both largely used in the manufacture of tartaric acid. The finer qualities form esteemed reagents in dyeing and printing operations, though, on the score of expense, their use is not as great as in former times. As a mild substitute for tartaric acid, cream of tartar forms a discharge on dipped blues and turkey reds, and is used in steam colours for blues and greens. In conjunction with alum and the salts of tin, it is employed to some small extent in mordanting, but it is in all these processes a very mild agent. It acts probably in two ways; (1), as a corrective of bad, hard waters, with regard both to lime and iron; (2), as a mild acidifying agent, enabling the fibre, especially woollen stuffs, to take the colour well. For inferior work, sulphuric and arsenic acids, and bisulphate of potash, have to a great extent superseded tartaric acid and cream of tartar, but where economy is not of the first importance, the finer sorts of bitartrate hold their own as a safe reagent.

Rochelle salt is a tartrate of potassium and sodium, forming large clear prismatic crystals, with a mild saline taste. They effloresce slightly in the air and dissolve in 1½ parts of water. The usual method of preparation is to saturate a hot solution of cream of tartar with carbonate of soda and evaporate to a thin syrup, from which the salt crystallizes out. It enters into certain medicinal preparations, forming a well-known purgative.

J. L.

Soda.—This term is applied scientifically only to the oxides of the metal sodium, but practically it covers several other sodium compounds, more particularly the hydrate and carbonates. Three oxides are known, the suboxide, monoxide, and dioxide. Of the suboxide little is known. The monoxide and dioxide are both formed when metallic sodium is heated in dry air or oxygen gas. The former may be prepared pure by heating sodium hydrate with sodium; thus:—

$$NaHO + Na = Na_2O + H.$$

It is a greyish-coloured substance, melting at low red heat, and undergoing volatilization at a higher temperature. Its specific gravity is 2·80. The dioxide is pure white, turning yellow when heated. It is not decomposed by heat, but is very unstable in the air. It absorbs moisture and carbon dioxide, and becomes converted into carbonate. Neither of the oxides are of any considerable importance in manufacturing or industrial operations.

Carbonate of Sodium. (Fr., *Soude, Carbonate de Soude;* Ger., *Soda, Kohlensaures Natron.*) Formula, Na_2CO_3.—This important salt exists in nature, but to no very great extent. A mineral, the sesquicarbonate, is found in several localities, notably in Egypt and South America, going by the names of *trona*, or *latroni*, and *urao.* It forms an incrustation half an inch or so in thickness, and probably results from the evaporation of mineral waters. Egyptian soda has about the following composition:—

Sodium carbonate	60·0	Water	7·0
„ sulphate	16·0	Insoluble	2·0
„ chloride	15·0		

Other varieties, with widely different constituents and properties, are found in India, Hungary, Mexico, &c. These soda earths are usually treated in similar fashion to the saltpetre earths, of which mention has been made when speaking of potash and its salts. A hard crystalline mineral, *Gay-Lussite*, is also known with the following composition:—

Sodium carbonate	34·5	Water	30·4
Calcium „	33·6	Insoluble	1·5

Formerly soda was largely obtained from the ashes of marine plants, or plants in the neighbourhood of saline springs, by calcination. The product has been known as "barilla," "varec," or "vraick," "kelp," &c. Some saline plants, the ashes of which yield carbonate of soda freely, are:—

Salsola clavifolia	giving 45·99 per cent.	*Salsola kali*	giving 34·00 per cent.
Salsola soda	„ 40·95 „	*Salsola brachiata*	„ 26·26 „
Halimocnemum capsicum	„ 36·75 „		

The *Salsola soda* is especially esteemed as yielding a good product, and the cultivation and treatment of this and other species is still an important industry in Spain, France, and other countries. The well-known *Narbonne soda* is the product of the *Salicornia annua*, and contains 15 per cent. of carbonate. Many of the marine and saline plants are of course chiefly valuable for the potash salts and iodine which they yield. Of carbonate of soda they contain down to 2 per cent. and as high as 40. The preparation is of the roughest character, very little in the way of purification being attempted. For a description of the process usually employed, the reader is referred to the article upon Potash—more particularly to that portion of it treating of "*Kelp-salt.*"

Many processes for the artificial production of soda have been from time to time proposed, but nothing of any importance was done until about the close of the eighteenth century, when Scheele, Guyton, Carey, and Hodgson worked out various methods for the decomposition of common salt by caustic lime, by lead oxide, by alum, and felspar. Of these, the oxide of lead process was worked for long by Losh, at Walker-upon-Tyne, more especially for the sake of the pigment known as "Turner's yellow," which was obtained. The use of sulphuric acid was first proposed by Higgings in 1781, who, after decomposing the salt, reduced the sulphate of soda formed to sulphide, by fusing it with coal, and, decomposing the sulphide by iron or lead, formed caustic soda and sulphide of lead, &c. The process known as Le Blanc's was patented in France in the year 1792, in response to an invitation from the French Government to the chemists of the day to provide a substitute for the barilla soda when the supply of that article was cut off by the wars with Spain. Of thirteen processes proposed, that of Le Blanc was selected. It consisted in the decomposition of salt by sulphuric acid, the conversion of the sulphate of soda formed into carbonate of soda and (roughly speaking) sulphate of lime, by means of carbonate of lime or chalk and coal, and the lixiviation and preparation of the soluble carbonate. The first establishment for carrying out the process on a large scale was set up in 1804, at St. Denis, by Le Blanc and his partners, Dizé and Shée, but was by no means a success, the proprietors eventually being forced to appeal for English aid in order to enable them to prosecute their enterprise. In this country the process was not adopted until the close of the French war, when Losh, in conjunction with Lord Dundonald, established the first works at Walker-upon-Tyne. The alkali trade, however, was of exceedingly small importance until the repeal of the salt-tax, in the year 1823, sufficiently reduced the cost of the staple raw material to enable the products to become of wide application in the industrial life of the world. The introduction of pyrites in place of the Sicilian sulphur, as a source of sulphuric acid, gave a second great impetus to the trade about twenty years ago.

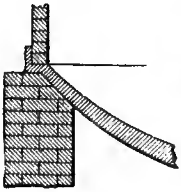
At the present time nearly the whole of the carbonate of soda of commerce, in various forms, is manufactured by Le Blanc's process, which has undergone, for such an intricate method, remarkably little modification.

The first part of the process consists in the manufacture of sulphate of soda, or "salt cake," from common salt and sulphuric acid, inasmuch as it is cheaper for the alkali-maker to produce his own material than to buy it. Some reference has already been made to this process when treating of hydrochloric acid, but it will probably be found useful to give further details here. The action of sulphuric acid upon chloride of sodium is extremely simple; thus:—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The salt most highly esteemed for the process is that obtained from the Cheshire or Worcestershire brine. It is both pure and cheap, containing about 95 per cent. of chloride, and very slight impurities except water—which averages about 4 per cent. The brine salt, moreover, is in fairly-sized and regular crystals, a formation which renders it peculiarly adapted to the decomposing process. Other kinds of salt have been often tried, notably the German rock, which can be imported at about 2*s.* per ton less cost than the Cheshire article. The grinding of the rock salt, however, causes considerable admixture of fine material, which is apt to cake on the bottom of the pan, and cause it to become overheated at that particular spot, and crack. Moreover, there is always an appreciable amount of calcium sulphate in rock salt, which goes through into the sodium sulphate and deteriorates the quality. Too much stress cannot be laid upon the importance of caring for the "life" of a decomposing pan, as the operation of replacing a broken one is both a great nuisance and a great expense. The sulphuric acid employed is ordinary "chamber" acid, preferably at about 135° Tw., and as hot as possible. Formerly it was necessary to heat and concentrate the acid in what was called an "evaporating pan," or "concentrating pan," but thanks to the introduction of Glover's towers, a sufficient supply of strong and hot acid is always available without any special means of preparation.

214.



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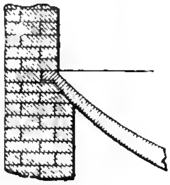

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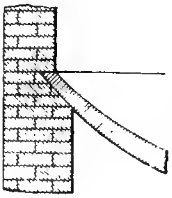

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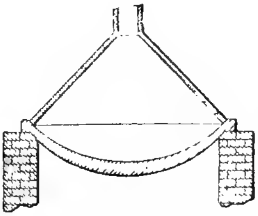

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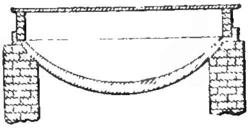
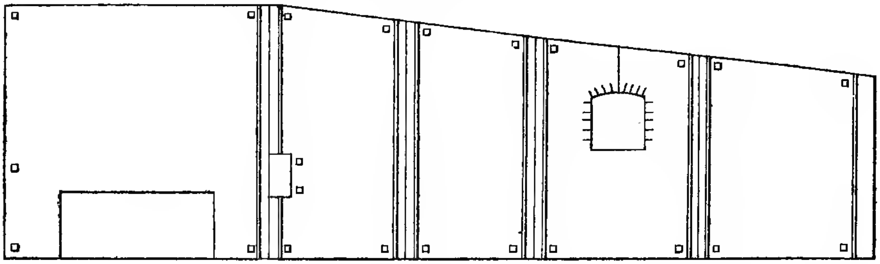


The process of decomposition has been sufficiently set forth in the article upon hydrochloric acid. The salt and acid are mixed in the "pan," thoroughly stirred up, and boiled for about forty minutes. The mixture, of a pasty consistency, and composed partly of sulphate and partly of bisulphate of soda, is then pushed over into the "drier" or "roaster," and subjected to further careful manipulation and furnacing, whereby the whole of the soda is obtained in the form of sulphate, and the remaining portions of hydrochloric acid gas driven off.

Details of apparatus in common use, and different from those already described under Hydrochloric Acid, are given in Figs. 214 to 233. It may be premised that the original sulphate furnace was built entirely of brickwork, and consisted of only one bed. When it was found that no brickwork would resist the wear and tear of the process and the ravages of acid substances, a lead lining was introduced, and this was employed until about thirty years ago, when metal pans and separate furnaces were introduced. In all probability, the pan now in common use will have, in its turn, to give way to some such mechanical contrivance as that of Messrs. Jones and Walsh. In Figs. 214 to 218 are shown five different pan settings. In Fig. 214 the edge of the pan is flanged and brought outside the brickwork arch, that any boiling over may be at once seen and rendered harmless. This method of setting originated with the alkali inspectors, who found considerable escapes of gas from the irruption of the contents of the pan into the underneath flues. It is also safer for the pan; but the small brick arch rendered necessary is difficult to keep in repair, and the necessity for its removal makes the replacing of the pan needlessly expensive and tedious. Figs. 215 and 216 show two methods of seating the pan in the brickwork. Figs. 217 and 218 show two forms of *iron* covers.

adapted to the exigencies of pans set with the rim visible, and intended to obviate the evils of this style of setting, already pointed out. The expense entailed by the wear and tear of these iron covers, however, need not be enlarged upon. Fig. 219 gives the elevation of a single-bedded furnace, an old style of finishing apparatus, but capable of turning out thoroughly good sulphate, if the batch be not too large. In Figs. 220, 221, and 222, the elevation, longitudinal section, and plan of an improved single-bedded arrangement are given. The pan has a furnace upon each side of it, the charge being pushed alternately into each. In this way, every batch of sulphate has about two hours allotted to

219.



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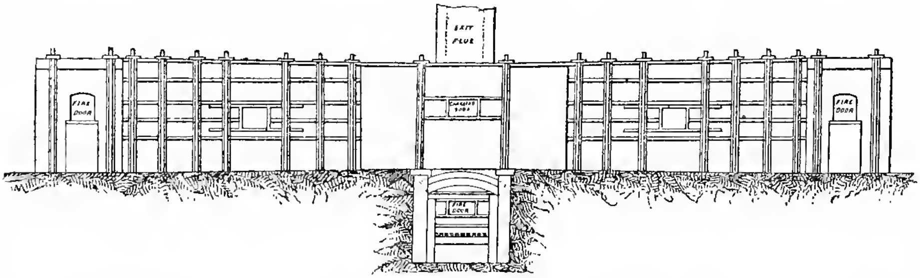

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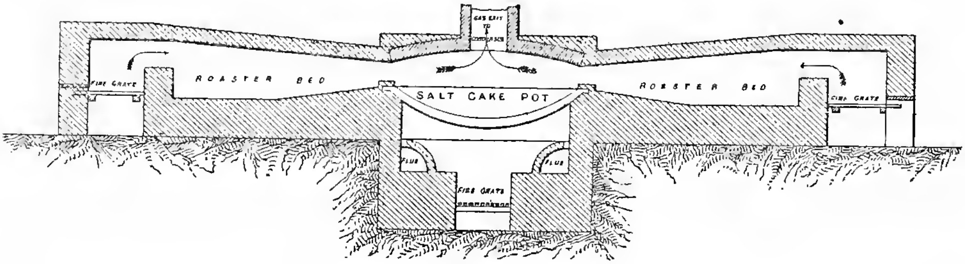

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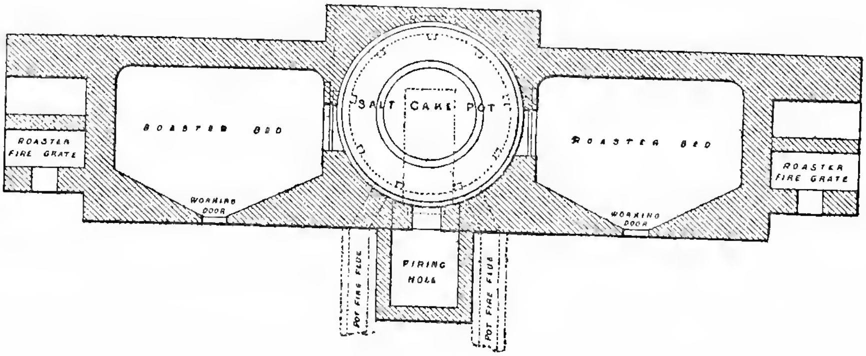
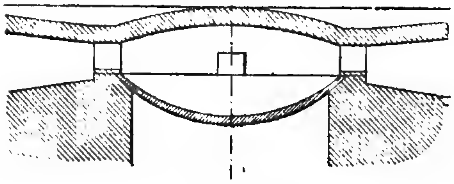
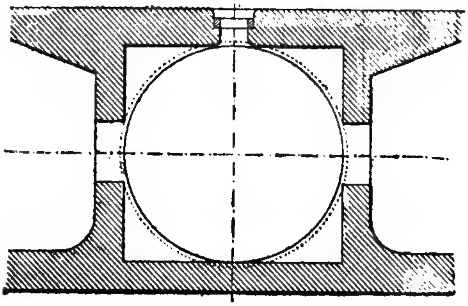


its finishing, and with a moderate expenditure of fuel can be "brought down" exceedingly fine, an operation that every manufacturer and intelligent consumer of sulphate knows the importance of. In Figs. 223 to 226 are shown different methods of setting a pan with two roasters. In Figs. 223 and 224, the rim is bedded solid in the brickwork; in Figs. 225 and 226, it is brought into sight all round.

223.





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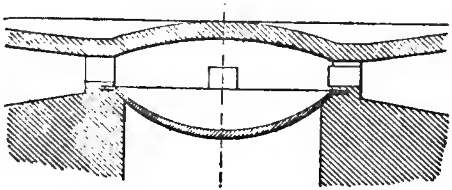
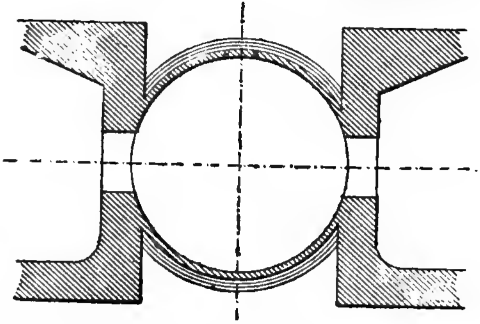
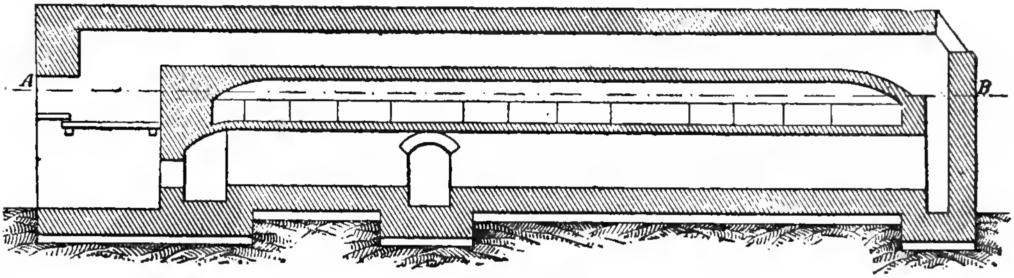




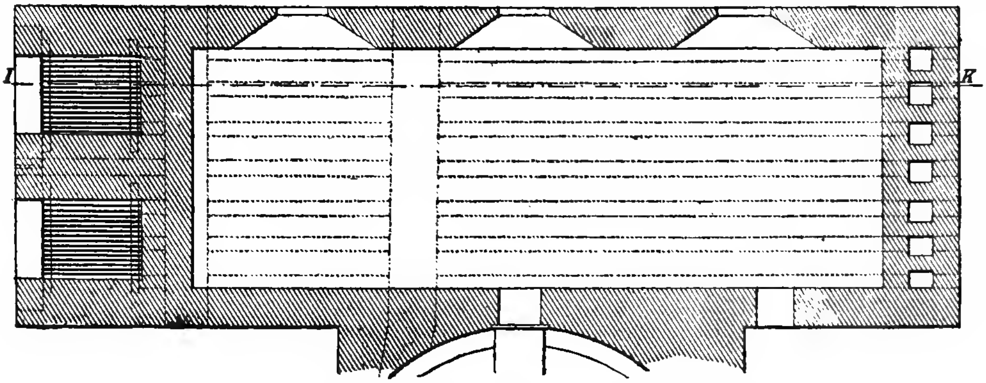
226.

The furnaces set forth hitherto have been all "open"; i.e., the flame acts directly upon the batch, and the products of combustion go with the hydrochloric acid gas into the condenser. To lessen this evil, coke may be used instead of coal, but is of course more expensive. In Figs. 227

227.

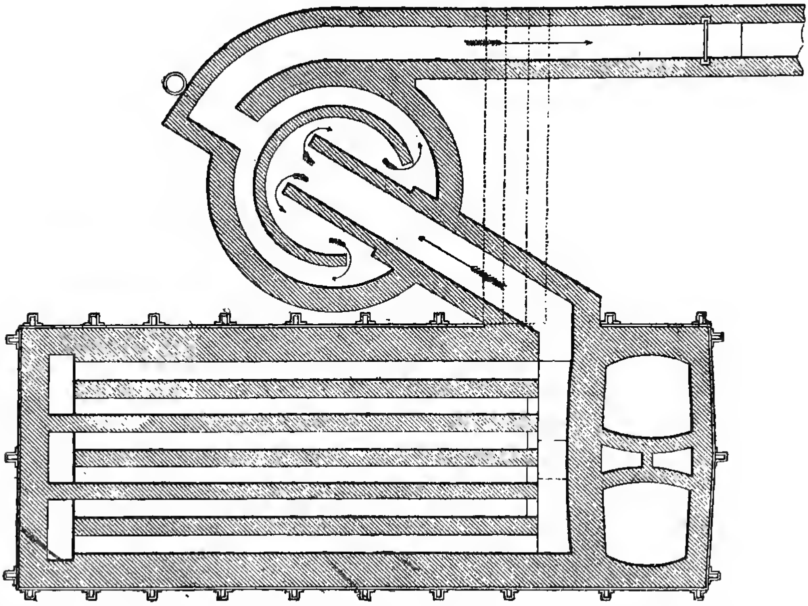


228.

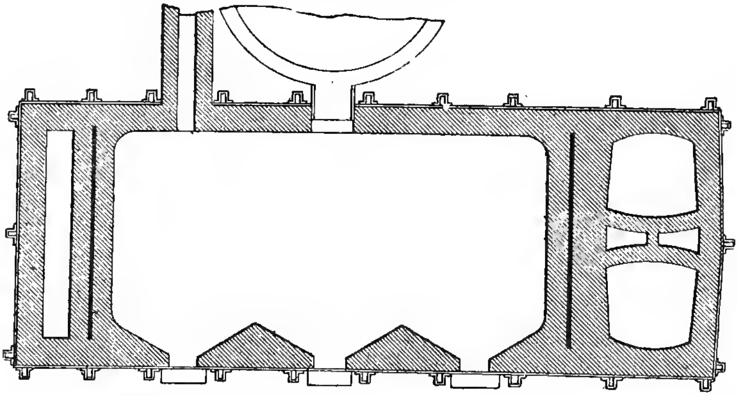


and 228, are given the sectional elevation and plan of the "close" roaster commonly used in Lancashire and most other centres of the trade, except the Tyne. It will be noted that here the heat and products of combustion pass over and under the furnace, never coming into actual contact with the materials. Two great evils attend this construction of furnace :—(1), the greater draught being in the smoke flue, there is constant liability to lose gas from leakage; (2), the sulphate, as a rule, is only imperfectly fired. From the first of these evils arises not only loss of gas, but damage to the surrounding vegetation, &c. To obviate this tendency to leakage, the late Mr. Deacon proposed the plan set forth in Figs. 229 to 232. The fireplace is built, as will be noticed, several feet below the sole of the furnace, and from this difference of level there is always a heated column of air and gases over the fire-bars; in fact, a chimney is interposed between the flues around the furnace and the fire. By this means the necessity for a great draught is avoided, the gases and products of combustion being actually checked while passing round the furnace, and, if escaping at all, finding their way into the interior of the muffle. At any rate all tendency on the part of the hydrochloric acid gas to leak into the flues is effectually prevented. A bye-flue leads the products of combustion direct to the chimney, instead of underneath the pan, whenever required, when the latter is empty or too hot. The draught of the chimney should be carefully regulated by a small damper, but the connections should be of large size, and the final stalk should have as *regular*

229.



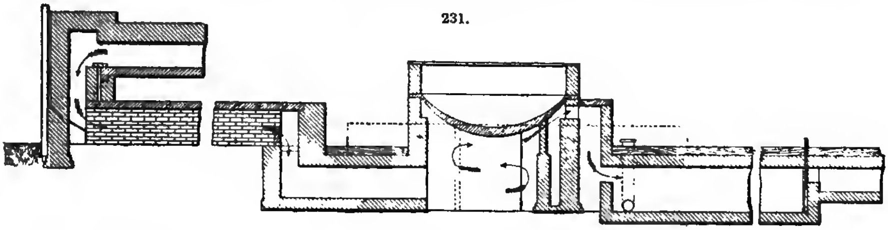
230.



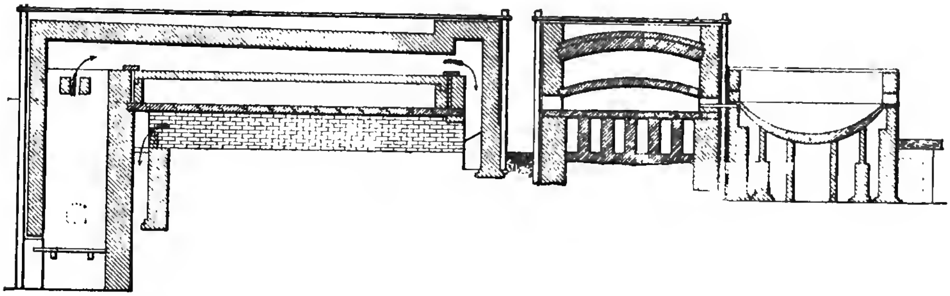
a draught as possible. This regulation of draught, so as to give sufficient power over the materials in the furnace, and turn out thoroughly fired sulphate, is the difficulty met with in working an exceedingly ingenious furnace.

It will be noticed that the roaster is sometimes fired from the end and sometimes from the side. The former is the better plan of the two, as giving a more regular heat over the sole, and admitting of better manipulation. A thoroughly good arrangement is shown in Fig. 233, two small fireplaces being arranged at the end of the furnace. Fig. 234 gives the end plates in section, with flanged joint and binder "runners."

231.



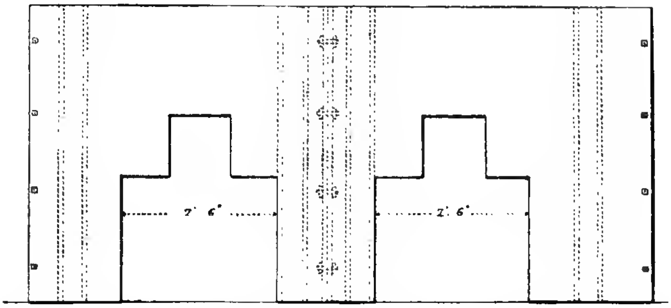
232.



A sectional elevation of pan, roaster, and condensing apparatus is given in Fig. 235. The connection between the furnace and its condenser should be of course much longer than is represented in the drawing, to allow the gases to cool before they enter the tower.

The weight of salt constituting a batch varies very much, depending chiefly upon the size and construction of the roaster. A good charge for a single-bedded furnace is 6½ cwt. per hour; when a large double-bedded roaster is used, the weight of salt may go to 10 or even 12 cwt. per hour. A batch of the latter size is however likely to be badly decomposed and worked. The manipulation of the pan is one of the most delicate operations in an alkali works, requiring not only great strength but judgment and long experience. The men at the furnace, on the other hand, can be readily trained to their work.

233.



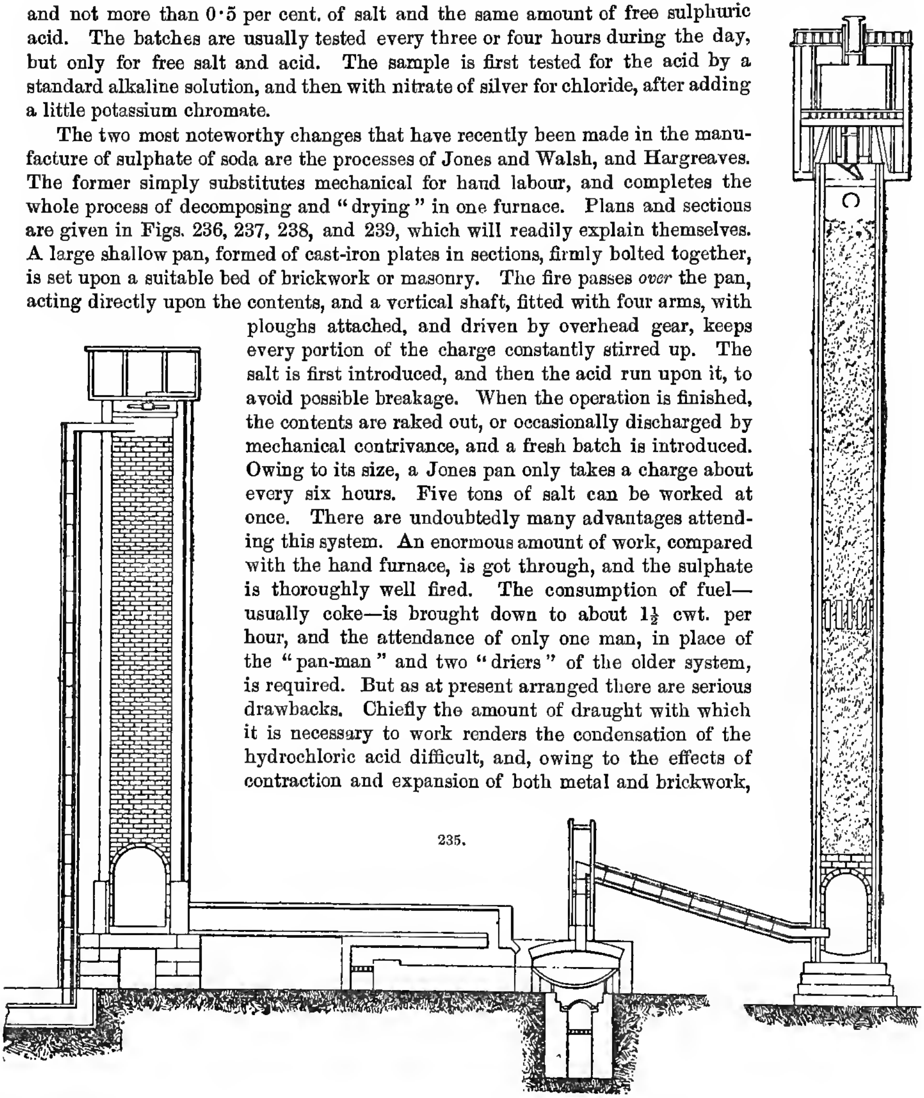
234.

Good sulphate should come out of the furnace red hot, and present when cool a bright canary colour, with no shade of green upon it. The lumps when broken should show no centres of undecomposed salt. Upon an average, about 112 parts of sulphate are obtained from 100 parts of salt, the rate of charging being usually one batch per hour. The work is continued, of course, day and night, the fires only being drawn at the week's end. The following is about the composition of an average English salt cake:—

Sodium sulphate	96·00	Sodium chloride	1·20
Calcium ,, ...	0·90	Free sulphuric acid	·80
Magnesium ,, ...	0·25	Insoluble matter	·25
Iron and alumina	0·25		99·65

A careful manufacturer, however, will keep the amounts of both sodium chloride and free acid below those set down. The best hand-made salt cake should test 97 per cent. of sulphate of soda, and not more than 0·5 per cent. of salt and the same amount of free sulphuric acid. The batches are usually tested every three or four hours during the day, but only for free salt and acid. The sample is first tested for the acid by a standard alkaline solution, and then with nitrate of silver for chloride, after adding a little potassium chromate.

The two most noteworthy changes that have recently been made in the manufacture of sulphate of soda are the processes of Jones and Walsh, and Hargreaves. The former simply substitutes mechanical for hand labour, and completes the whole process of decomposing and "drying" in one furnace. Plans and sections are given in Figs. 236, 237, 238, and 239, which will readily explain themselves. A large shallow pan, formed of cast-iron plates in sections, firmly bolted together, is set upon a suitable bed of brickwork or masonry. The fire passes *over* the pan, acting directly upon the contents, and a vertical shaft, fitted with four arms, with ploughs attached, and driven by overhead gear, keeps every portion of the charge constantly stirred up. The salt is first introduced, and then the acid run upon it, to avoid possible breakage. When the operation is finished, the contents are raked out, or occasionally discharged by mechanical contrivance, and a fresh batch is introduced. Owing to its size, a Jones pan only takes a charge about every six hours. Five tons of salt can be worked at once. There are undoubtedly many advantages attending this system. An enormous amount of work, compared with the hand furnace, is got through, and the sulphate is thoroughly well fired. The consumption of fuel—usually coke—is brought down to about 1½ cwt. per hour, and the attendance of only one man, in place of the "pan-man" and two "driers" of the older system, is required. But as at present arranged there are serious drawbacks. Chiefly the amount of draught with which it is necessary to work renders the condensation of the hydrochloric acid difficult, and, owing to the effects of contraction and expansion of both metal and brickwork, the pan is difficult to keep tight and in good repair. Still, the Jones furnace is the best mechanical contrivance that has yet appeared, and probably, with some modifications, is destined to supersede the old hand furnaces; unless, indeed, some such new process as the "Hargreaves' revolutionizes the whole operation of sulphate manufacture.



235.

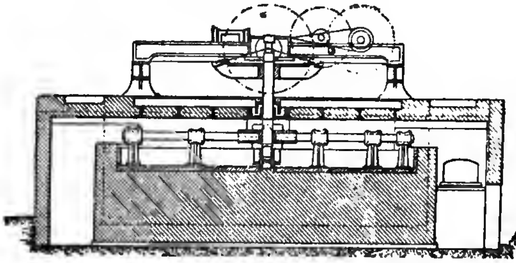
The process of Messrs. Hargreaves and Robinson aims at no mere modification of the present plan, but proposes to produce sulphate of soda by the direct action of sulphurous acid, oxygen (from the air), and steam, upon chloride of sodium. The idea is not altogether a new one, Longmaid having proposed, twenty-five years ago, to roast salt and pyrites in a reverberatory furnace, and obtain sulphate of sodium, oxide of iron, and chlorine,

$$4FeS_2 + 16NaCl + 19O_2 = 2Fe_2O_3 + 8Na_2SO_4 + 8Cl_2,$$

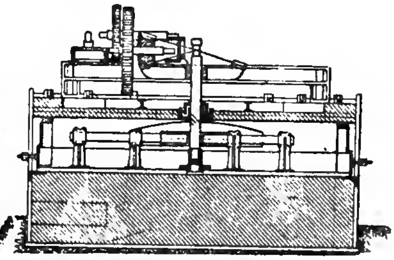
but his process was never successfully carried out. The reaction in the Hargreaves process is as follows, requiring a temperature of from 370° to 480° (700° to 900 F.);—

$$2NaCl + SO_2 + O + H_2O = Na_2SO_4 + 2HCl.$$

236.

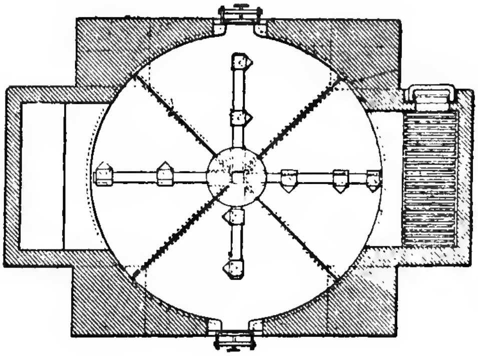


237.

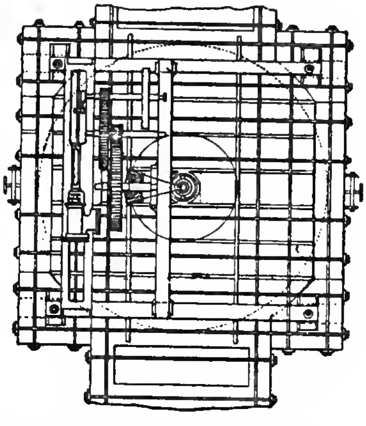


Two advantages are at once apparent:—no nitrate of sodium is necessary to effect the conversion of the sulphurous into sulphuric acid, and an inferior description of salt can be used. The form of apparatus employed is given in Figs. 240, 241, and 242. The salt is first prepared by being moistened with steam. It is then spread upon a suitable floor heated with underneath flues, dried, and broken up into small lumps, the fine being returned to the steaming-box. A better method of preparing these lumps has lately been introduced. It consists in spreading the steamed salt upon a series of iron plates set close together, and travelling upon endless chains over a flue inclined at an angle of 35° or so. As each plate, or flap, reaches the upper end it falls over, and the mass of caked salt falls upon a prepared floor, and shivers into fragments. In this way, comparatively little "smalls" is made. When prepared, the salt is charged into a series of huge iron cylinders, about 12 ft. high and 15 ft. in diameter—see A^1 A^2 A^3, &c., in Fig. 240. In these cylinders it lies upon a series of movable grids or bars, as H, Fig. 241. It is usual to have eight such cylinders, arranged in two rows, with a space between for flues and working the charges. The cylinders are connected with huge iron arms or siphons D, working upon pulleys fixed in the roof, with a flue C, conveying the sulphurous acid, &c., from the pyrites burners, and with each other by the circulating pipes E. The sulphate when finished is withdrawn by the door B, the grids H being knocked away from the tripods upon which they stand. The gas leaves the cylinders by an opening in the bottom of the drawing doorway, and passes into the flue G, from whence it is withdrawn by a Roots blower, or other suitable exhausting apparatus. Fig. 242 shows the brickwork foundation upon which the cylinders stand. The flues are covered over upon the top by a layer of ashes to keep in the heat, the burners being also constructed to prevent, as far as possible, loss of heat by radiation. The cylinders are heated, as may be required by fireplaces at the foot of each, the products of com-

238.

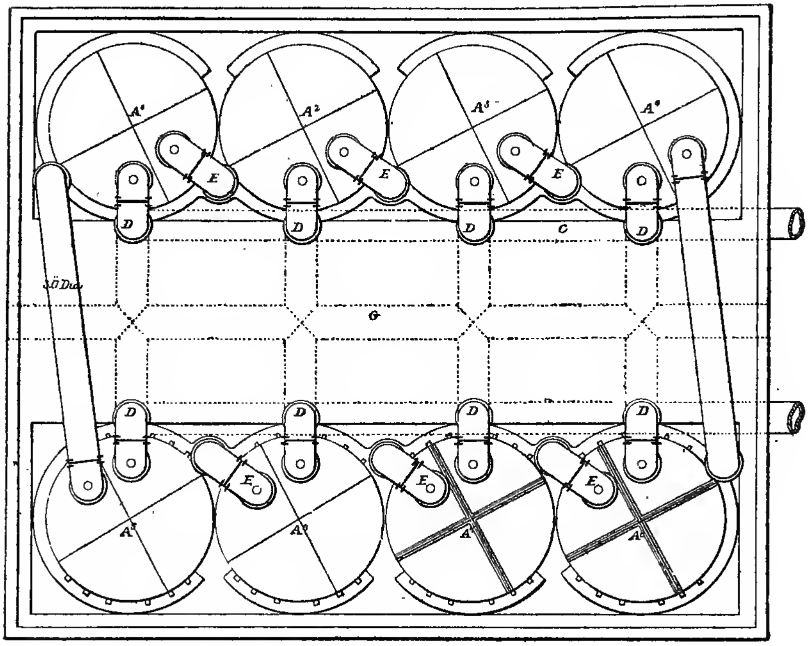


239.



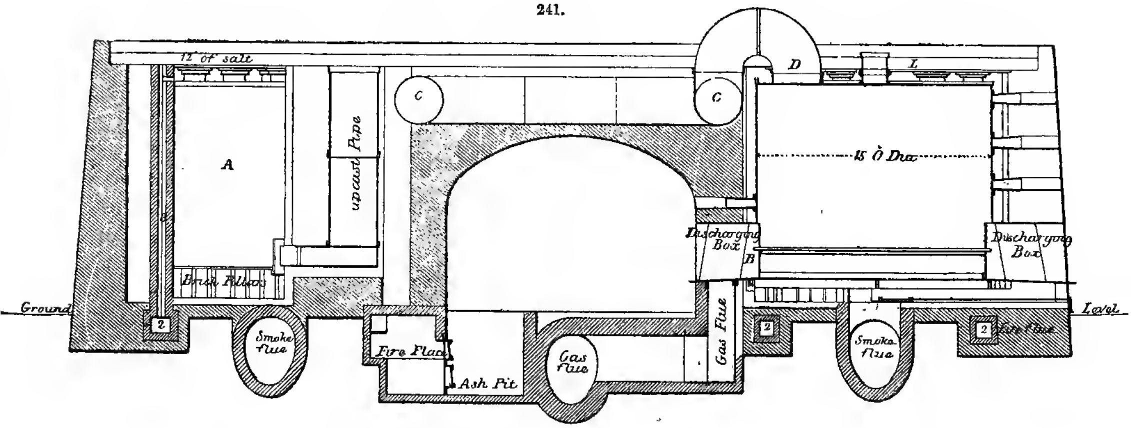
bustion passing up the small flues which will be noticed at the side of the cylinders, Fig. 240. These flues are only just of sufficient size to prevent choking. The heat is also sometimes admitted into a space some 10 in. high, left between the cylinder covers and a second covering plate, passing down the opposite side of the cylinder, and finally issuing to the chimney. The cylinders are so arranged that each one can become in turn the first, the last, and an intermediate one. The gases are admitted first into the cylinder whose contents are most nearly converted into sulphate, and pass from that through the intermediate cylinders, until they act upon the cylinder just filled with freshly prepared salt. When a cylinder is finished it is detached from the circle, emptied, recharged, and then becomes the last of the series.

240.



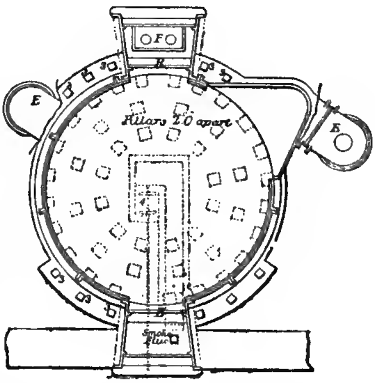
Although this process is beautifully self-acting, it requires most careful construction and watching. The heat must be well got up before the gas from the burners is admitted, and never allowed to fall below 750°. The contraction and expansion of the cylinders must be carefully guarded against, and the whole plant erected in as faultless and solid a manner as possible. Occasionally, the salt gets choked in the cylinder, and has to be entirely emptied out and worked

241.



over again at a great expense, or sold as half-finished sulphate. The management of draught by efficient aspirating apparatus is not so difficult a matter as might at first appear, and the sulphate produced when the process is carefully worked, is of most excellent quality, free from iron, and testing 98 per cent. of sulphate. The production and condensation of hydrochloric acid is equal to, and as easily managed as, the product of the hand furnaces, and the amount of fuel used is only about 8 cwt. per ton of sulphate. Upon the score of plant expense, there is nothing to choose between the "Hargreaves" and the old process, but the sulphate from the former process can undoubtedly be made at a reduced cost of 5*s*. per ton—35*s*. against 40*s*.

242.



The process of Messrs. Cammack and Walker, a revolving cylinder and continuous supply of salt and sulphuric acid, has already been noticed. Together with several other new devices, such as those of Mease (revolving pan), and Black, and Hill, it has not yet been placed upon a really working footing.

The second operation of the Le Blanc process consists of calcining the sulphate of sodium with chalk and small coal, producing the impure carbonate of soda known as "black ash," or "ball soda." It has already been shown what constitutes a good sulphate — freedom from uncombined salt and acid, and a good canary colour. The presence of reddish lumps, while showing, indeed, that the sulphate has been well fired, indicates also the presence of a considerable amount of free salt. The salt cake is then, technically, "weak." Two varieties of carbonate of lime are used, chalk and limestone. The former is the material chiefly used in the Tyne district, for the hand ball furnaces; the latter in Lancashire. The best chalk comes from the neighbourhood of London, Northfleet, Greenhithe, &c., and costs about 2*s*. 6*d*. per ton delivered to the works as block chalk. "Smalls" cost about 1*s*. 6*d*. per ton. The small cost results from the custom for small coasting vessels to take it in as ballast upon their return journey. Usually containing some 12 to 15 per cent. of moisture, a portion of the chalk is dried in kilns and mixed with the fresh, damp material, in quantity just enough to make the whole run well in the mill. It is then crushed between fluted rollers, or edge stones, and is ready for the furnace. If used in lumps, or wet, the sulphate in the furnace is fluxed and burned before the chalk is acted upon, and the "ball" spoiled. Moreover, it is necessary, when lumpy chalk has to be used, to put in a considerable excess, which in the tanks gives rise to caustic soda. Good limestone, Buxton, Irish, or Welsh, as used in Lancashire and other districts, has about the following composition:—

Organic matter	trace	Calcium carbonate	98·370
Silica	0·398	Magnesium „	0·756
Alumina	0·135	Manganese „	0·026
Ferrous carbonate	0·252	Calcium phosphate	trace

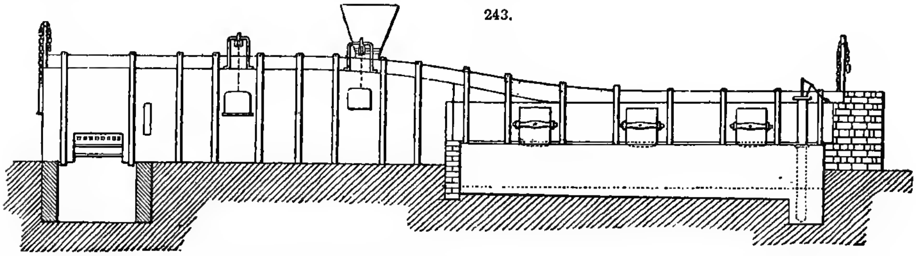
In revolving ball furnaces the use of limestone is universal.

The selection of a good "mixing" coal, as it is called, is an important matter, and the quality must be kept as uniform as possible. It should leave when ignited as small a quantity of ash as possible, and must be free from slaty and siliceous matter. A bituminous gas coal mixes well. The ash should not exceed 5 per cent., or the sulphur 0·75 per cent.

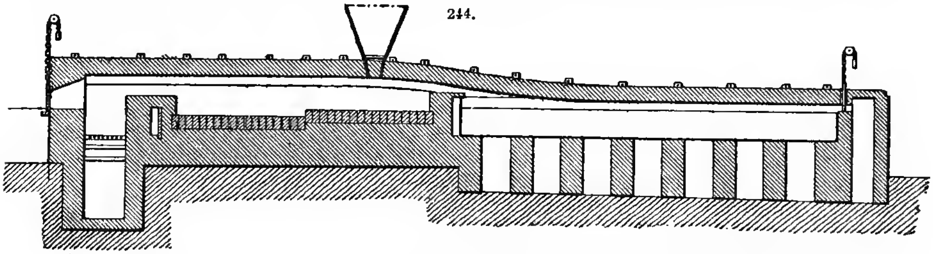
These three materials, in the proportion of 3 cwt. of sulphate to 3½ or 3¾ cwt. of chalk and about 1½ cwt. of small coal, are introduced into the ball furnace by means of a hopper, or thrown by hand upon the charging bed. The mixture varies with the judgment of the individual manufacturer or with the state and quality of the materials, but the above proportions represent the usual charge. The furnace is reverberatory; elevation, section, and plan are given in Figs. 243, 244, and 245. The fire is placed at the end, and is about 4 ft. by 6 ft. The two bars that will be noticed below the grates afford leverage to the poker which is used to break up the scars or "clinkers." When these scars are removed and fall into the "cave" or firehole, they must be cooled with water to prevent damage to the iron. It is usual to place a water-tap in the firehole for the purpose. Coal is introduced through the firehole at the end of the furnace, which is covered with a hanging door of cast iron lined with "half thicks." Between the fire and the first bed of the furnace a long narrow slit will be observed. This allows a current of cool air to pass continually under the bridge. One side of it is formed by what is called a "bridge plate"—a long cast-iron slab of peculiar construction, flanged at each end and bolted into the side plates of the furnace.

This keeps both bridge and furnace bottom in their places, and prevents any fluxed material from escaping from the bed of the furnace. It is usual to give the bridge plate sides about 2 in. high, and a lining of thin firebricks to strengthen it. The bed of the furnace is divided into two parts: the "working bed," that nearest the fire, is 6 in. or so lower than the "shelf" or charging bed; the hopper in which the charge of sulphate, coal, and chalk is contained, is built into the arch over the centre of the "shelf." Each bed is provided with a working door, closed by cast-iron covers lined with half thicks. Concerning the pan placed at the end of the furnace more will be said presently. A ball furnace requires very careful and substantial building to stand the heat (about 1200°), the wear and tear, and contraction and expansion. The walls are about 14 in. thick, the arch 9 in., the sole 9 in., formed of 9-in. firebricks, of best possible quality, set on end and "grouted in" with a thin mixture of finely ground fireclay and water. Below this bed a foundation of, first, concrete, and then brickwork is laid, with as thin jointings as possible. Bevelled portions of brickwork, as shown in Fig. 245, allow the workman to reach every corner of the beds with his paddle and rake. The arch goes in a nearly horizontal line over the first bed and then dips down towards the pan, so as to carry the heat well into the material. The connection between furnace and pan is formed of a bridge and air-course somewhat similar to the fire-bridge and its air-course, a large flat quarl, which projects some 4 in. over the edge of the pan, preventing the flames from coming into contact with the iron. The whole erection of furnace and pan is firmly bound up by strong iron binders running over upright bars set into the ground or foundation. The outside of the furnace is usually cased with plates of cast iron, as shown in Fig. 243, but in Lancashire it is customary simply to pass strips of metal behind the binders, as shown in Fig. 220, when describing a close or blind roaster. The bricks used in building a ball furnace, and especially in the beds, must be as free as possible from silica—to prevent the formation of silicate of soda, and *hard burnt*. The fireclay must be as well ground as possible so that all joints may be kept fine. The charging by hopper is a great improvement over the old custom of throwing the materials down in front of the charging door and shovelling them in by hand. Not only is a considerable saving of labour effected, but less cool air is admitted into the furnace. The best plan is to arrange the furnaces

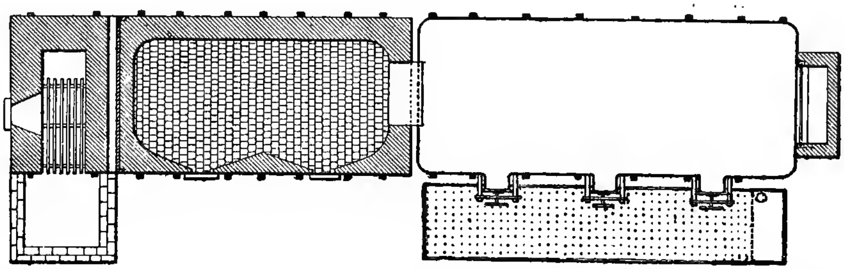
243.



244.



245.



so that one tramway, as direct as possible, may run overhead above the back beds and deliver its hourly charge into each hopper. By the old method, besides a "ball furnaceman," or man to work and draw the furnace, a "mixer" is required, whose business it is to fetch the charge of sulphate, chalk, and coal from the various depôts, throw the materials upon the shelf, and spread them to the flames. Adopting the hopper and tramway system, and arranging the depôts in contiguity to one another, half a dozen furnaces can be served by one boy. A fresh charge is always kept in the hopper to lute it, the simple withdrawing of a slide causing the materials to fall down upon the shelf of the furnace.

It has been said that the wear and tear of a ball furnace is very great. The working bed requires renewal about every three months, the arch immediately over the fire lasts about the same time, while the whole furnace, except plates and foundation, requires reconstruction about once in every three years. With inferior workmanship in the construction, or inferior materials, the life of a furnace is even shorter than three years, and the renewals from time to time of the several portions mentioned, very frequent indeed.

The placing of a pan at the end of the ball furnace, as set forth in the drawings, is simply a matter of convenience and economy, to utilize the waste heat of the furnace in concentrating the black ash liquors. The pan is usually of the description shown in Figs. 243, 244, and 245, a large rectangular vessel built of sheet-iron plates, three-eighths of an inch thick and thoroughly riveted together. The size varies from 18 to 24 ft. in length, from 2 ft. to 2 ft. 6 in. in depth, and is of the same width as the furnace. It is best to have it a little deeper at the fire end than at the damper. Round the top runs a strong angle iron which carries a 4½ in. (occasionally 9 in.) arch thrown across and joined to the sloping arch of the ball furnace. This arch also slopes down towards the far end of the pan to bring the heat well upon the liquors. Some manufacturers take the arch along almost level, and close down upon the angle iron, a custom that tends to yield burned salts. The arch and pan are bound together by square 2 in. iron binders, placed along the sides at intervals, and a series of cross rods, above and beneath, gripping the upright binders. The products of combustion, after passing over the surface of the liquor, finally pass to the chimney down the flue shown at the end of the pan, the draught being regulated by a hanging damper. In the front are constructed two or three doorways, depending upon the length of the pan, with projecting necks, closed by strong cast-iron slabs, which screw up against an angle iron rim running round the jambs of the doorways, and are further made tight by a bedding of clay. Through these doors the "black salts" are raked out into the "drainer," so placed in front of the pan, and at a lower level, that the projecting necks overlap by a few inches. The drainer is built of sheet iron in a manner similar to the pan, and is about 18 to 20 ft. long, 3 ft. wide, 2 ft. 3 in. deep at the end nearest the ball furnace, and 3 ft. at the other end. This sloping bottom allows the drainings from the salts to collect at the lower end, where a well, shown in Figs. 243 and 245, receives them. In this well, a pump is fixed whereby they are returned from time to time into the boiling-down pan. To assist the draining operation, a false bottom, perforated with a great number of holes, lies upon an angle iron running along the sides and ends of the drainer, about 6 in. from the bottom at the shallowest end, and level throughout. The pan is built upon pillars, as shown in the engravings, that all leakage may be readily apparent. The precise working will be detailed when treating of the lixiviation of the balls. After traversing the pan the waste heat from the furnace may be still further utilized by placing over the flue iron tanks of any suitable description, in which the liquor from the vats may be kept at the requisite temperature while settling.

The balling operations are as follows:—The required quantities of chalk, sulphate, and small coal are weighed off and introduced into the furnace—upon the *back* bed—by some such means as has been described. The workman with his "slice" then spreads the charge over the bed so as to thoroughly expose every portion to the action of the flames, and shuts down the door. After a short time the charge—already called a "ball"—is raked up, half of it transferred to the bed nearest the fire, and the other half again "spread." This splitting of the ball is not a universal method of working, but is upon the whole preferable. Again the doors are closed and the split ball exposed to the fluxing heat for about ten minutes. The second half is now transferred to the working bed, and the really hard labour of the ball furnaceman begins, hardly ceasing until his ball is drawn. As the materials begin to soften and flux—the sulphate first—every portion must be continually turned over so as to get an even fusion, and prevent any portion being burned. This is done with the paddle, and requires great experience, strength, and judgment on the part of the workman, as his materials are constantly varying, and, technically speaking, will "stand more fire" and need more fining down at one time than another. As soon as the fused mass begins to get stiffer, and the jets of flame, or "candles" begin to die down, the ball furnaceman takes his rake—the heavy cast-iron head about 10 in. by 7 in.—and after thoroughly mixing up every portion of the ball, draws it out as rapidly as possible into a wrought-iron barrow, or "bogie," placed under the furnace door, and just overlapped by the door-plate. All this finishing and drawing must be timed to a nicety, and calls into practice all the skill of the workman. If the ball be drawn a shade too soon, it is "green," and certain to contain undecomposed sulphate; if left for a moment too long exposed to the heat it is burned, and solidifies into a close hard mass, difficult to break up and lixiviate. A badly judged mixture is at once apparent at the finishing of the ball. If too little coal has been used, the whole mass remains soft; if too little chalk, it becomes thoroughly stiff and is difficult to draw. It takes about forty minutes to dry, work, and draw a ball. A fresh charge is introduced upon the shelf a few minutes after transferring the second half of the previous ball to the working bed, and, after drawing, this part of the furnace is left empty for ten minutes or so, to get up a thorough heat again, almost a white heat being required to flux rapidly. After the ball has been raked out into the bogie, it is left for a short time to cool and solidify, the "candles" or "pipes" rapidly dying out, and the mass assuming a creamy brown appearance; it is then wheeled away and tipped up in convenient contiguity to the lixiviating tanks.

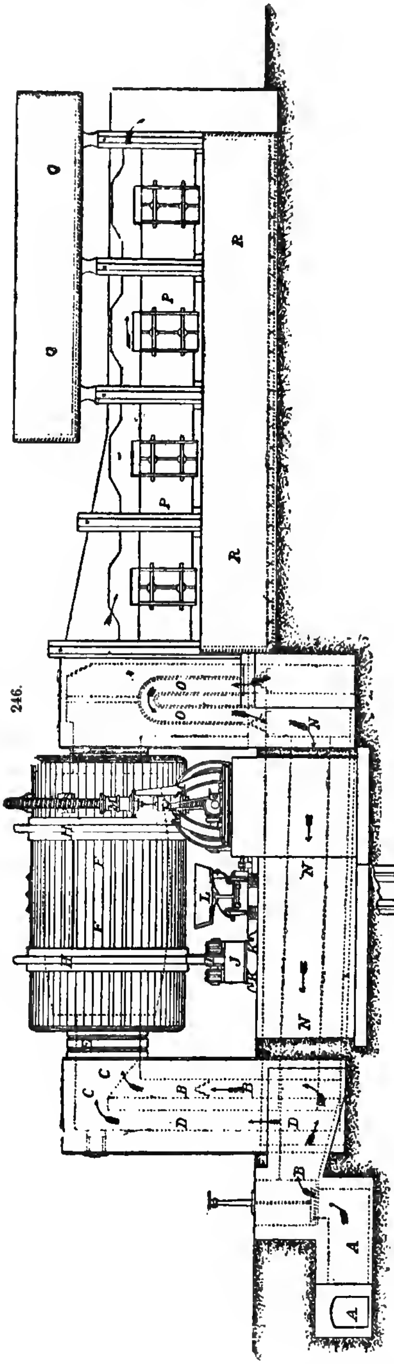
The amount of work got out of a ball furnace varies with all different circumstances and mixtures, but as a rule, a workman can draw nine balls in an eight hours' shift, well worked and fired, and weighing about 4 cwt. 3 qrs. each.

The exact nature of the changes wrought in the ball furnace is still but imperfectly understood. For a full description of all the chemical theories which have been from time to time advanced, the reader is referred to the many papers that have been published upon the subject. The simplest view is, that first the sulphate of sodium is reduced to sulphide by the action of the coal, and that then a mutual decomposition takes place between this substance and the calcium carbonate, sodium carbonate, carbon dioxide, and a mixture of calcium sulphide and oxide being produced. The analysis of black ash is not only very intricate, on account of the number of constituents, but is also exceedingly uncertain, from the variety of the materials used and the circumstances attending sampling and testing operations. The following, however, may be taken to represent the composition of a good and well-worked ball:—

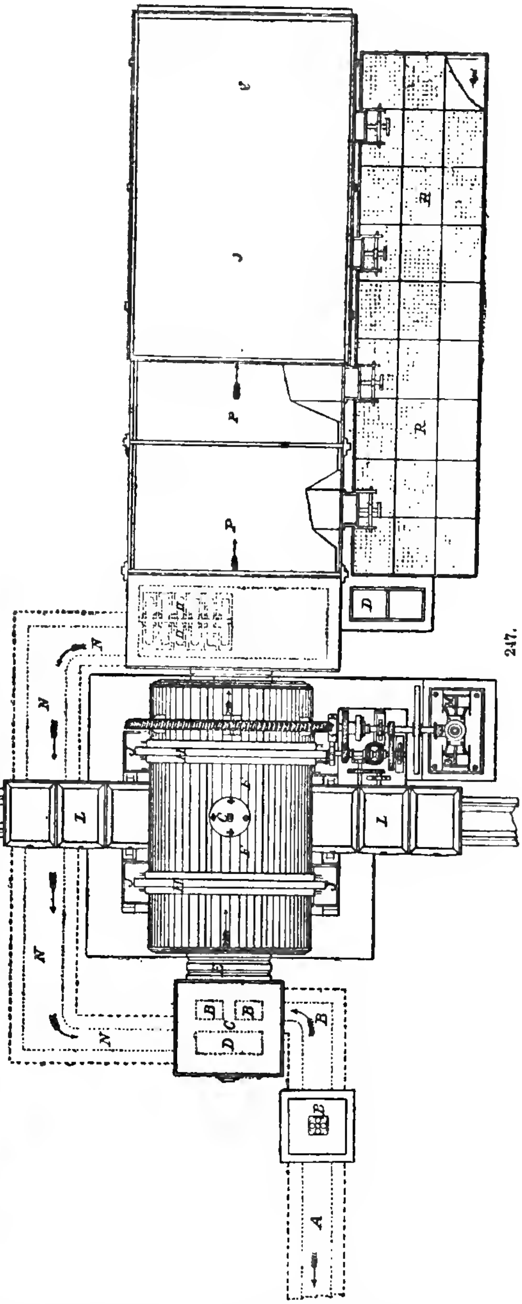
Sodium sulphate	1·00	Lime	0·35
„ chloride	1·50	Magnesia	0·50
„ carbonate	39·00	Iron water and alumina	6·00
„ silicate	trace	Silica	1·70
„ aluminate	trace	Sand	2·00
„ cyanides	0·5	Carbon	4·00
Calcium carbonate	4·00	Other lime compounds	3·00
„ oxysulphide	35·00		98·70

In the year 1853, the first "revolving," or mechanical, ball furnace was patented by Elliott and Russell. This apparatus is designed to do away altogether with the necessity for hand labour in the balling operation. Many difficulties have had to be overcome, but at length, thanks to the improvements of Messrs. Stevenson and Williamson, and James Mactear, and to more perfect mechanical contrivances, the "revolvers" bid fair, in large works at least, to supersede the old hand furnaces. The annexed drawings, Figs. 246, 247, and 248, show the complete apparatus as designed and constructed by Messrs. Robert Daglish and Co., of St. Helens. Heat is supplied by Siemens' patent gas arrangement in the plan set forth. The more usual custom is to employ the ordinary coal fire. Gas is being daily more and more applied to various purposes in the alkali manufacture, but its introduction is comparatively slow, owing to an expensive plant being required and the influences of deeply rooted prejudices. The saving of fuel effected is not very considerable, but for all purposes where an exact regulation of heat is an important point, the superiority of gas cannot be denied. Fig. 246 gives the side elevation of the revolver and boiling-down pan; Fig. 248, the end elevation; and Fig. 247, a plan of the whole. A A is the gas flue from the generator; B B the inlet for regulating the supply; C C the combustion chamber; D D inlet for heated air; E E a ring to allow of the contraction and expansion of the cylinder; F F the revolving cylinder itself, built of boiler plate, half an inch in thickness, lined with firebricks and blocks. The shell is about 15 ft. in length and 10 ft. in diameter, put together in the most careful and substantial manner possible, strengthened by two strong cast-iron rings riveted firmly to it, and hooped with solid cast-steel tyres shrunk hot upon the rings and securely bolted. G is the charging door when at the top and the discharging door when the position of the cylinder is reversed. H H are the friction rings working upon the steel-tyred friction rollers I I. J J are the bearers resting upon strong iron plates, K K. L L are waggons for receiving the ball when discharged, running upon a small tramway. M M a high pressure upright engine for driving the cylinder and working the tramway, the speed being capable of the most delicate regulation by suitable gearing. N N is a flue for supplying heated air to the combustion chamber. This air is introduced through the upright cast-iron heater O O, and warmed by the waste heat from the furnace. P P is the boiling-down pan; R R the drainer, and Q Q a tank for settling the black ash liquors and supplying them to the pan. This tank forms of course no integral part of the arrangement; its position is merely a matter of convenience and economy. When direct firing is adopted, the neck of the cylinder is formed with a loose iron rim lined with firebricks. Through the space on either side of this rim a constant indraught of air takes place, which materially assists in the complete combustion of the gases. It is also possible to ascertain through this opening the state of the charge within the cylinder. In

246.

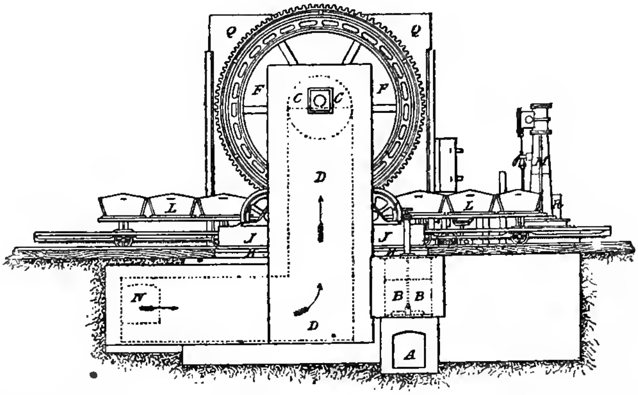


247.



place, too, of the heater O O is built a dust chamber between the furnace and boiling-down pan, to collect the waste from the fire, and prevent the sulphate, &c., from the charge, being drawn over into the black salt. It will be noticed, by referring to Fig. 246, that the interior of the cylinder is barrel-shaped, to assist in the concentration of the charge. This form is given by the brickwork lining. The entire cost of a first-class revolver, with pan, engine and over-head tramway complete, is about 2000*l.*

248.



The adoption of the over-head charging system, which has been described when speaking of hand furnaces, is of course imperative in the case of revolvers. This part of the operation differs materially from the mixing process already set forth. A usual charge for an ordinarily sized revolver consists of 30 cwt. of sulphate, 33 to 35 cwt. of chalk—or 27 cwt. of good limestone, and 17 to 19 cwt. of small coal. What is termed the "liming" process is still followed by many manufacturers. The chalk and two-thirds of the mixing coal are first tipped into the revolver. A slow motion is given to the cylinder, and after about three-quarters of an hour, a blue flame appearing at the pan end of the furnace denotes that a portion of the lime is causticized. The revolver is then brought with its charging hole under the hopper, or waggon, and the sulphate and remainder of the coal tipped in. While this is being done the pan damper is nearly closed, so as to prevent a rapid draught carrying the finely divided sulphate and coal away. For about twenty minutes the cylinder is turned with a slow motion until the workman judges that the sulphate is melted. A quicker motion, of about two revolutions per minute, is then given, and continued for half an hour or so, until the workman judges, from the appearance of the bright flame, the state of consistency of the charge, and the before-mentioned "pipes," that the decomposition is complete. The bogies have been in the meantime drawn up underneath the cylinder. A rapid motion is given for a few minutes, so as to collect the fused ball well down to the centre of the cylinder side, and as the speed is slackened the door is unhooked, and the charge falls out into the waggons. As each one fills, it is dragged forward, an empty one immediately taking its place. So rapidly is this discharging now accomplished, that eight or nine bogies are filled before the slowly revolving cylinder carries the discharging hole upwards. One revolution then suffices to collect the remaining portions of ball and discharge them into a couple of empty bogies.

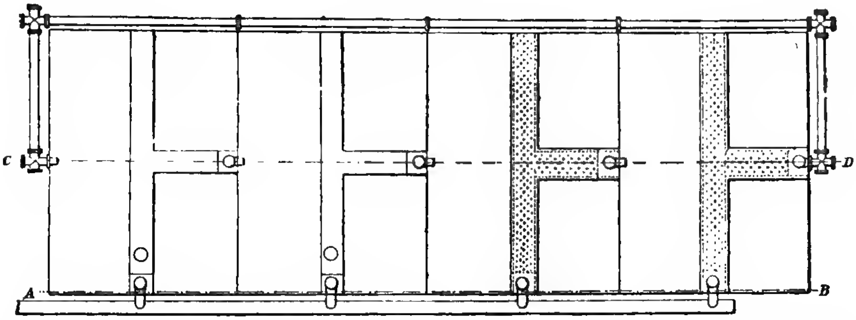
James Mactear, of Glasgow, to whom great credit is due for bringing the revolvers to their present perfection, has adopted a method of charging which obviates the necessity for this tedious "liming" operation. It should be premised that the greatest difficulty met with in the mechanical process has been the fact that the balls produced were so close and hard that no amount of steaming in the tanks could properly lixiviate them. By adding an excess of lime, and causticizing it, it was supposed that the balls would burst in the tanks and fall easily, and a very fair success has attended the operation. Mactear, however, has established the fact that little more than an equivalent quantity of limestone need be added at first, and that the whole charge may be tipped in at once. After decomposing the sulphate thoroughly, the cylinder meanwhile revolving slowly, a small quantity of caustic lime in lumps is dropped in. The cylinder is then made to revolve rapidly, the whole charge mixed up, and drawn without loss of time. Besides keeping the ball open, this addition of the caustic lime cools the cylinder to some extent, and prevents any burning of the ball while the last stages are being gone through. The addition of a small quantity of cinders, or coal, along with the lime tends to keep the ball still more porous and readily lixiviated. This simplification of the original process has done away with several of the evils attending mechanical balling. The output of the furnace is greatly increased, by shortening the time required to work off a ball; the quantity of alkali waste is reduced, and a proportional saving of lime and fuel effected.

The size of revolvers, and, consequently, their output, is being constantly increased. Mactear states that his last erected furnace is capable of decomposing 330 tons of sulphate per week. The ordinary revolver, however, with the usual method of working will not decompose above 150 tons per week. In this enormous capability lies one of the evils of the system. A small works, manufacturing only its 150 tons of sulphate per week, cannot afford to come to an absolute standstill, while repairs are being made in its one revolver. And the old evil of close hard balls is still not altogether cured. It requires a higher temperature to dissolve a revolver ball than one made in a hand furnace. The question of temperature of tank water will come up again when treating of the lixiviation of the balls.

Until a few years ago the length of time required for discharging presented an almost insuperable difficulty, the first portions of the ball being "green," while the last were burned. With better mechanical contrivances and more thorough experience in regulating the speed of the cylinder this evil has been practically done away with.

Lixiviation of the Black Ash.—The next process is to extract the sodium compounds from the black ash by dissolving the balls in warm water. It will be noticed by referring to the analysis given that about one half of a ball is soluble, and the remainder insoluble—the latter consisting of various impurities, but chiefly a mixture of various sulphides, sulphites, and oxide of lime. For the purpose of lixiviation, the balls are broken into pieces, and thrown into the series of tanks, shown in Figs. 249, 250, and 251. Water at about 35° (100° F.) to 43° (110° F.), and the second liquors, are then run upon them, the soluble compounds drawn off to the settlers, and the insoluble residue thrown out. During the process of breaking up, the quality of the balls may be judged by an experienced eye almost as correctly as by complete analysis, and the careful attention of the manufacturer should be specially and unremittingly devoted to this point of review. The interior of a ball should present a clear, steel grey appearance, well honeycombed. It should break readily with a sharp ring, preferably splitting right down the centre. The outer crust should not be loose, or too well defined, and lumps of undecomposed sulphate should be conspicuous by their absence A pinkish shade shows a green ball, a dull red a burned one. Irregularity of appearance, with white lumps and dark patches, shows want of work, a general soft "mushy" character, an ill-judged mixture, or too long exposure to the air. The exact amount of harm a ball receives by lying too long before lixiviation is a matter of doubt. If put into the tanks too hot, the temperature of the water is raised too high, if left upon the ground more than forty-eight hours or so, a certain

249.



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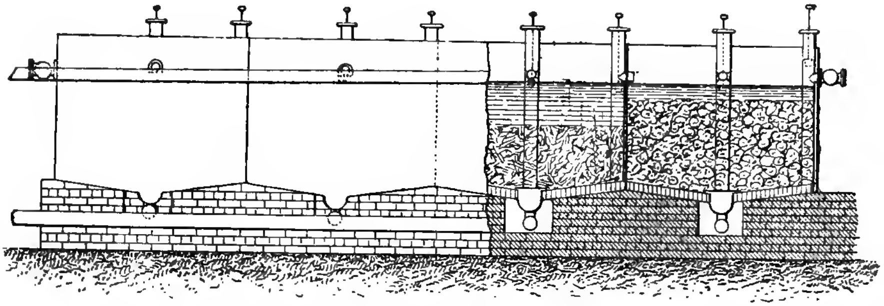
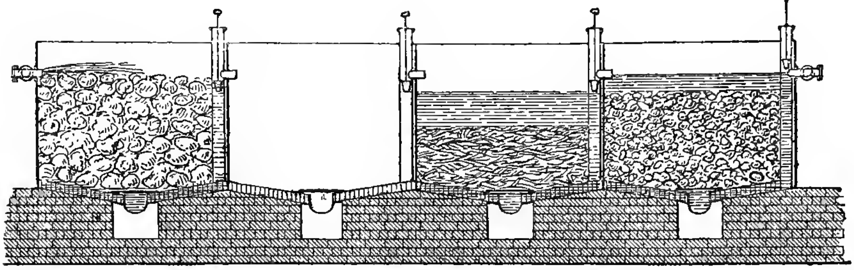


amount of decomposition, with oxidation of the lime compounds, takes place. As a general rule, twelve hours may be taken as the best time for a ball to lie before being tanked.

A description of the older apparatus for lixiviating black ash is only interesting to the alkali antiquarian. The ingenious method at present adopted was originally the invention of Shanks of St. Helens, and leaves little to be desired. It depends upon the different specific gravities of the water and liquor. The tanks vary in size with the experience and judgment of different manufacturers. Good dimensions may be taken to be 10 ft. long by 8 ft. wide and 7 ft. deep. They are usually arranged in sets of four—four tanks of the size named being sufficient for three hand ball furnaces, or a decomposition of 60 tons of sulphate per week—and are formed by placing partitions in one long tank. The sides, ends, and bottom are formed of $\frac{3}{8}$-inch iron plates well riveted together with angle-irons at all the corners. The bottom is sometimes flat, sometimes assumes for each tank the shape shown in the drawings, sloping down to a drainer, or "well," which runs along the centre of the tank. In either case a lining of 4½ bricks, on edge, is given to the bottom, leaving a cross drainer, as shown in Fig. 249. Over both longitudinal and cross drains are laid loose sheets of iron, well perforated. In each drainer, reaching just below the false bottoms, are fixed two "jugs," one of which communicates with the next tank and the other with a spout running along the whole range of pipes, which conveys the strong liquor to the settlers. These jugs consist of metal pipes, 3 inches bore in the lower part, widening to 4 inches in the upper part—shaped in fact like a pump. By means of a plug and seat arranged just below the outlet pipe, or "nose," communication with the neighbouring tank or settlers can be made or cut off at will. The outlet pipes of the jugs along the front of the tanks—those by which the strong liquor runs to the settlers—are placed slightly below the level of the communications between the tanks. By a pipe running back from the fourth to the first tank the whole operation is made continuous, each one becoming in turn the "strong" tank, an intermediary, and the "weak," or exhausted tank. Water is supplied to the surface of the tanks by any convenient apparatus, and is heated, *before it touches the liquor, or balls*, by waste or other steam. Some manufacturers put the steam direct into the tank, a method causing loss through the temperature of the tank at that particular spot being raised too high, and the sulphides dissolved. Finally, in the drainer of each tank is fixed a pipe and cock to carry off the waste liquors.

251.



The plan of working is as follows:—The tanks are filled with lumps of ball—not too large—to within about a foot of the top, a layer of dry ashes being placed upon the bottoms. Water heated to about 100° F. is then run on, which, percolating through the mass of black ash, rises up the jugs, and that one which communicates with the settlers being open, finds its way out in the shape of strong soda liquor. At first this liquor will test about 50° Tw., but the strength speedily advances to 55° or even 60°, and then rapidly falls down to 40°. The plug is then placed in its seat, and the tank left to itself for awhile. After a quarter of an hour or so the plug is withdrawn and a second "running" of liquor taken off, now testing up to 48° or so. Each tank should bear a third tapping, the liquor never being allowed to go to the settlers below 38°. This outlet pipe is then closed, and the communication between the first and second tanks opened. The liquor from the first tank flows over, percolates through the balls with which the tank is filled, and is drawn off to the settlers in the manner described. In the meantime a steady flow of water upon the balls in the first tank is kept up. This operation is repeated with all four tanks. By the time the last is reached, a sample of the liquor *drawn from the jug* of the first tank will be found to test not more than 1° or 2° Tw., showing that all the soda is, practically, dissolved out. The water is then turned upon the second tank, the first being shut off. The spent liquors are drawn off through the pipe at the bottom and run away, leaving a mass of insoluble residue—tank waste—about half filling the tank. This is shovelled out, the drainer cleaned, a fresh layer of ashes sprinkled over the bottom, and the tank is ready to receive a supply of broken ball and the liquor to be dissolved by the returned liquors from the fourth tank. Sometimes the weak tank is "run down," as it is called, to 0° Tw., but between 2° and 0°, the sulphides dissolve more rapidly than the carbonate of soda and spoil the liquor. Fig. 249 gives a plan of the tanks, showing the bottom drains and false bottoms; Fig. 250, elevation and sectional elevation through the line A, B, Fig. 249; Fig. 251, a section through the line C D. The last drawing shows a set of tanks as at work. No. 1 tank is just filled with ball, and is receiving the liquor running round from No. 4. No. 2 is empty, No. 3 spent, No. 4 about half through its work.

The working of the tanks is an operation requiring considerable care and judgment, much of the success of the after processes depending upon the securing of good liquor. The most important points are, to keep the temperature as low as possible; to take off the strong liquor speedily, that it may be kept from contamination, and not to allow the strength of the liquor running to the settlers to fall below 38° Tw. With regard to the first point, the water should not be run upon the tanks hotter than 32° (90° F.) in summer, and 42° (110° F.) in winter. The temperature of the mass in the tanks has always a tendency to rise owing to the hydration of the lime and other chemical reactions going on. If the liquors show any greater heat than 65° (150° F.), it is safe to conclude that the water has been run on too hot. Both strong and weak liquors, and tank waste should be tested daily—at least once on each shift. The waste should present no lumps of undissolved ball, and should be of a dirty green colour. It should be tested at any rate for soda, and from time to time should be subjected to complete analysis. The amount of soluble soda should not exceed 0·15 per cent. A fresh sample will give about the following composition:—

	Per cent.		Per cent.
Calcium sulphide	37·0	Sodium carbonate	0·25
„ hydrate	9·0	Iron, alumina, and magnesia	7·0
„ carbonate	16·0	Carbon	6·0
„ sulphate	6·0	Silica, &c.	5·0
Sodium sulphide	0·5		

It is of the greatest importance to keep both sulphide and carbonate of sodium as low as possible. A good manufacturer will not allow even as much of these salts as set down in the above analysis, 0·25 total soda being the point to be aimed at.

The liquor that is drawn off to the settlers should be of a yellowish brown colour and perfectly clear. It should be tested two or three times daily for sulphide of sodium, to make sure that the tanks are not being overheated or the liquor allowed to stand too long before being drawn off. The amount shown should never exceed 0·75 per cent., though where the weak liquors are pumped back upon the tanks, and used over and over again in place of water—a piece of poor economy—as much sulphide as 2 per cent. will be often registered. As this is simply converted into sulphate in the after processes, it is sheer loss of soda. An average tank liquor, not the best, will show about the following composition:—

Sodium carbonate	69·0	Sodium cyanide	trace
„ hydrate	15·0	„ ferrocyanide	trace
„ sulphide	1·0	„ silicate	0·5
„ sulphite	2·0	„ aluminate	0·5
„ sulphate	7·0	Iron and alumina	0·5
„ chloride	3·0	Insoluble	0·5

Many processes have been proposed to purify the tank liquors from cyanides, &c., and carbonate or peroxidize the sodium compounds. The method proposed by Gossage is perhaps the most extensively adopted. An iron tower, usually a large pipe, is loosely packed with coke, and the tank liquor run down. During its passage it is met with a stream of air, or impure carbon dioxide from a lime-kiln, or the waste gases from some furnace containing large quantities of both oxygen and carbon dioxide. The caustic soda is thereby converted into carbonate, the sulphide oxidized, and the aluminates decomposed with precipitation of alumina. Another process is to pass a steam blast into the liquor, under a perforated false bottom which ensures the division of the steam and its action upon every portion of the liquors. Upon the whole these processes do not repay for the trouble and expense incurred in adopting them, the best plan being to get as good liquor as possible, and then use it without further manipulation. The cyanogen compounds of the liquor have attracted a good deal of attention, but no practical result has ever been attained in the way of getting rid of them. Stevenson has proposed to heat the liquors under pressure to 150°. Probably the best plan is to use a mixing coal containing the least possible amount of nitrogen. The smell of ammonia which proceeds from well-worked balls when cooling, is the result of decomposition of certain of the cyanogen compounds.

The weak liquor, standing about 1° Tw., is, as has been stated, sometimes used over again in the place of water, but is usually run to waste. It contains very small proportions of sodium carbonate, hydrate, sulphide, hyposulphite, sulphate, chloride, silicate, and aluminate.

Various methods for utilizing the tank waste will be detailed hereafter. Usually it is removed as soon as thrown out of the tanks, and either carried out to sea or deposited upon waste land. Some use is made of it in building walls and laying foundations, the sulphate of calcium, or gypsum, which is formed by the action of the air causing it to set very hard. If allowed to remain in heaps, as loosely thrown out of the tanks, the mass speedily becomes hot, even red hot. The oxygen of the air, and the moisture present, cause the formation of soluble calcium hydrosulphide, bisulphide, and hyposulphite, &c., and the presence of carbon dioxide causes an evolution of sulphuretted hydrogen, which is most offensive and injurious. Much of this evil can be prevented by spreading the waste over the ground, or building it promptly into whatever shape may be required, keeping out all ashes or substances that would tend to porosity, and beating it down carefully with shovels so as to keep out the air as much as possible. The most abiding mischief is caused by the drainage from all "tank heaps." The sulphide becomes soluble, and is washed out by rain, &c., forming a yellow liquid, which gives off a well-known nauseous odour. The yellow coating that appears upon the surface of a heap of tank after exposure to the air consists mostly of free sulphur from the oxidation of iron sulphide.

The next operation is the boiling down of the soda liquors from the tanks. When they are drawn off from the balls, the liquors are run into a series of settlers, slightly warmed by waste heat, or a coil of steam piping, to prevent any deposit of crystals. Here any insoluble matter, mechanically carried over, subsides, the following being about the composition of the residue :—

Calcium sulphide	38·00	Iron compounds	6·00
Silica	26·00	Sodium, ditto	11·00
Alumina	19·00		

The settlers require clearing out about every five or six weeks, the residue lying upon the bottom being removed to the tanks, and mixed with fresh balls, so as to lose none of the soda. The clear, warm liquor is next run into the boiling-down pans, which have already been described, and exposed to the waste heat of the ball furnace. After a few hours' concentration, a barrowful or two of sawdust is thrown in, and as the body of liquor contracts a further quantity is run in, to keep the sides of the pan from burning. After about twenty-three hours the liquor is boiled down to a pasty mass. The doors are then removed, and the whole is raked out into the drainer placed in front, an operation requiring about a quarter of an hour. The doors are then fitted on and luted with moist clay, and a fresh charge of liquor is run in. The tanks, settlers, and boiling-down pans should be so arranged that the liquor runs from one to another without any pumping, &c., expense. As the salt crystallizes out and forms a crust over the liquor, a system of careful stirring should be commenced, and continued from time to time during the whole of the boiling-down process. As the mass gets more solid, the salts should be worked back from the fire, that no portion of them may become burned. If the supply of liquor runs short, one or more of the boiling-down pans must be filled with water, and the liquor reserved for the rest. As a rule, a hand ball furnace will boil down rather more than the liquor from its own balls. The salts are allowed to remain in the drainer for about twelve hours, during which time the greater part of the mother liquor drains out, runs along underneath the false bottom (see Figs. 243 and 245), and collects in the well at the low end. From here it is pumped from time to time back into the pan, or into a separate cistern if a particularly pure product be required. These mother liquors contain nearly all the absolute impurities from the liquor, the sodium salts consisting of carbonate, hydrate, sulphide, and sulphate. After being thoroughly drained, the contents of the drainer are wheeled away to a depôt or to the finishing furnace. These "black salts" should present a mixed appearance of black and white salt, glistening with small crystals. If very fine in grain, and white or yellow in colour, the liquor has been impure, or the heat in the tanks too great. The salt that is taken from the furnace end is called "strong"; that from the further end "weak," and for the finishing operation a judicious mixture should be made. If the workman takes all weak salt, it will not "stand the fire; "if all strong, it is found impossible to "clean" it. Upon this point more will be said hereafter. When the mother—technically termed "red"—liquors are separated from the salts—not pumped back into the pan—they are utilized in making caustic soda, or are worked up into an inferior greyish coloured carbonate. Separation of the red liquors is always adopted by manufacturers who work with revolvers, and by the majority of those who use hand furnaces. It is not, however, necessary, and the writer's experience is that a thoroughly good carbonate, testing 53 per cent., and pure white, may be made, even when the red liquors are pumped back.

Besides merely evaporating the liquors, the action in the boiling-down pan is to convert a large quantity of the sodium hydrate into carbonate, and oxidize the sulphides to some extent. All the sulphur is carried through the process, none being volatilized as is sometimes stated. A certain amount of finely divided sulphate of soda is carried over from the furnace, by the current of gases, and settles in the liquors.

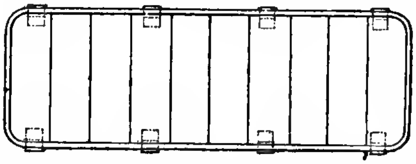
In France, the soda liquor is boiled down and calcined in the same furnace. This is a very primitive method, turning out a good carbonate, but expensive and only producing a very limited output.

To keep the salts from being contaminated by the products of combustion in the ball furnace and the carrying over of sulphate and insoluble matter, boiling down by bottom heat is very often resorted to. The various descriptions of pan and setting are shown in Figs. 252 to 257. The apparatus is usually termed a "boat" pan from its shape. It will be noticed that the pan is so set in brickwork that the fire only plays upon the sides about half-way up. Consequently the salt, as it crystallizes out, accumulates at the bottom of the pan and is then "fished" out up the sloping sides, being protected by the solid brickwork from being burned. "Fished" salts yield a very fine carbonate, 52 to 57 per cent.; the remainder, containing the caustic soda and certain other salts, forms a "caustic" ash, containing up to 10 per cent. of sodium hydrate, and on that account esteemed by paper makers and soap manufacturers, who, in any case, have to causticize their lye.

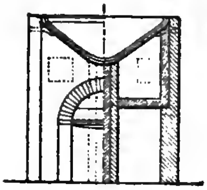
252.

253.

254.

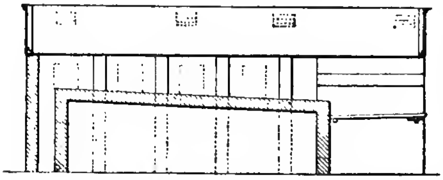


255.

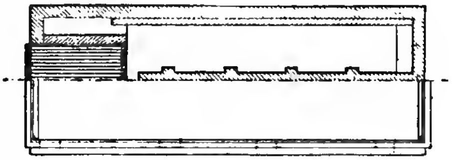


An ingenious form of pan has been occasionally tried. It consists of two compartments, the one heated and the other kept cool, connected by a large tube. The liquors are kept in constant circulation between the two compartments, crystallizing out in the cold one, and the mother liquors being pumped back. It has also been proposed to fish salts of different value from the boiling-down pan at different stages of concentration, leaving the mother liquors to be finally worked up into a caustic ash. Upon the whole the method of boiling down by the waste heat passing over the surface of the liquors is the most economical, proper care in the subsequent finishing process rendering it perfectly easy to produce a satisfactory carbonate.

256.



257.



It now remains to carbonate, or finish, the black salts. Wheeled from the depôt, or trainer, they are thrown into a reverberatory furnace, very closely resembling the sulphate of soda "roaster." The chief difference is that the bridge of the "carbonator" is carried higher so as to keep the flame from too immediate contact with the salt. Sometimes a single-bedded, sometimes a double-bedded carbonator is used, the latter undoubtedly doing the better work. In the case of a single-bedded furnace the charge of salt, weighing about 15 cwt., is thrown upon the bed and the fire kept well damped until the mass is thoroughly dried. As soon as this stage is reached, the damper is drawn up, the fire "cleared," and the charge carefully and almost continuously worked with a heavy paddle. If the fire is allowed to burn with a clear flame before the salt is dry, certain portions of it, especially in the neighbourhood of the bridge, will flux and be spoiled. The working of a batch of salt requires considerable skill. It must be sliced in thin portions and worked first towards the fire and then back again, so that every portion may be exposed to the heat, but none long enough to be fluxed. The work accomplished in the carbonator is to oxidize the sulphide of sodium into sulphate and carbonate the caustic soda. The latter is brought about both by the presence of carbon dioxide in the furnace and by the carbonizing of the sawdust which was thrown into the salt in the pan. Chiefly the former; the sawdust tends mainly to keep the salt open so that it is readily accessible to the influence of the heat of the carbonator. When the charge is cleared—when all appearance of sulphur has vanished from the manipulation of the paddle, the fire is urged to a strong red heat and the door shut down for a few minutes. The charge is then raked out into iron barrows.

When a double-bedded carbonator is used, and it is by far the more preferable furnace of the two, a charge of black salt dries upon the bed furthest from the fire, while another is being worked upon the first bed. Considerable economy of fuel and an increased output are thereby secured. A double-bedded carbonator closely resembles a double-bedded roaster in every particular.

The carbonating process is one requiring great care and judgment. If the "hard" and "soft" salts are not properly mixed—the salts from the furnace end of the pan, and the end nearest the flue—the charge either fluxes before being thoroughly finished or cannot be "cleared" at all. When the salt has been fished it requires only drying, the heat being kept sufficiently low not to melt the charge.

The carbonate when drawn, now called "alkali" or "soda ash," is weighed and tipped up in the "alkali house." The quality may be judged pretty accurately by its appearance. It should come out of the carbonator *red hot*, showing the heat well when tipped out of the barrow. When cool, the ash should have a bluish shade over the white, proceeding probably from some compound of sodium and manganese, and should not assume a dull, clayey appearance. Above all, it should not be grey. If the heat in the carbonating process has been set away too soon, the ash will assume a reddish "foxy" appearance, but will sometimes, even then, grind a very fair colour. A usual amount of work for a carbonating furnace is 30 cwt. of finished ash per shift, divided into two charges taking about five hours each to work off.

Every batch of soda ash should be carefully tested for carbonate and sulphide of sodium, and once a week or so, a complete analysis should be made of a mixed sample of all the week's work. The amount of sulphide of sodium should not exceed a trace—i. e. the merest brown coloration should be given when a few drops of acetate of lead are added to a solution of the ash. The sulphite should not exceed 0·10 per cent.; the insoluble residue 1 per cent.; the chloride of sodium 1·25 per cent.; the sodium sulphate 7 per cent.; the sodium hydrate 1 per cent.; except in the case of a caustic ash. The points chiefly to be attended to are the amounts of sodium sulphide and sodium sulphate. The former ought at any rate not to exceed ·01 per cent. If it does, the salts have been imperfectly worked, for however "dirty" they may be, it is perfectly possible to clear even the worst samples. If the sulphate of soda exceeds 7 or 8 per cent. the balls have been badly worked, the undecomposed sulphate coming through the process, or there has been an excess of sulphide of sodium in the tank liquors.

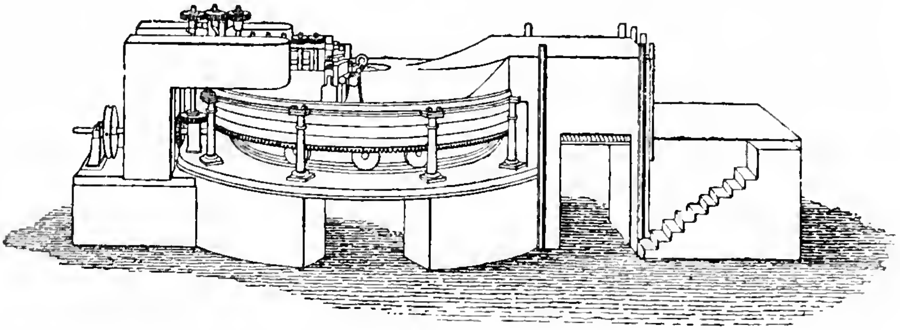
When the carbonating process is completed, a manufacturer can tell the result of the whole operation of soda making, not only as regards *quality*, but *loss* during the intricacies of the process. A considerable amount of loss is inevitable. The plant leaks in various directions, however well it may be cared for and looked after; a certain amount of soda goes away with the weak tank liquors, in the volatilization of sodium salts, in the formation of salts—e. g. sulphide and sulphate—which do not reckon as available soda, in incomplete work in the sulphate of soda process, &c. As a rule, the average production of carbonate from sulphate is not above 69 per cent.—perhaps hardly so much. In a carefully conducted works, 71 parts of ash of "natural strength"—i. e. 52 to 53 per cent.—should be obtained from 100 parts of sulphate. Theoretically, 75 parts should be obtained.

A very great improvement upon the ordinary carbonating furnace has recently been introduced by Mactear, of the St. Rollox Works, in the shape of a mechanical furnace. The apparatus is shown in Figs. 258, 259. It consists of a revolving circular bed, about 20 ft. in diameter, made of boiler plate, and supported upon cast-iron arms which radiate from a hollow central casting. The bed also has an opening in it corresponding to this centre piece. The arms, and consequently the bed, revolve with bevelled wheels upon a rail or race laid upon any substantial foundation, and are driven by suitable engine, allowing of perfect regulation of speed. Through the centre of the foundation a roadway is left, upon which travels a set of waggons to receive the finished carbonate. The arch of the furnace is supported from an angle iron carried by iron columns set in the foundations. The keystone of the arch is a cast-iron ring, corresponding to the centre of the bed, and forming an opening through which rises and falls, as may be required, a closing piece held in its position by a groove at the bottom and iron hoop at the top. By the raising of this centre piece, the opening in the sole of the furnace is uncovered, and the carbonate discharged into the waggons. The pan itself is lined with bricks, and round the outside a lute is formed, into which dips a cast-iron flange depending from the arch. As this lute gets immediately filled with portions of the charge, all ingress of cold air is prevented.

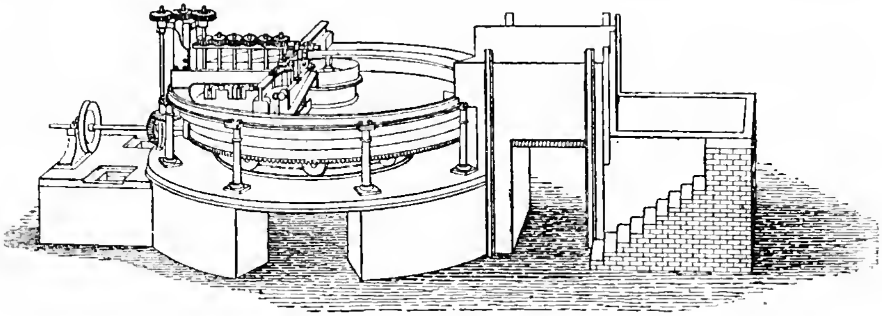
This mechanical carbonator has proved a great success, and is being rapidly adopted by the best alkali makers. A furnace of the dimensions stated can turn out 150 tons of finished ash per week, the cost of labour being 11*d.* per ton, and the amount of fuel on an average, 8 cwt. per ton of carbonate. The quality of the ash, too, is more certain than in a hand furnace, as the mechanical working can be absolutely relied upon. In decreasing the amount of caustic soda the superior working is especially shown.

Until about twenty years ago this first carbonate, or "soda ash," was looked upon merely as a crude product—a prelude to further processes. With increased knowledge, and skill, and more perfect apparatus, the quality has been so much improved that soda ash forms the great bulk of commercial carbonate of soda, having superseded refined alkali, to a great extent, in the soap, glass, and paper trades. It is rarely sold in the rough state in which it comes from the furnace, but is usually ground to a fine powder. For this purpose it is put through horizontal stones, similar to those of a flour mill, from which it runs into casks placed beneath the spout. Occasionally vertical, "edge," stones are used, but the ash requires then to be sifted before being packed. The best stones are blue lava from Italy and the Lower Rhine. These resist the heat of the ash better than the French "burrs" occasionally used. The carbonate, after being spread upon the floor of the packing house to cool, should be fed into the mill by a set of elevators, and the cask into which the finely ground product runs should be kept constantly rocked or shaken by any suitable contrivance so that it may be packed as tightly as possible. The cost of grinding and packing is about 1s. per ton, and the weight of cask when filled varies from 1 to 15 cwt., depending upon the requirements of the consumer. If a lower strength of ash be required than that produced from the furnace—say 48 per cent. instead of 52 per cent.—a certain quantity of dried chloride of sodium, or "kelp salt," is mixed with it. To keep this mixture, and the strength, right, it is necessary to test every cask.

258.



259.

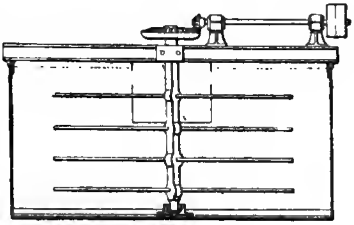


Soda ash is sold by the percentage of sodium carbonate it contains, and at so much "per degree." The testing is of the simplest description, by neutralization of a solution in hot water of a known weight of soda ash by a standard solution of pure sulphuric acid. It may be noted that all available soda—the hydrate, silicate, and aluminate—tests as carbonate. The equivalent of sodium is usually taken as 24 instead of the correct figure 23, and of the carbonate 108 instead of 106. Hence the correction to "English degrees" in the table annexed—the degrees upon which the carbonate is usually reckoned. The Decroizilles' degrees represent the French standard and show the number of parts of oil of vitriol neutralized by 100 parts of the sample. This alkalimetrical table has been drawn up by John Pattinson, of Newcastle-upon-Tyne.

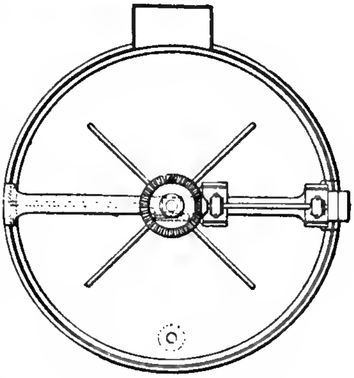
Percentage of Soda.	Carbonate of Soda.	English Degrees.	Decroizilles' Degrees.	Percentage of Soda.	Carbonate of Soda.	English Degrees.	Decroizilles' Degrees.
30·0	51·29	30·39	47·42	54·0	92·32	54·71	85·35
30·5	52·14	30·90	48·21	54·5	93·18	55·22	86·14
31·0	53·00	31·41	49·00	55·0	94·03	55·72	86·93
31·5	53·85	31·91	49·79	55·5	94·89	56·23	87·72
32·0	54·71	32·42	50·58	56·0	95·74	56·74	88·52
32·5	55·56	32·92	51·37	56·5	96·60	57·24	89·31
33·0	56·42	33·43	52·16	57·0	97·45	57·75	90·10
33·5	57·27	33·94	52·95	57·5	98·31	58·26	90·89
34·0	58·13	34·44	53·74	58·0	99·16	58·76	91·68
34·5	58·98	34·95	54·53	58·5	100·02	59·27	92·47
35·0	59·84	35·46	55·32	59·0	100·87	59·77	93·26
35·5	60·69	35·96	56·11	59·5	101·73	60·28	94·05
36·0	61·55	36·47	56·90	60·0	102·58	60·79	94·84
36·5	62·40	36·98	57·69	60·5	103·44	61·30	95·63
37·0	63·26	37·48	58·48	61·0	104·30	61·80	96·42
37·5	64·11	37·99	59·27	61·5	105·15	62·31	97·21
38·0	64·97	38·50	60·06	62·0	106·01	62·82	98·00
38·5	65·82	39·00	60·85	62·5	106·86	63·32	98·79
39·0	66·68	39·51	61·64	63·0	107·72	63·83	99·58
39·5	67·53	40·02	62·43	63·5	108·57	64·33	100·37
40·0	68·39	40·52	63·22	64·0	109·43	64·84	101·16
40·5	69·24	41·03	64·01	64·5	110·28	65·35	101·95
41·0	70·10	41·54	64·81	65·0	111·14	65·85	102·74
41·5	70·95	42·04	65·60	65·5	111·99	66·36	103·53
42·0	71·81	42·55	66·39	66·0	112·85	66·87	104·32
42·5	72·66	43·06	67·18	66·5	113·70	67·37	105·11
43·0	73·52	43·57	67·97	67·0	114·56	67·88	105·90
43·5	74·37	44·07	68·76	67·5	115·41	68·39	106·69
44·0	75·23	44·58	69·55	68·0	116·27	68·89	107·48
44·5	76·08	45·08	70·34	68·5	117·12	69·40	108·27
45·0	76·95	45·59	71·13	69·0	117·98	69·91	109·06
45·5	77·80	46·10	71·92	69·5	118·83	70·41	109·85
46·0	78·66	46·60	72·71	70·0	119·69	70·92	110·64
46·5	79·51	47·11	73·50	70·5	120·53	71·43	111·43
47·0	80·37	47·62	74·29	71·0	121·39	71·93	112·23
47·5	81·22	48·12	75·08	71·5	122·24	72·44	113·02
48·0	82·07	48·63	75·87	72·0	123·10	72·95	113·81
48·5	82·93	49·14	76·66	72·5	123·95	73·45	114·60
49·0	83·78	49·64	77·45	73·0	124·81	73·96	115·39
49·5	84·64	50·15	78·24	73·5	125·66	74·47	116·18
50·0	85·48	50·66	79·03	74·0	126·52	74·97	116·97
50·5	86·34	51·16	79·82	74·5	127·37	75·48	117·76
51·0	87·19	51·67	80·61	75·0	128·23	75·99	118·55
51·5	88·05	52·18	81·40	75·5	129·08	76·49	119·34
52·0	88·90	52·68	82·19	76·0	129·94	77·00	120·13
52·5	89·76	53·19	82·98	76·5	130·79	77·51	120·92
53·0	90·61	53·70	83·77	77·0	131·65	78·01	121·71
53·5	91·47	54·20	84·56	77·5	132·50	78·52	122·50

Refined Alkali.—For the finer sorts of glass, and for various other purposes, a purer article than soda ash is required, and this is readily obtained by dissolving the ash in hot water, settling, boiling down, and re-furnacing. All the insoluble impurities of the ash are thereby removed, the iron and the lower sulphur compounds thoroughly oxidized, while the sodium hydrate is converted into carbonate. The process of refining is as follows :—The soda ash in its rough state, as it comes from the carbonator, is thrown into some such dissolver as that shown in Figs. 260 and 261, and hot water run in. Any waste heat is utilized for warming the water, but it is also necessary to have a small steam pipe in the dissolver itself. The agitators shown greatly facilitate solution. The liquor, as nearly saturated as possible, is taken off by a pipe set about two-thirds up the side of the dissolver, a second outlet at the bottom serving to empty the vessel completely when requisite. If much sulphide be present in the ash, a few pounds of bleaching powder may be added in the dissolver, but inasmuch as this destroys also a certain amount of carbonate, its use is not recommended. The soda solution is drawn off as it forms and run through a series of shallow settlers, preferably half boilers, into the pumping well. From here it is pumped up into any convenient arrangement of tanks and left for about five hours to settle. The solution being run very hot from the dissolver, does not cool down to crystallizing point in the settlers, unless left too long, and therefore no loss need be feared upon this head. After thoroughly settling, the clear liquor, to within about 12 in. of the bottom of the tank, is run off into a pan almost exactly similar in construction to the boiling-down pan of a hand ball furnace The arch. however, is kept higher, the pan has two fireplaces, one at each end, and the products of combustion are taken out from the centre. This boiling-down operation results in a great waste of heat, as the flames must be kept from too close contact with the liquor, to prevent contamination with carbonaceous matter, and a rapid draught must be used. Sometimes a pan has only one fireplace, but this arrangement does not work well; nor can the boiling down be performed by any waste heat. When the salts assume a pasty consistency, with large lumps of nearly dried salt mixed through, the doors are removed and the whole mass is raked out into a drainer placed in front. The doors are then replaced and a fresh charge of lye is run in. The drained salt is treated precisely like the black salts—dried and furnaced in a double-bedded reverberatory furnace with a high arch. The finishing process requires great care to prevent fluxing, a clear flame being only allowed to play upon the charge when it is thoroughly dried. It is altogether more akin to the drying of fish salt in the carbonator. Nearly all the sodium hydrate is now converted into carbonate and the sulphite into sulphate. A loss of about 5 per cent. of material is incurred by the refining process, and a decrease of about ½ per cent. in strength, 53 per cent. ash making only a 52·5 per cent. refined alkali. Sometimes the "white salt" in the drainer is washed with water to obtain a purer carbonate, but such a process is entirely superfluous. The mud from the settlers and dissolver is washed with hot water, and the washings are run into the dissolver or the boiling-down pan. More usually, however, the whole of the residue is put upon the balls in the lixiviating tanks.

260.



261.

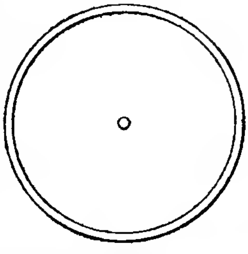


Refined alkali is ground and packed in manner precisely resembling soda ash. Formerly, nearly the whole of the alkali of commerce consisted of this refined article, but its use has given way to a great extent to that of a better prepared soda ash. The cost of refining is about 25*s.* per ton, the product being of a beautifully white colour, and containing from 48 to 53 per cent. of carbonate, depending upon the strength of the ash from which it is made.

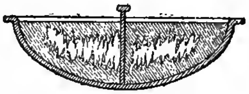
Soda crystals.—This well-known product of the alkali trade is a crystalline compound of carbonate of soda with ten atoms of water—$Na_2CO_3 + 10H_2O$. For most household and cleansing purposes, also in bleaching, tanning, and dyeing, soda crystals still hold their own, though probably, as purer forms of carbonate, such, for instance, as the product of the ammonia process, to which further reference will be made, are introduced, the use of crystals will be to a great extent superseded. A manifest disadvantage is the bulk of water of crystallization contained. Roughly speaking, 1 ton of soda ash makes 2 tons of crystals, so that all the expenses of freight, carriage, and manipulation are doubled. The greatest part of the trade in crystals is done with foreign countries where heavy import duties upon soda ash give the manufactured product the advantage. Also for all household purposes, crystals are esteemed, as being cleaner and more readily handled.

The manufacture of crystals is as follows:—Good, thoroughly carbonated soda ash, of as high strength as possible, is thrown, in the rough state, into a dissolver and treated in a manner similar to that set forth when speaking of refined alkali. The ash should be free from caustic soda because the presence of this salt spoils the appearance of the crystals, and increases the volume of mother liquor. If the ash contain any appreciable amount of sulphide of sodium, it must be cleared by introducing a small quantity of bleaching powder into the dissolver. The solution, having a specific gravity of about 1·225, is run from the dissolver into a series of settlers—large wrought-iron tanks about 10 ft. square by 7 ft. deep, well stayed with cross rods of iron. After thoroughly settling, the clear liquors are run off by any convenient siphon arrangement into a set of coolers or "cones," where they remain for a fortnight to three weeks, depending upon the state of the weather, until a pretty nearly solid mass of crystals forms. These crystallizing cones are of various shapes and description. The best form, upon the whole, is shown in Figs. 262, 263, and consists of a circular cast-iron pan, 2 ft. deep and about 9 ft. in diameter, by 1 in. thick. A hole in the centre serves to remove the mother liquor when the plug shown in Fig. 263 is withdrawn. The crystals form in the manner set forth. That which sets round the sides of the cone is called "block," and in cool weather is a solid mass 9 in. or so in thickness. Finer, larger crystals form in the centre and upon the surface, called "points," and are more esteemed. To assist these points to form, it is usual to place strips of iron or wood across the surface of the liquor. Crystals of a very large size may be "grown" by removing a few points and suspending them in fresh liquor, repeating the operation almost to an indefinite extent. When it is judged that all the available soda has crystallized out, the plug is withdrawn from the centre of the cone, the mother liquors are drained away, along a spout placed beneath, into a well or any convenient receptacle, and the crystals removed to the drainer. This is usually a long sloping bench or hopper, set with its top on a level with the bottom of the cones. At the bottom of the slope, are a series of small doors, and when these are raised, the crystals, after they have drained, are run into casks placed beneath, and packed ready for sale. The manufacture of crystals requires considerable experience and great care. The liquors must be allowed to settle thoroughly, the cones must be kept well filled, so as not to rust, and they must be emptied before the crystals "salt," or become opaque. The roof over the cones must be kept in perfect repair to prevent any disturbances of the liquor while crystallizing. Finally, the whole plant must be arranged so that a free current of cool air plays upon all sides of the cones. Neglect of this last-named precaution is a potent source both of bad crystals and bad yields. The mother liquors are pumped into a boiling-down pan, and treated exactly like refined alkali. The product—"weak alkali," as it is called—varies in strength with the amount of mother liquor. In hot weather, when less soda crystallizes out, the weak alkali will test up to 41 per cent. of carbonate. In winter, when the "crops" of crystals are large, and the mother liquors proportionately weak, the strength of the weak alkali will not run beyond 36 or 37 per cent. This product is highly esteemed by glass manufacturers, as they only pay for a small amount of carbonate of soda, and get a large amount of sulphate of soda—which of course remains in the mother liquor, and lowers the test—given to them. The mud from the settlers is washed or put upon the balls in the lixiviating tanks.

262.

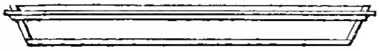


263.



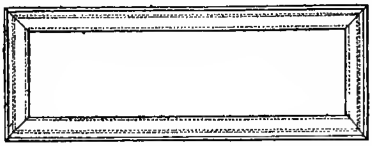
Other forms of cone are given in Figs. 264 to 269. In Fig. 270 is shown a convenient disposition of these small cones with a tramway running round each set to convey the crystals to the bench or warehouse. Occasionally rectangular pans of wrought iron are used, but these can hardly bear the picking and hammering required in order to remove the block crystal. The circular cone shown in Figs. 262 and 263 is the best. The yield from such a crystallizer is about 2½ tons.

264.



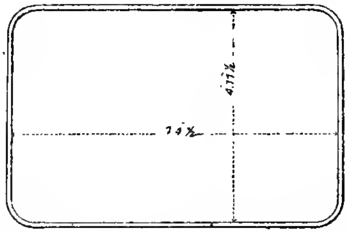
265.

266.

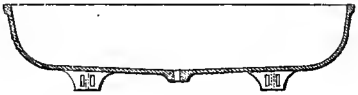


Soda crystals are packed in casks holding from 1 to 10 cwt. As a rule, 5 casks go to the ton, unless some particular size is indicated or bargained for. One cwt. casks fetch 20*s.* per ton extra price. The labour in crystal making is very small—half a dozen hands being capable of turning out 150 tons per week. The whole is usually let out to a "ganger" at about 2*s.* per ton, which includes all labour except the boiler and engine man. Cost and selling prices of soda crystals at the present time are about the same—2*l.* 15*s.* per ton. The price fluctuates very much with that of soda ash. Within the last few years, the selling price in London has been as high as 6*l.* 10*s.* per ton.

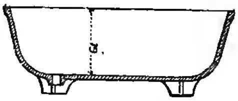
267.



268.

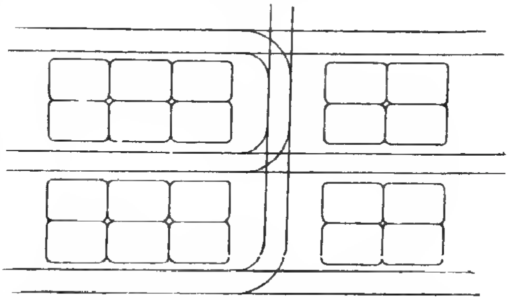


269.



In France and Belgium, it is customary to use very small crystallizing cones, not more than 2 ft. in diameter—more usually 18 in. square—and 9 inches deep. From these small cones better and purer crystals are obtained, but the labour is immensely greater. They are arranged in tiers, one above another, and only allowed to stand about forty-eight hours. The cone is then lifted up in the hands, the mother liquor poured out, and the crystals are loosened by placing the cone in warm water. They are then tilted out in one irregular block. Very often, too, the French crystals are dried in a warmed chamber without being allowed to effloresce.

270



The fact that English crystals after a short exposure to the air become opaque, and covered with a fine powdery substance, is no sign of inferior or deteriorated quality. The appearance is simply caused by a certain amount of the water of crystallization being given off and the original alkali forming upon the surface. If anything, the real value of the crystals is enhanced thereby.

Bicarbonate of Sodium. $NaHCO_3$.—This salt may be prepared by passing a stream of carbon dioxide through a cold solution of the neutral carbonate, or by exposing the crystals to an atmosphere of the gas. Bicarbonate separates in very fine crystalline grains.

This salt has only a feebly alkaline taste. It reddens litmus, and, exposed to a low red heat, loses carbon dioxide, and is converted into the neutral carbonate. It requires 10 parts of water at 15° for solution, giving off carbon dioxide when heated to 70°.

Bicarbonate of soda forms another branch of the alkali manufacture. It has been proposed to obtain it by mixing four parts of soda crystals with one part of commercial sesquicarbonate of ammonia. Upon being heated, the mixture gives off ammonia, and sodium bicarbonate remains. The usual method, however, is to act upon soda crystals with carbon dioxide, the process being as follows:—Pieces of chalk or limestone of any quality, but in not too large lumps, are loosely thrown into an underground well, or cistern, built of stone, and made tight with a good bedding of clay. In the well-cover is a man-hole, which serves as an entrance when clearing out is required, and for introducing the chalk or limestone. The weak hydrochloric acid from the roaster condenser—acid that is too weak to be utilized in the bleaching powder department—enters the cistern through a pipe near the bottom. As it rises through the chalk, it becomes saturated, carbon dioxide is evolved, and finally a neutral solution of chloride of calcium overflows through a pipe set in the side of the cistern near the top. The gas is taken off through a pipe stemmed into the cover, and conveyed to boxes in which the soda crystals are packed. These boxes, or chambers, are of various descriptions and material—stone, wood, or iron. The interior is provided with a false perforated bottom, or series of shelves, upon which the crystals are piled, the carbon dioxide permeating the whole mass. Absorption of the gas immediately takes place with considerable generation of heat, and disengagement of nearly all the water of crystallization, which collects at the bottom of the box, and is conveyed away by a U pipe, or any convenient luting apparatus. The operation is allowed to proceed until a rod passed through convenient holes in the box meets with no resistance from hard lumps of crystal soda. The finished bicarbonate is then removed in the form of opaque white lumps, retaining the shape of the original crystals. It is dried at a gentle heat in a chamber the temperature of which is kept to about 35° by any suitable arrangement of hot-air pipes. It is finally ground in an ordinary flour mill, and sifted through a fine brass or copper gauze, containing not less than 300 meshes to the inch. The finished product is a fine white impalpable powder, and is packed in 1 cwt. barrels, or 5 cwt. casks. The drying and grinding must be carefully effected to prevent loss of carbon dioxide. The mother liquor from the shelves contains a certain amount of bicarbonate and nearly all the foreign salts of the crystals. It is either added to the tank liquor, or boiled down and furnaced as weak alkali. For the bicarbonate process it is usual to employ the inferior crystals, or crystals that have been in any way damaged.

The commercial product nearly always contains a certain percentage of sesquicarbonate. It is used largely in the manufacture of baking powders, seidlitz powders, and effervescing drinks; also to some small extent in dyeing and printing as a mild alkali, where a more energetic carbonate might be hurtful. The total manufacture of the country reaches 20,000 tons per annum. At the present time, selling and cost price are about 8*l.* 15*s.* per ton. Roughly speaking, one ton of "bicarb." requires two tons of soda crystals.

Hydrate of Sodium. Caustic Soda. NaHO.—This substance is a white, opaque, hard solid, possessing a fibrous texture. Its specific gravity is 2·00. It is fusible below a red heat, and is less volatile than the corresponding potassium hydrate. It is very soluble in water, attracting moisture from the air. Upon drying, carbon dioxide is absorbed, and the hydrate becomes converted into the carbonate.

The saturated solution has a specific gravity of 1·5 at ordinary temperatures. At 18°, 100 parts of water, dissolve 60·53 parts of hydrate; at 70°, 116·75 parts; at 80°, 127·02 parts. The following table (Tünnermann) gives the amount of soda (Na_2O) in solutions of varying densities :—

Specific Gravity.	Per cent. of Na_2O.	Specific Gravity.	Per cent. of Na_2O.	Specific Gravity.	Per cent. of Na_2O.	Specific Gravity.	Per cent. of Na_2O.
1·4285	30·220	1·3198	22·363	1·2280	14·500	1·0855	6·044
1·4101	29·011	1·3125	21·758	1·2058	13·297	1·0675	4·835
1·3923	27·802	1·2982	20·550	1·1841	12·088	1·0500	3·626
1·3751	26·594	1·2843	19·341	1·1630	10·879	1·0330	2·418
1·3186	25·385	1·2708	18·132	1·1428	9·670	1·0163	1·209
1·3426	24·176	1·2578	16·923	1·1233	8·462	1·0040	0·302
1·3273	22·967	1·2453	15·714	1·1042	7·253		

The solution dissolves hair, wool, and most animal substances, also sulphur and the metallic sulphides, silica and alumina. It acts as a strong caustic, and is a powerful alkali.

It has already been stated that caustic soda is produced when water is added to the monoxide of sodium. Upon a large scale, however, it is manufactured by depriving the carbonate of its carbonic acid by the action of hydrate of calcium.

The credit of first preparing caustic soda upon a large scale is probably due to Weisenfeldt, who introduced at the St. Rollox Works, Glasgow, in 1844, a process of fusing the red liquors from the black salts with nitre. The caustic produced in this way was of good quality and white colour. Since that time the manufacture has been gradually improved, the most notable alterations being those of Gossage, in 1853, who proposed to utilize the tank liquors, fishing out the carbonate and other sodium salts during evaporation, and preparing caustic soda from the mother liquors; Stott, in 1855, who patented a process for removing the sulphides from tank liquor by means of oxide of iron, zinc, or manganese; Bakewell, in 1857, who first adopted the sheet-iron drum now in ordinary use; Thomas, in 1858, who patented the use of calcium hydrate and the oxidation of the sulphides by air; Ralston, in 1860, who first produced what is usually termed "white" caustic, by continuing the evaporation of the caustic liquors, until the iron separated out as oxide and precipitated to the bottom of the vessel, leaving a clear supernatant caustic solution. This introduction of a pure 70 per cent. white caustic was followed up by the publication, in 1872, of Pauli's process now in general use. He proposed to fuse the ordinary "cream" caustic, and keep up the heat until the oxide of iron and silicate of alumina separate out.

Soda liquor from three sources is employed in the production of caustic soda: (1) from the finished soda ash by dissolving it in hot water; (2) direct from the lixiviation of the balls; (3) from the red liquors. The first of these processes is a very roundabout and expensive plan; the dissolving of the ash is conducted in a similar manner to that described when treating of refined alkali, and the solution then simply takes the place of a pure tank liquor. Red liquors are chiefly employed in the production of *cream* caustic, on account of the impurities contained in them. The second method, the causticizing of tank liquors, is the most important process for the production of caustic soda, and to it the attention of the reader is directed.

The ball mixture is first adjusted to the process. A large excess of limestone or chalk is added, and the lime mud from the causticizer is usually worked up in the ball furnace. So the mixture may assume either of the following proportions:—

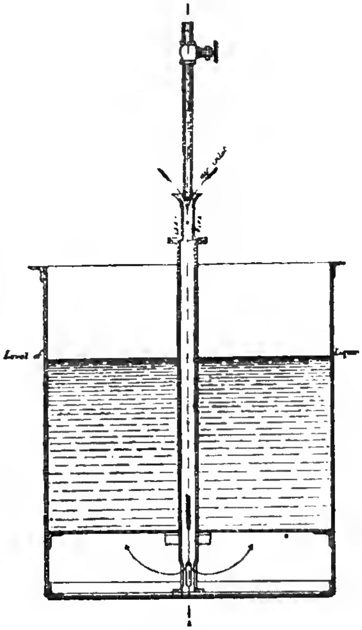
	a.	*b.*
	cwt.	cwt.
Sulphate of soda	2½	2½
Limestone	2¾	1¼
Lime mud	none	3
Small coal	1½	1½

The admixture of lime mud of course varies, and with it the amount of limestone or chalk.

The tank liquors after settling are pumped into the "causticizer." If white caustic is to be made this settling part of the operation must be thorough. The causticizers are extremely various in sizes and shapes. Often old boilers, cut in half crosswise, are used. The best apparatus, in which the liquors are both causticized and oxidized, and at the same time thoroughly agitated, is shown in

Figs. 271 and 272. But little explanation is necessary. The air oxidizes the sulphides and performs the necessary agitation of the contents of the vessel, and steam helps in the agitation and heats the liquors. Steam and air are admitted below a perforated false bottom, the plan of which is given in Fig. 272. Sometimes a previous oxidation by a special blower is resorted to before the liquors are introduced into the causticizer, and mechanical agitation, by an engine fixed to the side of the vessel, adopted. A sludge valve serves to run off the residue, or "lime mud," and the clear caustic liquors are decanted by any convenient form of siphon.

271.



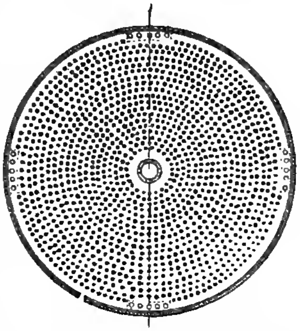
Before being causticized, it is usual to reduce the strength of the liquor to 20° or 22° Tw. Occasionally the reduction is carried down to 14°, but a liquor of 20° causticizes as readily as one at 14°, and the extra amount of water simply represents an after extra expenditure of fuel. Steam is blown in until a temperature of 100° is attained, and the mass of liquor begins to boil. A quantity of quicklime contained in a convenient cage, which keeps back all stones and big lumps, is then lowered into the vessel, and the steaming and agitation are continued until a sample of the liquor, filtered, gives no effervescence with dilute hydrochloric or sulphuric acid. A simple view of the reaction in the causticizer is the following:—

$$Na_2CO_3 + CaO = Na_2O + CaCO_3.$$

Besides this, the sulphide of sodium is converted into sulphate, and the alumina and silica are carried down with the calcium carbonate. A usual charge of well-burned lime consists of 14 cwt. per ton of 60 per cent. caustic soda, but the process is, as a rule, carried out in only a rough fashion, an excess of lime being put into the cage. About an hour and a half is required for the causticizing of a batch of liquors.

After completion of the operation, the contents of the vessel are allowed to settle for half an hour or so, during which time the insoluble portions rapidly subside. The clear caustic liquor is then drawn off, and a fresh lot of diluted tank liquor run in upon the lime mud, and the causticizing operation repeated. The mud is not removed after every operation, because a certain amount of undecomposed lime is always present, and serves to causticize the next charge to some extent. After a second operation, fresh water is run in upon the mud and the whole well agitated. The washings are run off to dilute the tank liquors, and the mud placed upon the "filter." This filter is usually a half boiler, cut longitudinally. The bottom is paved with bricks in somewhat similar fashion to that already described when explaining the construction of the lixiviating vats, a channel being left down the centre, and the bricks only loosely put in. The actual *filter* is formed by layers of coke to a depth of 9 inches or so, the bottom layer composed of good-sized lumps, the top of small pieces, and a covering of coarse sand or cinders. Over the filter are laid perforated iron plates or grids, upon which the mud is placed. When a batch is spread over the grids, it is allowed some little time to drain, and then thoroughly washed with water. The drainings and washings are utilized in diluting tank liquor, and the finally hard, close mud is shovelled out of the filter and wheeled away to the ball furnaces or mixing depôt. An ingenious mechanical contrivance is often used to assist the draining and washing of the mud. A 2-in. iron pipe is bolted upon the bottom of the boiler, below the filter, and communicates with a small air-tight tank placed upon a higher level, and connected in its turn with a vacuum pump. Upon the top of this tank is an air-cock, and set into the bottom a pipe to convey away the collected water and liquor. When a batch of mud is spread over the filter, the vacuum pump is set away, and draws up, first the drainings and then the washings. These collect in the tank and are run off to their destination. The completely washed mud should not contain above 1·5 per cent. of caustic soda. About 40 per cent. of it is calcium carbonate, 4 per cent. calcium hydrate, and 50 per cent. water. The remaining constituents

272.



are silica, alumina, oxide of iron, and magnesia, with traces of chloride, sulphate, and carbonate of soda.

To return to the caustic liquors. These are run from the causticizers into settlers, and, after clearing, transferred to a wrought or cast-iron concentrating pan. The best form is the "boat" pan already described. Two of these, or a boat pan and a boiler, may be conveniently built at the end of a ball furnace and worked with waste heat. Concentration in a boiler or wrought-iron pan is not advisable beyond 30° Tw., as the liquor eats the iron away rapidly. In any case, the liquor in these first "weak" pans should not be allowed to concentrate beyond 35° Tw. It is then transferred to cast-iron pans—usually called "strong," where evaporation is carried on till a density of 70° Tw. is attained. Heat in the "strong" pans is supplied by two fireplaces built in front of the two side flues running along the pan. A convenient arrangement is to place a "weak" at the end of a "strong" pan, and take the fire from the one under the other. Evaporation in both pans must be carefully conducted so that no boiling over may occur. If 70 per cent. caustic be required, concentration is continued up to 82° Tw. During this operation, occasionally in the "weak," but rapidly in the "strong" pans, the carbonate, sulphate, and chloride of sodium separate out, together with a little caustic soda. These salts are fished out and the liquor replenished from time to time. When the desired strength is attained the pans are allowed to cool down and the contents to settle. The clear liquor is then siphoned off into a series of settlers. The remaining salts and residue in the "strong" pans is shovelled out, drained, and worked up in the balls. The composition of these fished salts is about as follows:—

Sodium sulphate	27·00	Sodium carbonate	23·00
„ sulphide	0·10	„ hydrate	9·00
„ sulphite and hyposulphite	3·00	Insoluble	1·00
„ chloride	6·00	Water	30·00

Settling before running into the pots is often dispensed with, the liquors being allowed a further time to clear in the "strong" pans, but a better quality of caustic is made when separate settlers are used. Instead of judging by the density of the strong liquors, they are sometimes run off when a temperature of 138° (280° F.) is attained. A few pounds of nitrate of soda are usually added before running off. When previous and careful oxidation however has been performed, this second oxidation of the salts is not necessary, and involves some loss.

From the settlers, or "strong" pans, the liquor is run into the "pot." These pots are made of cast iron, about 9 ft. in diameter and 5½ ft. deep. In shape, they resemble the soda cone shown in Fig. 262, but are deeper and much stouter. They are set after the fashion of a sulphate pan, the fire not being allowed to play directly upon the pot, but escaping from an under arch and passing round the sides by a circular flue. With all precautions, the breakage of caustic pots is a constantly recurring evil. Sometimes the bottom rests upon a plate to facilitate the turning of the pot from time to time, by which operation a fresher surface is presented to the more direct action of the fire. An overhead crane is an advisable adjunct to assist in the turning or replacement of these pots, which weigh up to 6½ tons each. Instead of working a charge off in one pot, a common arrangement is to have three pots, and bale the liquor, as it concentrates, from one to another. The pots should of course be set successively one below the other. When a temperature of 121° (250° F.) is attained, the liquor begins to froth up, and a strong smell of ammonia is given off, from the decomposition of the cyanogen compounds. Soon after, at 143° (290°F.), a dirty black scum rises to the surface, and is skimmed off, very carefully if 70 per cent. white caustic be required. At 155° (311° F.) the liquor boils rapidly, and turns a very dark colour. The deposition of salts goes on, and if a 70 per cent. product be required, the pot is cooled down when a temperature of 160° (320° F.) is reached, and the salts are fished out. Concentration is continued to 224° and finally to 260°. About 182° (360° F.), the pot is very liable to boil over, and the workman in charge has to give every possible care to prevent this by heating down the froth or adding a little grease or oil. Between 200° and 260°, the liquor boils very gently, and contains at the former temperature 60 per cent., and at the latter 65 per cent. of alkali. The ammoniacal vapours, mixed with a little caustic soda which is mechanically carried off, are at this stage exceedingly irritating. The cyanides are destroyed with separation of graphite and also nitrogen. Soon all motion ceases. The pot is then covered up and the fire urged until the contents are at a red heat. This process is termed "clearing." The sulphur compounds are now finally oxidized, either by the addition of nitre, or by blowing in air. The addition of nitre must be made very carefully so as not to overdo it, or turn the caustic green. From time to time a small sample is taken out, allowed to solidify, and tested with a few drops of acetate of lead. As a rule 1 ton of caustic will require 40 lb. or so of nitre. If the pot has been over-oxidized—a trace of sulphide should be always left—a few balefuls of fresh liquor are added. Oxidation by a current of air is now very generally practised, an ordinary blowing engine being employed for the purpose, with a short quick stroke. All water is perfectly discharged from the cylinder when starting to blow, and the delivery pipe is then connected with a strong 1½ in. iron pipe, terminating in a perforated ring which is plunged into the liquor, and rests upon the bottom of the pot. The clearance of water is rendered necessary to avoid any possible explosion if it came in contact with the red-hot liquor. The same blowing engine which supplies the causticizer may be used for the finishing process. Blowing is continued for about three hours in the case of liquors which have been partially oxidized in the pans, and for about eight hours if the sulphides have been all allowed to come through. The testing with acetate of lead for complete oxidation is practised as the operation proceeds. When it is finished a sample is taken from the pot, and tested for alkali. If only 60 per cent. be required the necessary reduction is made by adding common salt in very small quantities at a time to prevent any violent deflagration. If 70 per cent. be required, the sample should test fully 72 in the pot. Anything under 70 per cent. is made into 60. After "salting," the pot is heated up again, and then allowed to stand for eight or twelve hours. The oxide of iron and aluminate of soda settle down, leaving clear caustic supernatant. If a fine quality is required this settling must be very thorough. The caustic is now ready for packing into the well-known sheet iron "drums," which hold about 6 cwt. each. The drums are ranged round the pot and filled slowly, preferably at short intervals, by means of an iron spout. This slow and intermittent filling is necessary to give absolutely full drums. The composition of 60 and 70 per cent. caustic is as follows:—

	White 60 per cent. Na_2O.	70 per cent. Na_2O.
	per cent.	per cent.
Sodium hydrate	72 to 73	82 to 89
„ carbonate	1·5	4
„ chloride	19	6
„ sulphate	5·5	5
„ silicate	0·3	0·5
„ aluminate	trace	trace

Only the clear liquor is baled out into the first set of drums. The residue, an impure caustic, is packed separately, and forms what is known as "bottoms"—an article containing from 54 to 62 per cent. of alkali—or is broken up when cool, dissolved to 48° Tw. *hot*, and the clear liquor, after settling out the iron, silica, and alumina, causticized again. Sometimes the "bottoms" are added to the red liquors, and go to make cream caustic.

Deacon has patented a process for obtaining crystals of caustic soda by evaporation until a temperature of 177° (350° F.) is attained, cooling down to 70° (158 F.), and crystallizing in cast-iron cones. The hydrate that separates has about the following composition:—

Sodium oxide	50·5	Sodium chloride	1·8
„ hyposulphite	0·5	Water	47·2

Parnell and Simpson have lately introduced a high-pressure causticizer, which seems to be a decided improvement upon the older, open plan. The waste of heat caused by the steam passing through the liquor and away from the top is avoided, and a considerable saving in fuel and labour effected.

Cream caustic is made either from roughly worked tank liquor, or red liquors—chiefly the latter. The colour of these liquors is probably due to the presence of a soluble double sulphide of iron and sodium. They are first allowed to settle well, then concentrated in any convenient self-fired pan to 70° Tw.—a temperature of 121° (250° F.) being attained. They are then allowed to cool, and the salts which have in the meantime separated, are fished out. The heat is again applied till the density reaches 95° Tw., and during this second stage, a quantity of nitre is added to oxidize the liquors. After settling a little, the liquors are run off into pans, and allowed to stand till quite clear. They are then transferred to a pot and fired until the batch tests 60 per cent., or thereabouts, for alkali. No oxidation in the pot is resorted to, and the contents are not fused as in the case of the white caustic. The whole of the pot is then baled out into drums, leaving no "bottoms." The colour, due to the presence of iron oxide, is very variable. If too red, the product is sold as inferior caustic, or worked up into white, by oxidation and fusion. Cream caustic usually contains about five per cent of carbonate, 7 per cent. of chloride of sodium, 2 per cent. of sulphate, and 15 per cent. of water. The salts from the settlers are washed and worked up in the carbonate process.

The cost of 70 per cent. caustic soda is about 11*l.* per ton; of white 60 per cent., 10*l.* per ton; of cream 60 per cent., 9*l.* 10*s.* per ton. The amount of bottoms average about 7 cwt. per 10-ton pot. 100 tons of salt cake should yield 55 tons of 60 per cent. caustic.

A few words more may be devoted to Bachet's process for manufacturing caustic soda, which produced some considerable stir ten years ago, but is now practically abandoned. It was carried out upon rather a large scale at the Walker-upon-Tyne works, and strangely enough, is based upon the old process of Dundonald and Losh, carried on in the same works eighty years ago, viz. the decomposition of salt by litharge. A mixture of 100 parts of litharge, 70 parts of salt, and 50 of lime, is ground into a paste in a mill. Decomposition ensues, chloride of lead and caustic soda being formed. The solution is pressed out, and freed from lead by filtration through hydrate of lime. It is then worked up to a 70 per cent. caustic in the usual way, the common salt which it contains being fished out during concentration. The cakes left in the press are dried at 300° to 350° F., the hydrate of lead being thereby converted into yellow oxide. The whole mass is then treated with boiling lime water to decompose the chloride, and the regenerated oxide used over again to decompose a fresh batch of salt. The reactions in this process have proved to be difficult and only partial. A considerable loss of lead also is sustained.

Such are, briefly, the details of the several branches of the soda manufacture as carried on in this country upon an immense scale. Starting from the commencement of the present century, the growth of the trade has been almost beyond belief. As nearly as possible 700,000 tons of salt per annum are worked up into sulphate, and the total statistics of the trade are probably about as follows:—2,500,000 tons of raw material, pyrites, salt, chalk, timber, coal, manganese, &c., costing 2,000,000*l.*, turn out finished products of the value of 3,500,000*l.*, even at the depressed prices of the day. The value of the plant is about 4,500,000*l.*, the number of factories about 120, and the number of hands employed about 40,000. In these estimates the allied branches of hydrochloric acid and bleaching powder, &c., are included.

Numberless other sources of soda have been proposed from time to time. Hunt and Gossage fluxed salt cake with small coal, lixiviated the sulphide of sodium cake obtained with water, and passed into the solution, heated with steam, a current of carbonic anhydride. Carbonate of soda is produced which may be crystallized out from the cooled liquors, and purified by dissolving and recrystallizing. The sulphide of sodium cake is, however, a material difficult to make, and uncertain in character. A considerable amount of soda is lost by volatilization, and the wear and tear of the plant is very great. The burning of the sulphuretted hydrogen evolved, and utilization of the sulphurous acid thereby produced for the manufacture of sulphuric acid, has been only a failure. It has been proposed in several patents to obtain sulphide of sodium in the manner described, and to manufacture caustic soda from it by the oxides of iron, manganese, zinc, or copper. Here, again, the sulphide of sodium difficulties have been insuperable. The decomposition of salt by silica and steam, by electricity, by superheated steam, and various other agencies, has formed a series of interesting but practically unsuccessful experiments upon a more or less large scale. The most likely process, excepting the ammonia method described above, consists in the extraction of soda from felspar, cryolite, and other minerals. Of the many patents bearing upon this idea, that of Julius Thomsen (1850), has been the most successfully worked. Cryolite is crushed to powder and mixed with slaked lime, or powdered chalk in large excess. These materials are then calcined at a gentle heat, for about two hours, fusion being especially avoided, and the resulting white powder is lixiviated by water. A solution of soda and sodium aluminate is obtained standing about 28° B. This is transferred to cylinders fitted with agitators, and a stream of pure carbonic anhydride passed in, which converts the soda compounds into carbonate, freeing alumina. The following equation represents, roughly, the reaction:—

$$2(Na_3AlO_3) + 3CO_2 = 3NaCO_3 + Al_2O_3.$$

The liquors are run off, the alumina is settled out, and the soda solution boiled down and calcined.

If caustic soda be required, about 15 equivalents of lime are added to 2 equivalents of cryolite, producing caustic soda, aluminate of lime, and fluoride of calcium. The decomposition is usually performed in a large upright cylinder of cast iron, heated by steam to boiling point. The mixture is thoroughly agitated and boiled for about three hours, and then settled, evaporated, fished, and calcined. Carbonate of soda may be obtained by this latter, wet, method also, by treating the liquors from the decomposers with carbonic anhydride, settling and calcining. About 20,000 tons of cryolite and allied minerals are annually consumed by this process.

It only remains to glance at some of the modifications and improvements of the soda manufacture which are engaging the attention of manufacturers. The discovery of enormous salt deposits in the Cleveland district has for many years past excited among the Tyne manufacturers the hope of procuring their supplies of salt nearer home than at present. Considerable sums of money have been spent by Messrs. Bell Brothers and Bolckow, Vaughan, and Company, in turning this discovery to practical account; but hitherto the nature of the deposits—the necessity for making an artificial brine, and the great depth at which the salt lies—has vetoed all attempts. Doubtless, before many years are past, unless the use of salt is superseded, more perfect mechanical contrivances than have yet been applied, will bring the Cleveland deposits into active competition with the brines of Cheshire and Worcestershire.

The salt question leads naturally to the consideration of a process that has been on its trial for many years with only a limited success—the ammonia soda process. So long ago as 1838, Harrison, Grey, Dyar, and John Hemming patented the use of ammonia in the production of soda, and since that time many specifications have been filed, having as their object the bringing of the discovery to the test of practice upon a large scale. The patents of Delaunay, Young, Rolland, Gossage, Schlössing, Deacon, and finally Solvay may be mentioned. All but the last named have failed to command even a moderate degree of success, owing to the delicate nature of the manufacture and the costly character of the materials employed. The simplicity of the process has, however, always tempted fresh investigators into the field, and to Solvay belongs the honour of finally establishing the manufacture upon something like a large scale. Solvay's first patents were taken out in 1861 and 1863. Previously to that time works had been established in Cheshire, at Widnes, Leeds, and Newton, in this country, by Messrs. Deacon, Gossage, Bowker, Muspratt, &c.; also near Nancy and at Puteaux upon the Continent. The Turck process was adopted at Nancy, and at Puteaux, Schlössing carried out his ideas assisted by Rolland, a scientific engineer. Solvay's works were first erected about the year 1866, at Couillet, in Belgium. About 1872, a second establishment was set up at Varangéville-Dombasle, and both works have been recently enlarged, the total output reaching about 25,000 tons per annum — 20,000 tons at Varangéville-Dombasle, and 5000 tons at Couillet. In England the only works in active operation are those of Brünner, Mond, and Co., at Northwich and Sandbach. At these two works, the turn-out of carbonate is about 10,000 tons per annum.

The process is founded upon the well-known laboratory reaction, that when carbon dioxide is passed into a solution of common salt and ammonia, bicarbonate of soda and chloride of ammonia are formed:—

$$NH_3 + CO_2 + NaCl + H_2O = NH_4Cl + HNaCO_3.$$

Or, in shorter form, bicarbonate of ammonia and chloride of sodium in solution produce bicarbonate of soda and chloride of ammonium. The former is decomposed by heat to yield neutral carbonate, the latter is, or may be, distilled with lime or magnesia, the ammonia recovered, and used over again. As a matter of fact, however, this part of the process has practically broken down, and, in the English works at least, has been abandoned. At the best a serious loss of ammonia is incurred, which tells fearfully against the costs. A thoroughly good article is undoubtedly produced, as the following analysis shows:—

Carbonate of soda	99·40	Iron and Alumina	0·03
Moisture	0·15	Lime	0·13
Silica	0·10	Magnesia	0·06
Chloride of sodium	0·13		

In this respect, the ammonia soda certainly has the advantage over the ordinary carbonate, which contains up to 7 or 8 per cent. of sodium sulphate, 0·25 of chloride of sodium, and 1 per cent. of caustic soda. It is, moreover, claimed for the process that the noxious exhalations of the Le Blanc manufacture are avoided, that there is little or no waste product to encumber and render offensive the land in the neighbourhood of the works, that the purity of the article and its freedom from caustic soda render unnecessary the manufacture of refined alkali and soda crystals, and that the absence of iron and sodium sulphate peculiarly fit it for fine glass-making. There is a great deal of truth in all this, but a good deal may be said on the other side. For many purposes, e.g. in the soap manufacture—the presence of sulphate of soda is a positive advantage and must be actually added if the ammonia soda is used. Where an article free from the ordinary impurities of soda ash is required, it can be produced in the form of refined alkali or soda crystals at a cost that is, still, lower than that of ammonia soda. Moreover, the attendant evils of the Le Blanc process, are capable of regeneration. Much has lately been done in this way, and much more will yet be accomplished. The present plant from its very roughness of structure is easily put right when any little mishap occurs, whereas the constant breaking down of the more delicate parts of the ammonia soda process seriously enhances the costs of the product. Upon this question of costs it may be stated that a ton of the purest alkali of the Le Blanc process—refined alkali—costs 6*l.* 10*s.*, against 8*l.* 5*s.* of the ammonia process, so that even allowing for the difference in strength—53 per cent. against 58 per cent.—there is still a considerable margin in favour of the former. The further consideration that the ammonia soda is a purer, as well as a stronger article, only lessens, does not remove, this disparity.

To sum up the whole:—Probably the ammonia soda will gradually supersede the *refined alkali* of the Le Blanc process. But this covers very little ground. Soda ash, crystals, and caustic soda, will probably hold their own against the new comer. And it must be remembered that improvements are daily being made in the old method. Weldon's manganese recovery process, Hargreaves' direct method of sulphate manufacture, revolving ball furnaces, and various other processes and improvements have done very much in the way of reducing costs and utilizing waste products.

The arrangements of the ammonia process differ in the various works. The best method, perhaps, is to introduce the saturated solution of common salt, testing 23° or 24° Tw., into a vessel fitted with a false bottom and saturate it with ammonia. A considerable amount of heat is generated, and the solution has to be cooled by a worm or any other convenient apparatus. It is then transferred to the absorbers—huge cylinders some 30 feet or so high—and a stream of carbon dioxide, obtained from limestone in the usual way, and washed, is introduced near the bottom. The liquid when saturated is drawn off, the bicarbonate of soda separated by filtration, washed, and passed down a tower where it meets hot air or steam and is converted into the neutral carbonate. The disengaged carbon dioxide is conveyed to the absorbers.

Utilization of Tank Waste.—Of all the evils and difficulties of the Le Blanc process, perhaps the greatest has been the enormous waste residue from the lixiviating vats, and how to deal with it. That it contains substances of great value has always been a patent fact, and many attempts at its utilization have been made. The most notable are the manufacture of hyposulphite of soda, and the various processes for the recovery of sulphur. The former will be treated of under the head of Hyposulphite of Sodium. It may, however, be mentioned here, that the demand for hyposulphite is so limited that only a small portion of the tank waste produced can ever be employed in its production. Only a portion, too, of the sulphur compounds in the waste, which form the objectionable drainings from the heaps termed "yellow liquor," are destroyed in the process. The regeneration of the sulphur has been dealt with in the patents of Gossage, Delamure, Kopp, Losh, Noble, Favre, Spencer, Mond, Leighton, Schaffner, Hoffman, Fowler, Duclos, Bell, Jullion, Mactear, and others too numerous to mention. Only four, however, those of Mond, Schaffner, Hoffman, and Mactear, have been worked with anything like success, and these only need be mentioned.

The process of Mond, patented in 1863, is the best known, and is as follows:—In addition to the tanks in ordinary use for lixiviating, one-and-a-half times as many more are provided. That is to say, six extra tanks for every set of four. In these extra tanks the waste is exposed to a strong current of air, forced through a false bottom with which the tanks are provided. This current is produced by any convenient form of fan blast, and is passed through the waste for a period of from twelve to eighteen hours, depending upon the quality and texture of the material. During the oxidation process the temperature rises to about 140° (220° F.,) and clouds of steam are given off. The surface of the waste becomes covered with bright yellow spots, their appearance being a guide to the workman as to the progress of the operation. Weak liquor from a previous lixiviation is then run upon the waste for eight hours or so, until, starting at about 18° Tw., the density falls to 10°. Water is then run on, and the product collected as weak liquor to be used for the next tank. This process of blowing and washing is repeated three times, the quantity of strong liquor obtained being less each time. If the operation be conducted in the ordinary tanks, a sufficient number of extra ones not being provided, only two blowings and washings can be got through, but the waste is then anything but exhausted. Any of the sulphur liquor left in the tanks, too, spoils the ball lixiviation. The liquors from the bleaching operation consist of sulphide, sulphite, and hyposulphite of lime, together with small proportions of similar sodium compounds. They are allowed to settle thoroughly in a series of tanks, and then run into a wooden vessel lined with lead, some 10 ft. in diameter, and 5 ft. deep, treated with weak hydrochloric acid from the condensers, and heated to 65° (150° F.) with steam. Viewed in the simplest possible form, the following reaction takes place:—

$$2CaS + CaS_2O_3 + 6HCl = 3CaCl_2 + 3H_2O + 4S.$$

The quantity of hydrochloric acid must be carefully gauged—continued till just a faint smell of sulphurous acid is apparent—and the contents of the "tub" must be well agitated from time to time. The liquors are next run into tanks where the freed sulphur settles out, and is washed, dried, and melted—usually by Schaffner's process, of which some further notice will be given. Ingenious though this extraction method is, and successful in so far as it deprives the tank waste of those constituents which make it an absolute nuisance, it must be confessed that it does not repay the expenditure upon plant, and the trouble of carrying out a delicate operation. It is, however, carried on to some considerable extent by manufacturers who, from the situation of their works, are specially compelled to guard against nuisance. Unless carefully watched, both in the oxidizing and decomposing operations, an appreciable amount of sulphuretted hydrogen is given off. The average amount of sulphur recovered is two-fifths of the total amount in the waste.

Schaffner's process is, in the matter of oxidation, very similar to Mond's, except that the waste is first separated into small heaps in the open air and left to natural oxidation for some weeks. After lixiviation of the heaps the residue is again oxidized by mechanical means, and this time in the tanks in which it has been lixiviated. After a second lixiviation, the operation of blowing and washing is a third time performed. The liquors, containing polysulphides and hyposulphites are run into a pair of stone or cast-iron cisterns, and treated with hydrochloric acid. The polysulphides are first decomposed and converted into chlorides, with liberation of sulphur and sulphuretted hydrogen. The hydrochloric acid so far is run only into one of the cisterns. After decomposing the polysulphides the acid acts upon the hyposulphites, freeing sulphur and, now, sulphurous acid. The latter passes over into the second cistern and converts all the sulphur compounds of the liquor contained therein into hyposulphites. The contents of the first cistern are freed from sulphurous acid by blowing in steam, and are then run off from the bottom and a fresh charge of yellow liquor is introduced. The hydrochloric acid is now run into the second cistern. Sulphur is freed and generated, the latter returning sulphurous acid to No. 1 cistern, and converting the polysulphides of the fresh liquor into hyposulphites. So, after the first operation, the process is continuous, sulphur and sulphurous acid being only freed, the former drawn off with the liquor and the latter returning to the other cistern to act upon the sulphides. The liquor drawn from the cisterns contains besides the freed sulphur, calcium chloride, sodium chloride, and calcium sulphate. The sulphur is freed by filtration and washed. The purification of the product has already been mentioned when speaking of Mond's process. A cylinder of cast-iron is enclosed within an outer cylinder of wrought iron, with a small space between, the whole being inclined at an angle of some 15°. The washed sulphur, mixed with a little water and milk of lime, is introduced into the inner cylinder, and steam at a pressure of 1½ to 2 atmospheres blown into the space between the cylinders. Finally entering the inner cylinder, through the charging door, it melts the sulphur and passes off through an exit pipe loaded with a suitable safety valve. A mechanical stirrer, revolving with the axis of the cylinder, materially assists in the melting operation. The fused sulphur collects in the lower part of the cylinder and is run off into moulds. The supernatant, lighter liquor is then run to waste. The addition of lime is made to neutralize any acid there may be in the mixture of sulphur and water. This process is exceedingly ingenious, and doubtless Mond has drawn a great deal upon it. Owing, however, to imperfect oxidation, only about one-half the total sulphur contained in the waste is regenerated.

Hoffman's process is, so far as the oxidation of the tank waste is concerned, exactly similar to Schaffner's. The yellow liquors, however, are treated with waste still liquor (chloride of iron and manganese), the free acid and chloride of iron decomposing the sulphides and hyposulphites. The first resulting sulphuretted hydrogen is burned, while the sulphurous acid converts the polysulphides into hyposulphite. Since the adoption of Weldon's process for the recovery of manganese from still liquors, Hoffman's process has been abandoned.

The last process to be mentioned is that of Mactear, of the St. Rollox Works. It depends upon the decomposition of the sulphides of calcium of the tank waste by hydrochloric acid in the presence of sulphurous acid. The drainings from the tank heaps, or the waste itself (old or new) ground into a milk with water, are treated with a solution of sulphurous acid in water, and hydrochloric acid. The sulphurous acid solution is obtained from the combustion of pyrites, or refuse sulphur, the product being passed up wooden towers packed with coke, down which a stream of water is run. The solution mixes with the yellow liquors on its way to the decomposing vessel, the polysulphides are converted into hyposulphites, and the whole is treated with hydrochloric acid with the result already described when describing other processes for the regeneration of sulphur. During decomposition the temperature is kept at 63° (145 F.) by passing in steam. Mactear's process certainly has the advantages of a more perfect purifying of the waste, and a lower cost of sulphur over its rivals. The detailed cost of one ton of sulphur is as follows:—

	Quantity.			Cost.
	cwt.	qrs.	lbs.	*s.*
Pyrites sulphur	8	0	25	16·03
Salt	35	1	18	28·33
Vitriol	29	3	27	45·00
Coal	114	2	7	25·20
Repairs		..		4·00
Wages		..		38·50
				157·06
Deduct sulphate of soda ..	39	0	21	96·01
Net cost of 1 ton of sulphur				61·05

A plant to produce 30 tons of sulphur per week costs about 2000*l.* Mactear states that he obtains about 90 per cent. of the sulphur contained in the waste, or drainings, using the one or the other as may best suit—when the drainage is plentiful old waste, when small the fresher material.

Acetate of Sodium.—See Acetic Acid and salts.

Arsenate of Sodium.—This salt is used to a considerable extent in calico-printing, as a "dung" substitute. Formerly the dunging, or fixing of the mordants, was accomplished by passing the cloth, after being dried, through a bath of cow-dung, the alkaline quality of which neutralized the acid of the mordant, and promoted its fixation. The exceedingly variable quality of cow-dung, however, led to various attempts after substitutes, and those now most commonly used are the arsenate, arsenite, silicate, and phosphate of sodium, or a mixture of these salts. Arsenate of sodium is prepared by fusing white arsenic with sodium nitrate. The arsenious acid is first dissolved in caustic soda, and the arsenite formed. Nitrate of soda is then added, and the mixture heated in a reverberatory furnace to dryness, with evolution of ammonia and nitric oxide.

These dung substitutes are better in every way than the old material. They not only "cleanse" the cloth, but throw down the metallic base of the mordant, neutralizing the acid. The arsenite enters into the composition of certain "ageing" liquors.

Messrs. Roberts, Dale, and Co. prepare alkaline arsenates by adding a solution of arsenic acid to nitrate of potassium or sodium.

Borates of Sodium.—See Borax.

Chloride of Sodium.—See Salt.

Hyposulphite of Sodium.—This salt is an article in somewhat limited demand for paper-making, photographic and printing purposes. In paper-making it is used to discharge the bleach from the pulp, going by the name of "antichlor." In printing, it forms a red mordant with muriate of alumina, hyposulphite of alumina being produced. When the mordanted cloth is heated, the alumina is precipitated with liberation of sulphur and sulphurous acid.

There are several ways of procuring hyposulphite of soda. Very fine crystals may be obtained by passing sulphurous acid gas, well washed, into a strong solution of sodium carbonate, forming neutral sulphite of soda, and then digesting the solution with sulphur at a gentle heat. Upon a fairly large scale, the usual method of manufacture is the following:—Tank waste is exposed in small heaps to the influence of the air for about a fortnight, the heaps being turned over occasionally. The sulphide of calcium is thereby converted into hyposulphite. The heaps are then thrown into small wooden tanks and treated with water. The dissolved hyposulphite of calcium is drawn off and agitated with a quantity of impure carbonate of soda—refuse soda ash, or the sweepings of the alkali houses, &c. The hyposulphite of calcium is thereby converted into hyposulphite of sodium, calcium carbonate being precipitated. The hypo-solution is pumped up into a wrought-iron pan about 15 ft. long, 3 ft. deep, and 5 ft. wide, heated by an underneath fire. Here it is concentrated and run into deep iron pans to cool. An impure sodium hyposulphite crystallizes out, which is removed and dissolved in the mother liquors of the succeeding crystallization. This solution is concentrated and again crystallized. The hyposulphite now separates out in clearer and almost colourless crystals. They are, however, redissolved, the solution concentrated in a small open pan, filtered through cloths, and run into small circular glass basins ranged upon long wooden benches. Here pure, colourless, transparent crystals form. The basins are then inclined so that the mother liquor falls into a spout running below the bench, and after being left for a while to drain, the crystals are removed to the drying house, heated by a hot air flue running underneath a series of sloping benches. Here they are dried at a gentle heat, and packed into casks holding from 1 to 5 cwt. If the final crystals dry with an opaque yellowish appearance, they are returned to the second dissolving stage. For paper-making purposes, a sufficiently good article may be produced from the second crystallization, in iron vessels. In place of the glass basins described, square wooden boxes lined with sheet indiarubber may be used, or small wrought-iron basins. Upon the whole, however, the glass crystallizers are the best.

A modification of this process has lately been introduced, consisting in the treatment of tank waste liquor, or red liquors, with sulphurous acid obtained by the combustion of pyrites. The sulphurous gas is passed up a wrought-iron tower packed with coke, down which the liquors are run. This process yields a cheaper product, and is therefore upon the whole to be preferred. The older method has been abandoned on account of its high cost—caused principally by the heavy repairs of pans, &c., and the limited demand for the salt. About 10 tons per week are being made at the present time in Liverpool, by the sulphurous acid process.

A third process that has never been worked upon any large scale, consists in reducing sulphate of soda to sulphide by calcination with coal, lixiviating the product and passing sulphurous acid gas into the settled solution. The sodic hyposulphite is then crystallized out by concentrating and cooling.

Iodide of Sodium. NaI.—This interesting salt is contained in the mother liquors of kelp. Its preparation is similar to that of the corresponding potassium salt. It crystallizes from aqueous solutions at 20° in anhydrous cakes. At lower temperatures, the crystals present the appearance of rhombic prisms, and contain two equivalents of water of crystallization. When heated, the hydrated crystals melt in their water of crystallization and become anhydrous. At a high temperature the salt volatilizes, giving off a portion of its iodine. The crystals are deliquescent, and readily soluble in water, 100 parts at 14° dissolving 173 parts of salt. The following table gives the different densities of various solutions at 19·5°.

Quantity of NaI in 100 parts of Water.	Specific Gravity of Solution.
24·5	1·1752
50·2	1·3362
79·4	1·4962
115·6	1·6659
149·7	1·8047

Iodide of sodium forms a source of iodine. It is occasionally used in dyeing and printing, but the colours formed are all more or less unstable.

Nitrate of Sodium. (Fr., *Nitrate de Soude ;* Ger., *Würfelsalpeter.*) Formula, $NaNO_3$. Synonyms, nitre, cubic saltpetre, Chili, or Chili saltpetre.—Nitrate of sodium occurs very largely as a natural product, chiefly in South America. Large beds of it, many feet in thickness, associated with gypsum, common salt, sulphate of sodium, &c., are met with, extending 40 leagues at one stretch. The richer deposits lie about 2 ft. below the surface of the ground, and are covered with "costra," a hard rocky formation of somewhat similar constitution to the crude nitrate of soda below, and utilized to some extent in the manufacture. The nature of the salts, and remains of old shells, point to a time when the land was submerged in the ocean, or some huge inland salt lake. From the method of deposition, it will be readily understood that the constitution of the crude salt—"caliche"—varies widely. It has been found in the natural state as pure as the following :—94·3 per cent. of nitrate of sodium; 2 per cent. of chloride; 0·2 sulphate of potassium ; 0·4 nitrate of potassium; 0·9 nitrate of magnesium; 2 water, and 0·2 insoluble matter. About an average sample will test as follows :—

Nitrate of sodium	43·00	Chloride of sodium	16·00
Sulphate of sodium	26·00	Iodide of sodium	0·50
„ calcium	2·00	Insoluble	7·00
„ magnesium	trace	Water	5·50

Nitrate of sodium crystallizes in obtuse rhombohedra, whence its name of cubic saltpetre. Its specific gravity is 2·24. It is hygroscopic, and readily soluble in water ; in 1·25 parts at 0° C., in 1·136 parts at 18·75°. According to Schiff the composition of solutions of various densities and at 20·2° is as follows :—

Specific Gravity.	Percentage of Nitrate.	Specific Gravity.	Percentage of Nitrate.
1·0342	5·16	1·1478	20·66
1·0698	10·33	1·2326	30·89
1·1075	15·50	1·3806	46·48

The salt is also soluble in alcohol, the solubility decreasing rapidly with an increase in the strength of the solvent. Thus spirit containing 10 parts of alcohol in 100 dissolves 39·5 parts of nitrate, but with 80 parts of alcohol only 2·7 parts of nitrate are found in 100 parts of spirit. At about 310°, nitrate of sodium fuses, solidifying upon cooling to a white mass. At a strong red heat, oxygen gas is given off and then free nitrogen, the salt being reduced first to nitrite, and finally to a mixture of protoxide and peroxide. It deflagrates with charcoal and other combustible bodies, but somewhat slowly.

Commercial nitrate of sodium is obtained from the caliche in the manner already described when treating of the potassium salt—by lixiviation in boiling water, concentration, and crystallization. As usually brought into this market, it contains from 92 to 97 per cent. of nitrate, with from 1 to 2½ per cent. of sodium chloride, a little sulphate of soda—occasionally iodide and iodate—lime, magnesia, and water. To obtain really pure crystals, the commercial salt is crushed and heated with nitric acid. The chlorides present are thereby destroyed, and by dissolving and recrystallizing perfectly pure nitrate separates out.

The Peruvian and Chilian deposits are practically inexhaustible, sending out about 300,000 tons of commercial nitrate per annum. Probably the plant and apparatus now established could readily double the produce if desirable. The price varies very much with the state of the freight market, and with a constantly renewed threatening on the part of the Peruvian Government to impose a heavy duty upon the trade. At the present time the market value is about 13*l.* per ton. England and France are the largest consumers of nitrate, taking about one half the total production.

The uses of this salt are many and important. From it is made the bulk of nitric acid, being preferred to nitrate of potash on the score of cheapness, and because it produces about 7 per cent. more nitric acid weight for weight—60 as against 53. To some small extent sodium nitrate takes the place of potassium nitrate in the manufacture of explosives, but on account of its hygroscopic propensity and slow deflagration it forms but a poor substitute for the more energetic potassium salt. It is very extensively employed as a fertilizer, and in the artificial preparation of nitrate of potassium by decomposition with chloride of potassium in the manner described elsewhere. Perhaps the greater part of the salt is consumed by the manufacturers of sulphuric acid in the "potting" operation. Finally, it enters to some small extent into certain medicinal preparations. It may be mentioned that as a manure the virtue of nitrate of sodium lies in the nitrogen, of which about 15 per cent. is contained in good samples. It is principally used as a top dressing to grasses and young corn.

Phosphates of Sodium.—Several compounds of phosphoric acid and sodium are known. The principal are the subphosphate, the neutral phosphate, the pyrophosphate, and the metaphosphate. The first has $Na_2HPO_4+12H_2O$ as a formula, with a crystal density of 1·618. It is prepared from the neutral phosphate by adding caustic soda in excess to its solution, until a soapy feeling is apparent. The crystals effloresce in the air, are soluble in 5 parts of water at 15·4°, and melt in their own water of crystallization at a higher temperature. The salt is not of much importance.

The neutral phosphate is the best known compound of phosphoric acid and sodium. From it the other phosphates are made, and it enters into a variety of medicinal preparations. Its formula is $Na_2HPO_4+12H_2O$. Specific gravity of the crystals 1·525; of the anhydrous salt, 1·619. Phosphate of soda forms large colourless transparent crystals, which effloresce in the air, and are soluble in 4 parts of cold water. They fuse in their own water of crystallization at 37°. The solution has a faintly alkaline reaction. The best method of preparation is to treat powdered bone ash with about four-fifths its weight of dilute sulphuric acid, and neutralize with sodium carbonate until a faint alkaline reaction is visible. The solution is then concentrated, the insoluble phosphate of calcium settled out, and the clear liquor run into suitable vessels to cool and crystallize.

The pyrophosphate of sodium—$Na_4P_2O_7$, specific gravity 1·836, and the metaphosphate—$NaPO_3$—are of no interest outside of the laboratory.

What is commonly called "microcosmic salt," a phosphate of soda and ammonia, is used to some considerable extent in laboratory operations as a flux. It crystallizes in large transparent prisms, which are efflorescent in dry air, and is prepared by mixing 2 parts of water, 1 part of ammonium chloride, and 7 parts of the neutral phosphate. Chloride of sodium is deposited, and the clear solution is drawn off, concentrated, and crystallized.

Silicate of Sodium.—The soluble silicates, both of potash and soda, are of considerable importance in the arts and manufactures. They are all more or less soluble in boiling water, and when heated pass through a peculiar viscous stage before liquefying. Fused with other silicates of the earths or metallic oxides they impart this viscidity, also their transparency, and destroy all tendency to crystallization upon cooling. To these properties the transparency, and ductility of glass when cooling, are due.

The silicates are prepared by igniting sand, or any other convenient form of silica, with caustic potash or soda, or with the carbonates or nitrates of these bases which contain volatile acids. A monosilicate is produced by fusing 1 part of silica with 2¼ parts of potassium carbonate. The product deliquesces in the air, and is readily soluble in water. Treated with hydrochloric or nitric acid, the monosilicate parts with a portion of its silica in gelatinous flakes. What is commonly called "soluble glass" is a silicate with the formula $Na_2O, 4SiO_2$. This was the original silicate of Fuchs of Munich, who first published in the year 1825 a paper describing the preparation of various silicates of potassium and sodium, and the applications thereof. Soluble glass is prepared by melting together 8 parts of sodium carbonate, or 10 parts of purified pearl-ash, with 15 parts of pulverized quartz and 1 part of powdered charcoal. A black glass is obtained, after heating for five or six hours, which is cooled, pulverized, and boiled to dissolution with five or six times its weight of water for about three hours. The boiling is continued until a specific gravity of 1·26 is obtained. A voluminous gelatinous precipitate is produced—consisting of "water glass"—by adding to the solution ammonia, nitrate of sodium, and many other salts. Soluble glass is largely employed in fixing and preserving fresco colours, in the manufacture of various earthenwares, and in the preservation and preparation of stone. This last purpose, however—the production of artificial stone—has not been a success, on account of its high cost.

A double water glass, consisting of a mixture of potash and soda silicates, has received some considerable application. It is prepared by fusing together 100 parts of quartz and 121 parts of

Rochelle salt; or a mixture of quartz, nitre, and saltpetre; or, again, 100 parts of quartz, 28 parts of pearl-ash, 22 of carbonate of sodium, and 6 of powdered charcoal.

The silicates of sodium have been employed to a considerable extent as a dung substitute, in dyeing and printing. For this purpose the solution should be as neutral as possible. They have also been used to fix ultramarine blue and other pigments. The colour is well ground up with the silicate solution at about 90 Tw., and printed without any thickening.

Stannate of Sodium. Formula, Na_2O, SnO_2.—Prepared by dissolving stannic acid in soda lye; this salt crystallizes out from the solution on heating. It is less soluble in warm than in cold water, 100 parts of water dissolving 67·4 parts of the salt at 0°, and 61·3 parts at 20°. There are several methods of preparation, the best being that invented by Young. Native peroxide of tin is pulverized and fused with a solution of caustic soda. The mixture is thoroughly agitated, and a temperature of 516° (600° F.) kept up, the tin, or oxide of tin, combining gradually with the soda. When it is judged that the operation is complete, the contents of the pot are baled out into another vessel, cooled, broken up, and dissolved in water. The iron and other foreign metals being insoluble in the alkali readily settle out, and a clear solution of pure stannate is obtained. This may be used in the state of solution, or evaporated to dryness, or concentrated and crystallized.

Another method of preparation is to heat 22 lb. of caustic soda in an iron crucible to a low red heat, then add 8 lb. of sodium nitrate and 4 lb. of common salt. When the whole is fluxed, 10 lb. of block.tin are introduced, and the mixture kept well agitated. It soon assumes a dark colour and thick consistency, with free evolution of ammonia—from partial decomposition of the water of the caustic soda and of the nitrate. Finally, the mass becomes red-hot. It is then baled out, cooled, broken up, and treated in the manner already described.

A third method is to fuse tin ore with 1½ time its weight of sodium nitrate, and pass a current of steam over the mixture, which is kept in constant agitation. Nitric and nitrous fumes are given off and condensed. The stannate left in the pot is treated as before described. If chloride of sodium be substituted for the nitrate, hydrochloric acid is obtained as a bye-product.

Haeffely's process for the production of sodium stannate may be finally noticed. Litharge (80 lb.), or red lead (54 lb.), is heated in an iron pot with about 45 lb. of 70° caustic soda in solution, and sufficient water or weak washings added to hold the stannate when formed in solution. Plumbate of lead is first produced, and in this is suspended 16 lb. of feather block tin. The lead precipitates presently as a spongy metallic mass, and stannate of soda remains in solution. When all the tin is dissolved, the contents of the pot are transferred to a suitable vessel, and the lead settled out. The clear solution is drawn off, and worked up into a pure stannate. The lead precipitate is washed—the washings being put into the decomposing pot—and heated nearly to redness upon an iron plate. It is thereby oxidized, and re-converted into litharge or red lead. Instead of the lead compound, hydrated sesquioxide of iron, or binoxide of manganese, manganate of soda, or other oxidizing substances may be used.

Stannate of sodium is largely used in the dyeing and printing trades, going usually by the name of "preparing salts." Its value and its applications depend upon its giving up stannic acid when an acid is mixed with it. The method of preparing the cloth is to pad it in a stannate solution and then pass it through a souring bath. The sulphuric acid forms sulphate of soda with the base of the salt, and the stannic acid remains attached to the cloth. The value of stannate of soda depends upon the amount of tin which it contains. In the hydrated or crystalline salt, there should be 25 to 27 per cent. of water and no common salt. This latter substance is often added as an adulterant.

Stannite of Sodium.—To prepare this salt 4 lb. of chloride of sodium, 13½ lb. of caustic soda, and 4 lb. of feathered block tin, are fused in an iron pot. The mixture is kept well stirred and boiled to dryness. Stannite of sodium is used in dyeing and printing to some slight extent.

Sulphate of Sodium. (Fr., *Sulfate de Soude;* Ger., *Schwefelsaures Natron.*) Formula, Na_2SO_4. Synonyms, Glauber's salts, salt cake.—Sulphate of sodium was discovered about the year 1658, by Glauber. It occurs in nature in certain mineral waters—e. g. at Cheltenham—and in the minerals mirabilite and glauberite. The former is found in Spain, Hungary, Switzerland, Austria, and many other countries, also in lava, and as an efflorescence upon the Caspian steppes. Glauberite is a mixture of crystallized sulphate with gypsum, and occurs in Spain, Bavaria, Chili, &c.

Sulphate of sodium when pure, crystallizes in right rhombic prisms, with either 8 or 10 equivalents of water. The crystals effloresce in the air, and lose water. Heated, the salt fuses into a white solid, again becoming liquid at a red heat. The crystals are soluble in twice their own weight of cold water at 15·5°, the solubility rapidly increasing with an increase of temperature up to 33°. At that point, 100 parts of water dissolve 117·9 parts of the salt, corresponding to 52 parts of anhydrous sulphate. Beyond 33°, the solubility decreases, and a portion of sulphate is deposited. At 100°, water dissolves its own weight of the salt. It is insoluble in alcohol.

Sodium sulphate is a bye-product in many chemical operations—in the preparation of nitric acid, sal-ammoniac and magnesium carbonate; also in the slags from various glass processes. Its production by the action of sulphuric acid upon chloride of sodium, has already been set forth. Pure sulphate may be prepared in this way from pure materials, any excess of sulphuric acid being neutralized by carbonate of sodium, after dissolving the sulphate in water. The solution is then filtered, concentrated, and crystallized. A pure salt is also obtained from the evaporation of sea-water, in the process of Balard and Merle described when treating of potassium chloride. The magnesium sulphate and sodium chloride at a low temperature react upon one another, and produce magnesium chloride, which remains in solution, and sodium sulphate which crystallizes out. The bye-product obtained from the nitric acid and hydrochloric acid processes, called respectively "nitre cake," and "salt cake," is of very poor quality, containing large amounts of either free acid or free salt. A good Glauber's salt is produced from the "pan scales" of salt works, by separating the sodium sulphate from the gypsum with hot water. The solution is concentrated and run into shallow coolers of wood lined with lead. As soon as the liquors are cool a rod is drawn along the vessel. This causes small single crystals to separate out which afterwards grow into masses of fine needle-shaped prisms. The liquor is kept shallow to prevent the formation of too large crystals. On the other hand any violent agitation causes very small crystals to separate out—"flour" as they are termed. When the liquors are cold, the mothers are siphoned off, the crystals washed with cold water, and dried at a very gentle heat.

Besides the enormous consumption of sulphate of sodium in the alkali manufacture, the salt is used in the production of various kinds of glass—chiefly bottles; in certain medicinal preparations; and, to some small extent, in dyeing and printing, to fix lead mordants preparatory to dyeing them orange or yellow.

Tungstates of Sodium.—Several of these salts are well known, but only two possess any interest to the general reader—the neutral salt, Na_2O, WO_3, and an acid salt, $3Na_2O$, $7WO_3$. The latter is prepared by fusing the neutral salt with tungstic oxide, and boiling the product with water; or by fusing wolfram with one-third its weight of sodium carbonate. It forms large prismatic crystals, specific gravity 3·8, containing 16 atoms of water of crystallization, and with a bitter saline taste. The crystals effloresce in dry air, giving off nearly all the water of crystallization and being converted into the anhydrous salt. It melts at a red heat and is readily soluble in water.

The neutral salt is the tungstate commonly used. With two atoms of water, it crystallizes in colourless transparent rhombic tables, which have an alkaline reaction and bitter taste. The crystals do not effloresce, are soluble in 4 parts of cold water and half the quantity of hot, and insoluble in alcohol. At a red heat, the water of crystallization is given off and a fused mass of the anhydrous salt is obtained forming a colourless liquid, which assumes a crystalline appearance when cold.

Upon a fairly large scale, the neutral tungstate is produced from an ore of tungsten, called *wolfram*, found in considerable quantities in Cornwall, usually associated with tin ores. The mineral, a native tungstate of iron and manganese, is mixed with sodium carbonate, or salt cake, and thrown into a reverberatory furnace. The proportions vary considerably with the amount of wolfram present in the stone operated upon, which must be ascertained by actual analysis. The mixture is then regulated according to the chemical equivalents, about 10 cwt. forming an ordinary charge for the furnace. The batch is worked thoroughly after the manner of a sulphate furnace, soluble tungstate of soda, tin and manganese oxides, and silica being produced. When the charge is cooled, it is broken up and lixiviated with water in small wooden vats. Tungstate of soda is dissolved, drawn off, concentrated in iron pans, and crystallized.

The chief use of this salt is in calico printing and dyeing, where it takes the place of stannate of soda to some extent. Its cheapness is, however, the chief recommendation. Some of the tungsten compounds give good colours, but they are exceedingly unstable. It has also received some application in rendering ladies' dresses and other fibrous materials uninflammable. J. L.

ALKALIMETRY.—Alkalimetry is the name given to the various processes by which the quantity of real alkali in alkaline salts and solutions is determined. As in the case of acidimetry, these determinations may either be made by gravimetric or by volumetric analysis.

Gay-Lussac's alkalimetric method is based upon a titrated solution of carbonate of soda with a corresponding solution of sulphuric acid. Instead of the carbonate, it is preferable to use caustic soda, in order to avoid the objectionable interference caused by the presence of carbonic acid. The indicator employed is a solution of litmus, made by digesting about 10 grammes of litmus in half a litre of distilled water for a few hours; the clear liquid is decanted and kept in a small, tightly-corked wash-bottle, from which a few drops can be expelled when required. A very small quantity of dilute nitric acid may be advantageously added to the solution, in order to produce a violet colour, which increases the sensibility of the indicator.

The standard solution of sulphuric acid contains 49 grm. of real sulphuric acid per litre, and may be made in the following way :—Thirty cc. of the pure acid, of sp. gr. 1·840, is diluted with water in a beaker, and the mixture is left to stand; when perfectly cool, it is washed into a litre flask, and diluted to the containing-mark. The solution is next to be tested with a standard solution of carbonate of soda, containing 53 grm. of the pure carbonate to the litre, carefully weighed and measured. Ten cc. of this latter solution is placed in a beaker with a little distilled water and a few drops of the litmus solution, and the acid is run in carefully and slowly until the point of saturation is reached. If more than 10 cc. be required, the solution is too weak; if less, it is too strong, and it must either be strengthened or diluted, as the case may be, until 10 cc. of each solution *exactly neutralize each other*. In order to ensure perfect accuracy, larger quantities of the two substances, say 50 or 100 cc., may be employed, when the difference, if any, will be more readily detected.

If it be preferred to use caustic soda instead of carbonate, about 42 grm. is to be dissolved in water (about 800 cc.); the above test is applied, and small quantities of water are added until equal volumes exactly correspond. All these solutions are kept in tightly-stoppered bottles.

The method of procedure is as follows:—The necessary quantity of alkali being weighed or measured, as the case may be, it is diluted with distilled water in a flask, and enough litmus is added to produce a distinct, but not too deep, blue colour. The acid from the burette is then run in until the contents of the flask have been changed to a bright red colour. In order to expel the carbonic acid, the flask is boiled until the blue colour reappears; the acid solution must now be run in, a few drops at a time, with continued boiling, until, by the addition of a single drop, a distinct pink colour is produced. In order to obtain a very accurate result, it is well to run in an excess of acid, boil the liquid well, and then add, drop by drop, the standard alkaline solution until the liquid suddenly changes from pink to violet blue. The quantity of the alkaline solution required to effect this change is subtracted from the volume of acid originally run in, and the exact volume of standard acid required to neutralize the amount of alkali previously taken from analysis is thus determined at once.

It will be readily seen that the converse of this process may be applied to the estimation of the amount of *acid* contained in acid liquids or mixtures (see Acidimetry).

Mohr recommends the use of oxalic acid instead of sulphuric or hydrochloric, because it is more readily weighed than a liquid, and because its solution may be kept for a much longer period than these without undergoing change in strength. The weight required is 63 grm. per litre of water.

In making determinations of the quantity of alkali contained in samples of crude carbonate of potash and soda by gravimetric or weight analysis, the apparatus used in acidimetry, and shown in Fig. 2, may be employed. The weighed carbonate is dissolved in warm water in the flask A, and a quantity of acid, more than sufficient to neutralize the alkali, is placed in the short tube in the interior. The apparatus is then weighed, and the tube *d* closed by a plug of wax; the flask is tilted gently, so as to cause the acid to flow into the flask upon the carbonate. Carbonic acid is thus evolved, and the apparatus should be gently warmed until the evolution of gas completely ceases. When this is the case, the plug is removed, air is drawn through, and the whole is again weighed. The loss indicates the quantity of carbonic acid evolved, from which the amount of real carbonate contained in the sample may be calculated at once. The acidity of the solution, at the conclusion of the test, should be determined by adding a drop of litmus solution; if it be not acid, more acid must be added, and the operation repeated.

The apparatus devised by Fresenius and Will, and shown in Fig. 3, may also be employed in making alkalimetrical estimations. It is used in precisely the same way as in acidimetry. The alkali to be tested is carefully weighed, and dissolved in water in the flask A; concentrated sulphuric acid is placed in the flask B, and the apparatus is accurately weighed. After closing the end of the tube *c*, suction is applied to the tube *a*, so as to draw over a small quantity of air from A into B through the tube *b*; on withdrawing the lips, the pressure of air forces a little of the acid over into A, by which means the alkali is decomposed. This is continued until the evolution of carbonic acid ceases, when heat is applied gently for a few moments. Air is then drawn through, and the apparatus is cooled and weighed. The loss in weight gives the amount of carbonic acid evolved, as in the previous case.

Works for reference:—Fresenius's 'Quantitative Analysis'; Sutton's 'Volumetric Analysis.'

ALLOYS.—Alloys are compounds of two or more metals; thus brass is an alloy of copper and zinc, type-metal an alloy of lead and antimony, bell-metal and gun-metal alloys of copper and tin. Although there are fifty-one metals known to the chemist, only a comparatively small number have been largely used for industrial purposes. Every alloy may, however, be regarded as a new metal, since it generally possesses properties entirely different from those of the metals of which it is composed. Hence, as the properties resulting from the combination of two metals rarely represent the mean of those metals, it is impossible to foretell the nature of a new alloy, and it is therefore probable that such combinations may be made as will adapt themselves to every imaginable want created by our advancing civilization. Only a few hundred alloys have been prepared up to the present time, and only about sixty have really been carefully studied, although there is scarcely a limit to the number which might be made; so that there is yet much to be learnt on this interesting and important subject.

All true alloys consist of compounds of metals in their definite chemical proportions; it is, however, a matter of some difficulty to obtain them in a separate state, owing to the readiness with which they dissolve in the excess of that metal which may happen to preponderate. There are some alloys also in which the constituent metals seem to be merely mechanically mixed, but these are exceptions rather than the rule. Alloys possess the properties which are characteristic of metals, such as metallic lustre, conductivity of heat and electricity, and, in a greater or less degree, malleability, ductility, and tenacity. The specific gravity of an alloy appears to depend upon the amount of cohesion or attraction exerted by the constituent metals for one another, and to bear no reference whatever to the high or low specific gravity of those constituents in their free state. The specific heat of alloys was found by Regnault to be very nearly the mean of the specific heats of the constituents. The following rule for obtaining the specific heat of alloys gives a very close approximation to the figures obtained by actual experiment:—Multiply the specific heat of each constituent into the percentage amount of it contained in the alloy, and divide the sum of the products by 100. Alloys are not as a rule such good conductors of heat and electricity as the metals of which they are made. Their fusibility does not at all depend upon that of their constituents, but is generally greater; thus the melting point of tin is 230° C. and that of lead 334° C., whereas a compound of 5 parts of tin and 1 part of lead melts at 194° C., and a compound of equal parts of both metals melts at 241° C. The ductility of alloys is usually slightly less than that of their most ductile constituent, and their hardness is greater than the mean hardness of both or all the metals. The tenacity of an alloy is often much greater than that of either of the metals alone.

To make an alloy, the metals must be melted together. This operation may be carried on in an earthenware crucible when very small quantities are being operated upon; but when large masses of metal have to be dealt with, as in the case of statues, &c., a reverberatory furnace must be employed to effect the melting. As a rule, the least fusible metal is placed in the crucible first, unless it be in very small quantity and will dissolve readily in the other metal, in which case it goes in last; and if, as in the case of zinc, the volatilization of the metal be extremely rapid, it is introduced only the moment before the fused mass is ready to be poured into the mould or other receptacle. The order in which the metals are melted has a material effect upon the nature of the resulting alloy, for it has been proved by experiment that the latter often possesses different properties when the mixing has taken place in a different order. The fused metals should be kept thoroughly well stirred up until the mixture is complete; otherwise the heaviest metal will sink to the bottom of the mass, and the alloy will not be of uniform composition. This contingency is sometimes avoided by melting the mass a second time. When three metals have to be united together, they should first be melted in pairs, and afterwards together.

The following are some of the most important alloys which have yet received an extensive application in the arts and manufactures.

Aluminium Bronze.—This alloy is composed of 90 parts of copper and 10 parts of aluminium. It is a definite chemical compound, and was discovered by Dr. Percy. It was manufactured for many years at Washington, near Newcastle, by J. L. Bell, who obtained it by melting the copper in a crucible made of plumbago or some other highly refractory material; the correct proportion of metallic aluminium was added to the melted copper, the two metals uniting with evolution of intense heat. Aluminium bronze is of a yellow colour, resembling gold; it is extremely hard and tenacious, and possesses great malleability and strength. It is admirably adapted for the working parts of machinery where great durability is required, and has a power of withstanding compression nearly equal to that of the best steel. Aluminium bronze containing 10 per cent. of aluminium possesses the maximum degree of hardness, strength, and tenacity; a larger proportion of aluminium renders the alloy weak and brittle. It has a specific gravity of 7·68; the weight of a cubic inch is 0·276 lb., and the tensile strength 32 tons per square inch.

Bell-metal.—An alloy of copper and tin in proportions varying from 3 to 5 parts of copper to 1 part of tin. It is of a yellowish-grey colour, hard, brittle, and sonorous, and exhibits a fine-grained fracture. Cooled suddenly from a red heat, it becomes soft, but regains its hardness after being re-heated and cooled very slowly. Small house-bells are usually made of an alloy of 2 parts of copper with 1 part of tin; but for larger bells a higher proportion of copper is needed.

The larger the proportion of copper in the alloy, the deeper and graver is the tone of the bells formed from it. The addition of tin, iron, or zinc causes them to give out a sharper tone. Where the quality of the tone is the chief object sought after, care must be taken to employ only commercially pure copper. The presence of lead, even in very small quantities, affects prejudicially the sonorousness of the alloy. Silver, on the contrary, is said to give sweetness to the tone. The presence of this metal has been detected in many old church bells, which, according to tradition, were cast from crucibles into which articles of silver had been thrown as votive offerings.

The composition of some varieties of bell-metal is shown below :—

(1) Copper, 39 parts ; tin, 11 parts. This is the most sonorous of all the alloys of copper and zinc. ('Standard.')

(2) Copper, 77 parts ; tin, 21 parts ; antimony, 2 parts. Paler, and inferior to the above. ('Founders' Standard.')

(3) Copper, 4 parts ; tin, 1 part. Very deep-toned and sonorous.

(4) Copper, 3 parts ; tin, 1 part. Used for church and other large bells.

(5) Copper, 17 parts ; tin, 8 parts. Best proportions for house-bells, hand-bells, &c.

(6) Copper, 72 parts ; tin, 26½ parts ; iron, 1½ parts. Used by the Paris houses for the bells of small clocks.

Brass.—Brass is perhaps the most useful and important alloy known. Its composition varies widely with the uses for which it is intended, but its constituents are copper and zinc, usually in the proportions of nearly two parts of the former to one part of the latter. Brass may also contain small quantities of tin and lead. The qualities which render this alloy so valuable may be briefly enumerated as follows :—It is harder than copper, and consequently better able to resist wear and tear. It is very malleable and ductile, and therefore admits of being either rolled into thin sheets, shaped with the hammer, drawn into fine wire, or raised by stamping into objects of various forms. It is readily fusible, and therefore easily cast at a lower temperature than copper. It resists the influences of the atmosphere better than copper, although, if unprotected by lacquer or varnish, it rapidly tarnishes and blackens on exposure to the air. Finally, brass has a fine yellow colour, and is capable of receiving a beautiful polish.

The malleability of brass varies with its composition and with its temperature ; it is also affected, to a sensible degree, by the presence, even in minute quantities, of certain other metals. Some varieties of brass are malleable only when cold, others only when hot, and others, again, are never malleable. At a temperature just below its fusing point, brass, like copper, is brittle, and may be powdered in a mortar. Alloys of copper and zinc present a great variety of colour, ranging between the reddish hue of the former and the bluish-white of the latter ; the transition is gradual, and passes through all the intermediate stages of yellow. The following table represents the intensity of colour, hardness, and fusibility possessed by these different alloys :—

Atomic Constitution.	Percentage Composition.	Colour of Fracture.	Inverse order of Hardness.	Inverse order of Fusibility.	Nature of the Brass.
Cu	100·00	Tile red	20	15	Copper.
10Cu + Zn	90·72 + 9·28	Reddish-yellow, 1	21	14	Similor, &c. Several of these are malleable at high temperatures.
9Cu + Zn	89·80 + 10·20	„ „ 2	20	13	
8Cu + Zn	88·60 + 11·40	„ „ 3	19	12	
7Cu + Zn	87·30 + 12·70	„ „ 4	18	11	
6Cu + Zn	85·40 + 14·60	Yellowish-red 3	17	10	
5Cu + Zn	83·02 + 16·98	„ „ 2	15	9	Bath-metal.
4Cu + Zn	79·65 + 20·35	„ „ 1	16	8	Dutch brass.
3Cu + Zn	74·58 + 25·42	Pale yellow	14	7	Rolled sheet brass.
5Cu + 2Zn	71·43 + 28·57	..	..	..	Ordinary brass.
2Cu + Zn	66·18 + 33·82	Full yellow 1	13	6	British brass.
19Cu + 12Zn	60·00 + 40·00	„ „	15	6	Muntz's metal.
Cu + Zn	49·47 + 50·53	„ „ 2	12	6	German brass.
Cu + 2Zn	32·85 + 67·15	Deep yellow	10	6	„ (watch-makers').
8Cu + 17Zn	31·52 + 68·48	Silver white 1	5	5	Very brittle. Too hard to file or turn. Lustre nearly equal to speculum metal.
8Cu + 18Zn	30·30 + 69·70	„ „ 2	6	5	„
8Cu + 19Zn	29·17 + 70·83	Silver grey 1	7	5	„
8Cu + 20Zn	28·12 + 71·88	Ash grey 3	3	5	Brittle
8Cu + 21Zn	27·10 + 72·90	Silver grey 2	9	5	„
8Cu + 22Zn	26·24 + 73·76	„ „ 1	8	5	Very brittle
8Cu + 23Zn	25·39 + 74·61	Ash grey 4	1	5	Barely malleable.
Cu + 3Zn	24·50 + 75·50	„ „ 1	2	4	Brittle.
Cu + 4Zn	19·65 + 80·36	„ „ 2	4	3	White button metal.
Cu + 5Zn	16·36 + 83·64	Very dark grey	11	2	Brittle.
Zn	100·00	Bluish-grey	23	1	Zinc.

During the process of stamping brass, it must be hardened or tempered from time to time. At the end of the process it has lost its colour, owing to the formation of a coating of oxide during the tempering operations. This coating is easily removed by plunging the metal into nitric acid, and then washing it thoroughly with water. A brilliant metallic surface is thus produced, ready to receive the customary layer of lacquer or varnish. This cleansing process is known as "dipping." If the brass contain any impurities, dipping will not impart to it a brilliant surface. The colour produced by dipping varies according to the strength of the acid ; this is due, it is believed, to the fact that the metals constituting the alloy are acted upon to a greater or less degree by acids of different degrees of dilution. The operation of dipping is performed in the following way:—The object, coated with a black coat of oxide, is plunged into nitric acid containing 1 part of the pure acid to 7 or 8 parts of water. It is allowed to "pickle," as it is termed, in the acid solution until the crust can be detached by rubbing the surface of the metal gently with the finger, when it is withdrawn, and washed immediately in water. It is next dipped into a much stronger acid solution, where it remains until the "curd" appears, or until the surface of the metal is entirely covered with minute bubbles of gas. This solution should be about twice as strong as the one previously used. The brass must then be washed with a plentiful supply of water, and roughly dried in cold sawdust. It is afterwards dipped, with the particles of wood still adhering to its surface, into strong nitric acid, where it remains only a few moments, then rinsed with a little water, and immediately afterwards thoroughly washed with water containing argol in solution. It is finally dried in hot sawdust, after which the surface is ready for the lacquer or varnish.

Brass which is required for rolling into sheets should contain no antimony, as this metal renders the alloy very brittle, and extremely liable to crack. That which has to be turned contains invariably a small proportion of lead, usually about 2 per cent; this addition is made when the crucible containing the fused metals is taken out of the furnace. The following is an analysis by Chaudet of a brass which is well adapted for this purpose:—

Copper	65·8	Lead..	2·15
Zinc	31·8	Tin	0·25

The presence of tin was believed to be accidental. Brass required for engraving upon should always contain a little tin, in order to render it sufficiently firm.

Brass may be made either in a crucible, as in the ordinary Birmingham brass-foundries, or in a reverberatory furnace. The crucibles commonly used are circular, and made of fireclay; they are about 1 ft. in depth, 8 in. in diameter at the top, and 6 in. at the middle, internal measurements; they are also ¾ in. in thickness at the top, and 2 in. at the bottom; they contain about 84 lb.

The copper is first placed in the crucible, and the zinc is added to it bit by bit with much caution, as soon as the former metal is in a state of incipient fusion. The ingots of copper should be heated to redness before being put into the crucible. In Birmingham, the chief seat of the brass manufacture, the furnaces employed are square, their dimensions being 10 in. in the side and 24 in. in depth. Those used in London are circular in form. The flue between the furnace and the chimney should be narrow, and should lead out from the top of the furnace; its dimensions vary with those of the chimney, and with other conditions. Coke of the very best quality is the fuel employed. When the mixture is well fused together, the cinders are removed, and it is poured, if required for casting, into sand-moulds; if, on the contrary, it is to be used for rolling, it is cooled in close iron ingot-moulds, previously heated, oiled, and dusted lightly over in the interior with powdered charcoal. A loss of zinc invariably occurs by volatilization, which is always taken into consideration when weighing out the metal.

The following formulæ show the composition of different varieties of brass:—

For *fine brass*, an alloy of 2 parts of copper with 1 part of zinc is the correct proportion; the metals are melted separately, poured suddenly together, and united by vigorous stirring. By slightly raising the proportion of copper, as 7 parts of copper and 3 parts of zinc, a bright-yellow and malleable alloy is obtained. More copper still, as 4 parts of copper and 1 part of zinc, yields a metal of darker colour than the last.

For *malleable brass*, good proportions are: copper, 33 parts; zinc, 25 parts; or, copper, 3 parts; zinc, 2 parts. These are malleable when hot.

For *button brass*, an alloy of 8 parts of copper and 5 parts of zinc is commonly used by the Birmingham makers, under the name of "platin." An alloy paler in colour, and used for the common buttons, consists of 25 parts of copper, 20 parts of zinc, 3 parts of lead, and 2 parts of tin.

Brass for *fine castings* is an alloy of 62 parts of copper, 35 parts of zinc, 2 parts of lead, and 1 part of tin; this is rather pale and brittle. An alloy used for the same purpose, and of a deep, rich colour, consists of copper, 90 parts; zinc, 7 parts; tin, 2 parts; lead, 1 part.

For *gilding*, good proportions are: copper, 64 parts; zinc, 32 parts; lead, 3 parts; tin, 1 part.

For *soldering*, an alloy of fine brass, 12 parts; zinc, 6 parts; tin, 1 part, melted together, is most commonly employed.

For *turning*, the proportions are: fine brass, 98 parts; lead, 2 parts, both melted together; or, copper, 65 parts; zinc, 33 parts; lead, 2 parts.

For *wire*, an alloy of copper, 72 parts; zinc, 28 parts, is commonly used; this alloy must be afterwards hardened by tempering.

Bronze.—This alloy has been known and employed since very remote ages. It was used exclusively by the ancients for making swords and other sharp instruments, for coinage, statues, and many other useful and ornamental purposes. It is composed of copper and tin, sometimes with the addition of a little zinc and lead. Great variations are made in the proportions of the two chief constituents, according to the nature of the application for which it is destined. For statuary, the proportions used by the Brothers Keller, the most noted bronze-founders of modern times, were copper, 91·40; zinc, 5·53; tin, 1·70; and lead, 1·37. The bronze coinage of this country contains 95 parts copper, 4 of tin, and 1 of zinc. The addition of a little zinc to the alloy is an advantage, but too much diminishes its tenacity; lead is objectionable, owing to its tendency to sink after casting, thus destroying the homogeneity of the alloy. The metals should be melted rapidly to prevent loss of metal by oxidation, and the melted mass should be covered with a layer of charcoal, and kept constantly stirred. The operation is generally carried on in refractory crucibles, heated in a reverberatory furnace of suitable form. The cooling in the moulds must be as rapid as possible, in order to prevent the separation of the metals.

The composition of different kinds of bronze is shown below:—

For *edge-tools:* copper, 100 parts; tin, 14 parts. When properly tempered, this alloy is capable of taking nearly as fine an edge as steel.

For *gilding:* (1) copper, 82 parts; zinc, 18 parts; tin, 3 parts; lead, 2 parts. (2) copper, 83 parts; zinc, 17 parts; tin, 2 parts; lead, 1 part.

For *medals:* (1) copper, 89 parts; tin, 8 parts; zinc, 3 parts. This alloy takes a sharp impression by stamping. (2) (Chaudet) copper, 95 parts; tin, 4 or 5 parts.

For *mortars:* copper, 93 parts; lead, 5 parts; tin, 2 parts.

For *statuary:* (1) copper, 88 parts; tin, 9 parts; zinc, 2 parts; lead, 1 part. (2) copper, 82½ parts; zinc, 10½ parts; tin, 5 parts; lead, 2 parts. Nearly the proportions of the celebrated statue of Louis XV. (3) copper, 90 parts; tin, 9 parts; lead, 1 part. (4) copper, 91 parts; tin, 9 parts.

German Silver.—This alloy is much used as a substitute for silver; it is composed of copper, zinc and nickel. The proportions of the three metals are various; when intended as a substitute for silver, they are 50 parts copper, 25 parts zinc, and 25 parts nickel; castings, such as candlesticks, &c., are made of an alloy containing 60 parts of copper, and 20 parts of each of the other two constituents. German silver is harder than silver, and susceptible of a high polish. It is of a greyish-white colour; fuses at a bright-red heat, the zinc being volatilized in the open air. The three metals, in a state of division and intimately mixed, may be melted together in a crucible, having copper at the top and bottom. The whole is covered with a coating of fine charcoal and strongly heated in an air furnace with a strong draught. Or the copper and nickel may be first melted in the crucible, fragments of hot zinc being afterwards added. To aid the fusion of the nickel, the mixture should be well stirred. Lead is sometimes added, and also iron, for the purpose of whitening the alloy.

Actual analyses of various kinds of German silver show the following proportions:—

(1) Copper, 50 parts; nickel, 20 parts; zinc, 30 parts. Very malleable, and takes a high polish.

(2) Copper, 50 parts; nickel, 26 parts; zinc, 24 parts. Good imitation of silver.

(3) Copper, 41 parts; nickel, 18 parts; zinc, 41 parts. Rather brittle.

(4) Copper, 50 parts; nickel, 25 parts; zinc, 25 parts. Good imitation of silver; white and malleable.

(5) Copper, 60 parts; nickel, 25 parts; zinc, 20 parts. For rolling and wire; very tough and malleable.

(6) Copper, 40½ parts; nickel, 31½ parts; iron, 2½ parts; zinc, 25½ parts. Made from Hillburghausen ore; equal to best Chinese sample.

(7) Equal parts of copper and nickel. Recommended by Pelouze as being superior to any alloys containing zinc.

(8) Copper, 55 parts; nickel, 24 parts; zinc, 16 parts; tin, 3 parts; iron, 2 parts. White metal spoon, sold as German plate.

Gun-Metal.—This is also an alloy of copper and tin, in the proportions of 8 or 9 parts of the former to 1 of the latter. It is a very tenacious metal, easily forged, and possesses a considerable amount of resistance; it is the metal of which large guns were formerly cast, whence the name. In order to make a perfectly uniform alloy, the melted metals should be cooled in the moulds as rapidly as possible. Gun-metal of the above composition has a specific gravity of 8·462; the weight of a cubic inch is 0·304 lb., and its tensile strength 15·2 tons to the square inch.

Muntz's Metal.—An alloy of copper and zinc. For rolling into sheets, the best proportions are 60 parts copper to 40 parts zinc; but for other purposes its composition is variable. It was patented in 1832 by Muntz of Birmingham, and has since superseded copper for sheathing the bottoms of ships. The alloy is made in a reverberatory furnace, the copper being melted first and the zinc added afterwards. The fused mixture is run into clay-lined vessels and ladled from these, while still hot, into iron ingot-moulds. It is rolled into sheets or worked into bolts at a red heat; the sheets are subsequently "pickled" in weak sulphuric acid, and then washed with water.

Pewter.—Pewter is an alloy of lead and tin, containing sometimes copper, zinc, or antimony. There are three distinct kinds of English-made pewter, viz. (1) Plate pewter, used for dishes and plates, an alloy usually made without lead, and containing principally tin with small quantities of antimony, bismuth, and copper; (2) Trifle pewter, employed for casting drinking vessels, &c., an alloy of 82 parts tin with 18 parts lead, and containing variable quantities of antimony; and (3) Ley pewter, containing 4 parts tin and 1 part lead, employed for the larger wine measures. Owing to the poisonous nature of lead, which is apt to be dissolved by the acetic acid always present in beer, the French government has prohibited the use of an alloy containing more than 18 per cent. of lead; if the lead be not in excess of this quantity, the tin seems to have the effect of neutralizing its poisonous properties. When made in the above proportions, pewter has a specific gravity of 7·8, so that any specimens of a higher specific gravity than this may be known to contain too high a percentage of the heavier metal. Pewter is a soft metal resembling tin, but duller and darker in colour. Plates and dishes are hammered out of the variety called plate pewter, but drinking vessels, &c., are always cast into moulds from the common variety.

Solders.—Alloys employed for joining metals together are termed "solders," and they are commonly divided into two classes: hard and soft solders. The former fuse only at a red heat, but soft solders fuse at comparatively low temperatures.

The most easily fusible metal known is an alloy of 2 parts bismuth, 1 part tin, and 1 part lead; tin is the most fusible of these three metals, melting at 228°, but this alloy melts at 93°, or a little below the boiling point of water. By diminishing the quantity of bismuth in the alloy, the point of fusion may be made to vary between 100° and 200°, and thus it is an easy matter to form a solder which shall fuse at any required temperature between these limits, for electrical purposes, steam-boiler plugs, &c. The following are the best recipes for the common solders:—

Hard spelter solder: copper, 2 parts; zinc, 1 part. This solder is used for iron-work, gun-metal, &c.

Hard silver solder: silver, 4 parts; copper, 1 part; or, silver, 2 parts; brass wire, 1 part. These are employed for fine work; the latter is the most readily fusible.

For *brass-work:* equal parts of copper and zinc; or, for the finer kinds of work, silver, 1 part; copper, 8 parts; zinc, 8 parts.

For *steel:* silver, 19 parts; copper, 3 parts; zinc, 1 part.

For *pewterers:* bismuth, 2 parts; lead, 4 parts; tin, 3 parts; or, bismuth, 1 part; lead, 1 part; tin, 2 parts. The latter is best applied to the rougher kinds of work.

For *jewellers:* fine silver, 19 parts; brass, 10 parts; copper, 1 part; or, for joining gold, gold 24 parts; silver, 2 parts; copper, 1 part.

Type-metal.—This alloy, used for printers' type, is composed of 6 parts lead, and 2 parts antimony. It is of a blackish-grey colour, and is softer than tin and copper, but a little harder than lead.

Platinum is capable of being united to most other metals, the alloys being as a rule more fusible than platinum itself. It occurs in nature in combination with a rare metal called *iridium*, with which it is often alloyed; the resulting metal is called *iridio-platinum*, and, though still malleable, is harder than platinum, and unattacked by aqua regia. It is also much less readily fusible than platinum itself, and is therefore likely to be largely used in place of this metal for the purpose of electric lighting by incandescence. Silver is hardened, but rendered brittle, by being alloyed with very small quantities of platinum.

The following is a table of the proportions of the various metals in the alloys most commonly employed in the arts and manufactures.

	Cu.	Zn.	Sn.	Pb.	Sb.
Metal for frictional parts of locomotives (extremely hard)	87	5	8	..	..
Bearings of carriages	97	3	..	..	..
Bearings of driving wheels, also for steam-engine whistles giving a clear sound	80	2	18	..	..
Steam-engine whistles giving a deep sound	81	2	17	..	..
Cross-heads of connecting-rods	82	2	16	..	..
Cylinders of pumps, valve-boxes, and taps	88	2	10	..	..
Eccentric collars	84	2	14	..	..
Bearings of axles and trunnions; eccentric collars	84	2	14	..	..
	85	2	13	..	..
	84	7	9	..	..
	68	4	28	..	.

	Cu.	Zn.	Sn.	Pb.	Sb.
Pistons of locomotives	88	9	3	..	..
	84	8·4	2·9	4·7	..
Axle-boxes	88	2	10	..	..
Mathematical instruments, arms of balances	90	2	8	..	..
Machinery, bearings, &c.	67	..	14	19	..
Steam-engine whistles	30	..	18	..	2
Metal to withstand friction (Stephenson)	79	5	8	8	..
Rivets	64	24·6	3	9	..
Metal for coffins	15	..	40	45	..
Metal to withstand friction	2	..	72	..	26
Cylinders of pumps	7	72	21	..	..
Metal for bearings of locomotives	2	..	90	..	8
White brittle metal (for buttons, &c.)	10	6	20	..	64

The proportions of the several ingredients in the various alloys given above must be regarded as only approximative in many cases. Every manufacturer adopts the proportions which experience has taught him to be the most suitable for the purposes for which the alloy will be used, or perhaps, in some instances, which accident or caprice first led him to make use of. If we take, for example, half a dozen samples of that variety of pewter known as Britannia-metal from as many different manufacturers, we shall probably find that we have half a dozen alloys widely different in their composition, though similar in appearance, and applicable to the same uses. The same remark holds good of such alloys as pinchbeck, tombac, Manheim gold, and some others. More than this, even the products of the same manufactory may vary considerably in composition at different times, when these products are not required to possess in a high degree any given quality. It is therefore not surprising that the proportions published in many works are so absurdly different and contradictory. Thus we have, for example, one acknowledged authority giving the composition of Britannia-metal as equal parts of brass, tin, antimony, and bismuth; while another gives the composition as 150 parts of tin, 3 parts of copper, and 10 parts of antimony, omitting the bismuth altogether. It would be easy to find a third authority giving a composition of this alloy widely different from the above two. From out of this chaos it is impossible to evolve anything like order, or to give information that shall not be at variance with all that has preceded it from sources acknowledged to be trustworthy. Hence the recipes we have given must be regarded as having only an approximate value generally, though for the cases we have in view they are exact, i. e. they are the proportions which have been actually adopted in practice. Many of them have been ascertained by analysis of the finished product, while others have been obtained from sources that are worthy of confidence.

ALUM. (Fr., *Alun;* Ger., *Alaun.*)—The name alum is applied in science and the arts to a class of double salts containing sulphate of alumina (see Alumina), which plays the part of an acid, in combination with an alkaline sulphate, representing the base. The salts are composed of one equivalent of each of these constituents, together with 24 equivalents of water of crystallization, and are represented by the following formulæ:—

Potash alum	$AlK(SO_4)_2 + 22H_2O$.
Ammonia alum	$Al(NH_4)_2SO_4 + 12H_2O$.

Other alums exist in which the acid is represented by the oxides of chromium, iron, and manganese, which are isomorphous with alumina; and besides potash and ammonia, the base may be constituted by soda, alumina, or the oxides of iron and chromium. These acids and bases are found to replace each other singly, and also, in combination with one another, to form alums of more or less complexity. In each case, however, 12 equivalents of water are required for the constitution of the crystal.

The only alums known in commerce are those of potash and ammonia, the latter being now manufactured very extensively. Ordinary potash alum, commonly called "alum," to distinguish it from ammonia alum, consists of white, diaphanous, octahedral crystals, of the following percentage composition:—

Potash	9·95	Sulphuric acid	33·71
Alumina	10·83	Water	45·51

The crystals have a specific gravity of 1·71; they are slightly efflorescent in the air, have an acid, astringent taste and an acid reaction. One hundred parts of water at 0° dissolve about 4 parts, and at 100° about 360 parts of the salt. When heated, the crystals melt in their water of crystallization, the solid residue left on cooling being called *rock-alum.* Calcined at a low red heat, alum loses the sulphuric acid combined with the alumina, the latter remaining behind with the sulphate of potash. If the heat be raised to whiteness, the sulphate of potash is decomposed also, the residue consisting of a mixture of potash and alumina. A neutral variety of this alum, commonly called cubical or Roman alum, on account of the cubical form of the crystal, is made by boiling 12 parts of ordinary alum with one part of slaked lime in water. It is preferred to the common variety for some dyeing and printing operations, as it does not affect certain colours. It is prepared in the neighbourhood of Rome from a mineral called *alumite*. According to Schmidt, its percentage composition is:—

Potash	9·04	Sulphuric acid	33·95
Alumina	11·48	Water	45·61

Ammonia alum possesses many of the properties characteristic of ordinary alum, and may be applied to all the purposes for which the latter is used. When heated to redness, both the sulphuric acid and the ammonia disappear, nothing but pure alumina being left; this latter substance is often prepared on a large scale by this method (see Alumina). One hundred parts of water at 0° dissolve about 5 parts of this alum, and at 100°, 420 parts. Its percentage composition is:—

Ammonia	3·89	Sulphuric acid	36·10
Alumina	11·90	Water	48·11

Of the remaining alums, the most important is soda alum; it is, however, not yet largely used in industrial operations, on account of the difficulty experienced in obtaining the crystals in a pure state; it is analogous in constitution to the two above-mentioned alums.

Alum is found native, like saltpetre and carbonate of soda, in volcanic districts in the form of a white incrustation upon rocks and stones. In this form it occurs in the neighbourhood of Naples; in the Solfatara; in Sicily, and in the south of France. In these districts it has long been the custom to collect the white efflorescence and dissolve it in water; this solution is allowed to stand in order that mechanical impurities may settle out, and it is then evaporated in leaden pans by the natural volcanic heat of the soil, without the necessity of having recourse to fuel. The residue recrystallized affords a very pure product, which was for many centuries the only alum known in commerce. At the present time, native alum forms only a very small portion of that consumed in this country. The chief source is a bituminous clay called "alum shale," found in Norway, Bohemia, and the Hartz; in England, near Whitby; and in Scotland, near Glasgow. The shale undergoes a series of processes by which the sulphate of alumina is extracted and combined with sulphate of potash or sulphate of ammonia, in solution, as the case may be, the resulting mixture being evaporated down to obtain crystals of alum. In the neighbourhood of Manchester, large quantities of the coal-shales are employed for this purpose. Another important source of alum is the alum rock or alum stone, found in volcanic districts, and produced by the action of sulphurous vapours upon aluminiferous rocks. The mineral is calcined in large kilns, and then lixiviated with boiling water, the lye being evaporated down and crystallized out; this process is only employed in the volcanic districts, where the rock is extensively found. Other sources are clays of different kinds, notably fireclay and pipeclay; the minerals cryolite and bauxite are also used, and various mineral phosphates. These contain alumina only, and require the addition of both sulphuric acid and an alkaline sulphate in order to produce alum. All shales and clays selected for the manufacture of alum should be as free as possible from carbonate of lime and from iron.

Owing to their extensive application as mordants in the processes of dyeing and calico-printing, and to the comparatively economical methods which have been introduced from time to time for their preparation, potash and ammonia alum have risen to a position of much commercial importance during the last thirty years. There are also other applications of this useful substance to be mentioned later, in which the quantity annually consumed is rapidly increasing.

THE MANUFACTURE. 1. *From Alum Rock.*—This rock, which occurs in the volcanic districts around Naples, and at Muszag in Hungary, is composed principally of silica and sulphate of alumina. Analyses of four samples taken from different places have shown it to have the following composition:—

	From Tolfa, by Klaproth.	From Beregszag, by Klaproth.	From Montione, by Descotil.	From Mont d'Or, by Cordier.
Silica	56·5	62·3	..	28·4
Alumina	19·0	17·5	40·0	31·8
Sulphuric acid	16·5	12·5	35·6	27·0
Potash	4·0	1·0	13·8	5·8
Water	3·0	5·3	10·0	3·7
Oxide of Iron	..	..	..	1·4

The rock is piled up in heaps in a furnace or kiln, and heated to low redness, the flames being led in an upward direction through the mass. After a short time the sulphate of alumina is decomposed into alumina, oxygen, and sulphurous acid, and the calcination is known to be complete when white vapours of this latter gas exhibit themselves. The calcined mass is then placed in cisterns, and constantly moistened with water for three or four months, during which time it crumbles up and is converted into a soft mud. This mud contains a considerable quantity of alum which is dissolved out with water, the liquor being evaporated down until it attains a specific gravity of about 1·114 at 45°. The crystals of alum which separate out on cooling are of a reddish tinge, owing to the presence of iron, and must be subjected to recrystallization, which yields the salt in a very pure state. This product is much valued in commerce. Cubical or Roman alum is prepared in the same manner, except that the pure mineral, alumite, is employed, instead of the alum rock.

2. *From Aluminous Shale or Alum Ores.*—These are a kind of schismatic clay, containing much iron pyrites and bituminous matter, and very closely resembling the ordinary clay slate. Large beds are found in the Scandinavian peninsula; in Bohemia, the Hartz, and the mountainous districts of the lower Rhine. In Great Britain, they occur at Hurlet and Campsie, near Glasgow, and near Whitby, in Yorkshire. For many years, these places were the chief seats of the manufacture, alum works at the latter place having been established since the year 1600. The following table represents the composition of different shales from Glasgow and Whitby :—

	Whitby (Richardson).			Campsie (Ronald).	
	Top Rock.	Bottom Rock.		Top Rock.	Bottom Rock.
Sulphide of iron (*pyrites*)	4·20	8·50	Sulphide of iron (*pyrites*)	38·48	9·63
Silica	52·25	51·16	Silica	15·41	20·47
Protoxide of iron	8·49	6·11	Protoxide of iron	..	2·18
Alumina	18·75	18·30	Alumina	11·64	18·91
Lime	1·25	2·15	Lime	2·22	·40
Magnesia	·91	·90	Magnesia	·32	2·17
Oxide of manganese	trace	trace	Oxide of manganese	..	·55
Sulphuric acid (SO_3)	1·37	2·50	Sulphuric acid (SO_3)	..	·05
Potash	·13	trace	Potash	..	1·26
Soda	·20	trace	Soda	..	·21
Chlorine	trace	trace	Carbon or bituminous matter	28·80	(?)
Water	2·88	2·00	Coal	..	8·51
Coal	4·97	8·29	Water	..	8·54
Loss	4·60	(?)	Loss	3·13	1·59
	101·00	99·91		..	..

The process is conducted in the following way :—The mineral is piled up in heaps, which are moistened every now and then with water; it then becomes heated, and gradually crumbles up into a pulverulent state. This is usually carried on, either wholly or in part, on the floor of the mine. If the ore fails to attain this condition upon mere exposure to air and moisture, it must be broken to pieces and piled up in heaps upon a bed of brushwood and small-coal, in layers of about 4 feet in thickness. Fire is then applied, and when the mass is thoroughly kindled, fresh quantities of the broken shale are thrown upon it until it attains a considerable height and thickness. The bituminous matter contained in the shale is generally sufficient to produce the required heat provided that it be continued long enough; in some cases, when the shale is not very bituminous, it is necessary to employ slack or sawdust in order to assist the combustion. Calcination is then effected by means of a smothered fire; care must be taken to prevent the mass from becoming fused and from disengaging sulphurous vapours. To this end, the mass is after a time covered with a coating of calcined ore, or "mantled," as it is termed, in order to shelter the burning heap from wind and rain, and to moderate the heat and prevent it from progressing too rapidly, thus causing the sulphur to be lost by volatilization. When the process is complete, a thicker "mantling" is laid on, and the mass is allowed to cool, when it is found to have lost about one-half in bulk and to have become open and porous. It is then laid open to the air and moistened again with a little water. The time occupied by the process of calcination varies, according to the size of the mass and the state of the weather, from three to nine months.

The next part of the process consists in digesting the calcined ore in warm water in a large stone or brickwork cistern, until the soluble portion has been totally extracted; the lye is then run into another stone or brick cistern, placed in close proximity to a reverberatory furnace, so that the flame and products of combustion are led over the surface of the liquor in the cistern.

When it has been boiled down until it stands just above the point at which crystals are deposited, it is run off into coolers in which crystals of sulphate of iron separate out. The mother liquor from these is run off into another cistern. When pure potash alum is required, a saturated solution of chloride or sulphate of potash is run into the cistern; but for ammonia alum, impure sulphate of ammonia (usually in the form of gas-liquor) is employed; the ordinary alums of commerce are, however, generally mixtures of the two. The correct quantity of these solutions has been added when the addition ceases to produce a cloud or milkiness in the cistern. To produce 100 parts of alum from the sulphate of alumina liquor, the theoretical quantities are:—

Chloride of potash	15·7 parts.
Sulphate of potash	18·4 „
Sulphate of ammonia	13·9 „

The exact proportions required may be determined by testing a small quantity of the aluminous liquor before introducing the alkaline solution, but in practice the above indication is a sufficient guide. The mixture is next allowed to become perfectly cold, when the mother liquor is pumped or siphoned off, and the residue, consisting of alum in fine crystals, or "flour," is well drained, and washed several times with a little cold water. The alum flour is then placed in a leaden boiler, and dissolved in boiling water. While still boiling, or having just ceased, the liquor is run into large casks or tubs. These tubs are built in pieces; at the bottom is a large flagstone, and the pieces, each of which is lined with lead, are built round it, and kept in their places by strong iron hoops screwed together. The diameter of the tubs is greater at the bottom than at the top, and they are about 6 ft. high. When the hot solution is drawn off into these tubs, they are covered with wooden covers. In about four days, the sides of the tubs may be taken down, as there will then be a sufficient thickness of alum to hold the mother liquor. It now stands in this condition for fourteen days more, and a hole is made near the bottom of the block through which the mother liquor is drained out. This block is afterwards broken up and packed into casks for the market. The bottom part, which is not so pure as the rest, is usually redissolved.

3. *From Coal Shales* (Spence's process).—By this process, which was patented by Peter Spence, of Manchester, in 1845, about two-thirds of the alum produced in this country is manufactured. The shales used, which are black owing to the presence of from 5 to 10 per cent. of carbonaceous matter, are found underlying the coal seams in South Lancashire. They are calcined in the following way:—

A number of air-channels, one or two feet apart, are constructed by laying two parallel lines of bricks, each line about 4 in. distant from the other, and then laying bricks across the top of these so as to form a channel of about 4 in. section, the bricks being laid loosely in order to permit the air to pass freely between them. Upon these channels, one workman throws a layer of burning coal, while another covers the coal with the more bituminous shales, broken up small. When combustion commences, more shale is laid on gradually, care being taken not to put out the fire, and at the same time keeping down the heat to low redness, the object being to render the alumina of the shale soluble in sulphuric acid. If the temperature be raised too high, the clay will vitrify, and the alumina become insoluble. Calcination usually occupies about ten days, and when complete, the shale is of a pale red colour. It is then placed in long tanks or pans, made of sheets of cast-iron, screwed together, lined with lead, and about 40 ft. long, 10 ft. wide, and 3 ft. deep. Before being charged with shale, the bottoms of these pans are covered with tiles, about 9 in. square, in order to prevent the shale from coming in contact with the lead, because the heat would dry the shale and burn the lead. The charge of each pan is about 20 tons. The shale is then digested with about 10 tons of sulphuric acid, of sp. gr. 1·25. During four or five days the contents of the pan are kept at a temperature of 105° (220° F.), partly by means of a fire underneath the pans, and partly by the introduction of ammonia in the form of gas-liquor, which is boiled down in boilers. Steam is also driven in, in order to maintain the temperature. From time to time the liquor is tested to see if it be of the proper strength. A small quantity is put into a square, shallow leaden dish, and according to the time it takes to crystallize, it is known whether the liquor is ready to be drawn off into the coolers. These coolers are large, rectangular leaden vessels, about 29 ft. long, 17 wide, and 1 ft. 9 in. deep. While the liquor is in the cooler, it is constantly agitated by means of a long wooden arm, which is worked by steam; this prevents the formation of large crystals. On an average, the liquor remains in these coolers about fourteen hours, at the end of which time there is a bed of small crystals deposited, several inches in thickness. This deposit is greenish in colour, owing to the presence of sulphate of iron. The crystals are then thrown into a large, square box, lined with lead; in this they are washed well with mother liquor and then allowed to drain, the operation taking about two hours. When thoroughly washed, the crystals are thrown upon an iron grating, the bars of which are about ½ in. apart; this is done in order to break the lumps and wash out the mother liquor. The crystals are then ready to be dissolved, which is effected by means of steam in a strong cylindrical vessel, 2 to 3 ft. high, and

2 ft. in diameter. It has two divisions; one part is open to allow the crystals to be thrown in, and the other part has a division and is closed. This division is to prevent large crystals from passing through undissolved. At the bottom of the open part of the cylinder is a coil of lead pipe, perforated with small holes, through which a current of steam (about 20 lb. pressure) is driven. This, passing through the alum, dissolves it as fast as one man can throw it in. At the top of the cylinder is a pipe, which communicates with a wooden tank, lined with lead, called the dissolving box. This is 14 ft. long, 8 ft. broad, and about 3 ft. deep. It is to receive the solution of alum before it is drawn off into the crystallizing tubs or roaching pans; the solution remains in this tank about 3 hours, and is covered over with boards, the joints of which are loosely packed with cotton-waste. When this tank is nearly full, and under full pressure of steam, about four quarts of size is poured in through a pipe, in order to cause the mechanical impurities to settle out. When the solution is ready to be tapped off into the tubs, those which are at the furthest end of the shed—say 60 ft. from the tank—are filled a few minutes before those at the nearer end. The appearance of the alum after crystallization depends largely upon the temperature at which the boxes have been filled. When it is too hot, the liquor forms large crystals outside, but when the temperature is about right, the exterior of the block of alum should resemble a loaf of sugar. The processes of crystallizing and removing the crystals are precisely the same as described above.

4. *From Clay.*—The process of obtaining alum from sulphate of alumina prepared artificially from clays was first practised by Alban and Chaptal. The clays selected should be altogether free from iron and carbonate of lime. Ordinary clays consist of silicate of alumina and free alumina; china or pipe-clay being much the best for the above purpose. The clay is first calcined in order to peroxidize any iron which may be present, and to render it perfectly porous; it is then ground and sifted, and digested with 45 per cent. of sulphuric acid at 45° B.; this digestion is conducted in a pan or cistern heated by the waste heat from the calcining furnace to about 70° (158° F.). When the mass has become thick from separation of silica, it is removed from the pan and exposed for a long period to the atmosphere, by which means the conversion of the alumina into sulphate is completely effected; it is then lixiviated in stone or brick cisterns and precipitated by the addition of an alkaline sulphate in the manner previously described.

The following process was patented by H. D. Pochin, and is still employed in his works at Salford, Manchester:—Fine china clay, as free as possible from iron and carbonate of lime, is calcined in a furnace in order to remove the water and render the clay porous. It is then mixed with a suitable proportion of sulphuric acid, which must be considerably diluted (sp. gr. 1·52), in order to prevent its action being too energetic. The mixture is then run into a cistern having movable sides, where in a few minutes it becomes hot and boils violently. It now becomes gradually thicker until it is converted into a solid but very porous mass. In this form it is called "alum-cake," or "concentrated alum." It contains much water, although it appears perfectly dry, and also much of the silica contained in the original clay, in a state of very fine division. A solution of pure sulphate of alumina is readily obtainable from this substance by lixiviation; the solution so obtained is allowed to deposit its silica before being further used, though for many purposes the presence of silica is not objectionable. As the potash or ammonia contained in ordinary alum is a wholly unnecessary constituent, being only added to facilitate the purification and crystallization of the salt, the solution obtained by the above process may be adapted to all the processes of dyeing and calico-printing in which alum is so largely consumed. In order to convert the porous alum-cake into alum, a concentrated solution must be made and precipitated with potash or ammonia, or both, the process being then conducted as described above. If the proper quantity of sulphuric acid has not been used in the preparation of the cake, it must be added before precipitating with the alkaline solution.

Pipe-clay has also been largely used by Taylor of Bristol, in the manufacture of alum. The clay is calcined in the ordinary way, and mixed with about an equal weight of sulphuric acid (sp. gr. 1·20). This mixture is run into a tub and heated for about twelve hours by means of a coil of leaden pipe, lying on the bottom of the tub, through which steam is made to pass; the heat attained should be about 90° to 100°, or rather below the boiling point of water. The solution should then have a sp. gr. of about 1·3, and is run off through a pipe into other vats, where it is precipitated with an alkaline solution in the usual manner.

5. *From Mineral Phosphates.*—In the year 1870, a patent was secured by Peter Spence for obtaining alum from a mineral consisting of phosphates of iron and alumina, and obtained from the island of Rodonda, near Antigua, in the West Indies. The mineral is taken in pieces, as it comes to hand, and calcined in kilns similar to those used for lime, at a red heat, being previously mixed with coal or coke; or it is ground until it passes through a sieve of, say, twenty meshes to the inch; but the former plan is preferred by Spence, as it facilitates the solution of the mineral substance, and renders a portion of the iron insoluble by oxidation. The mineral having been prepared by these or similar means, it is placed in leaden vessels together with an equal weight of sulphuric acid of sp. gr. 1·6 if the mineral contain 20 per cent. of alumina, but only three-fifths of

its weight if it contain 12 per cent., and in similar proportions for other degrees of richness. Heat is then applied by blowing steam into the vessel containing the mixture. The mineral dissolves and the specific gravity rises. It is then cautiously reduced by water or weak liquors from subsequent parts of the process (especially the washings of the sediment hereafter to be mentioned), constantly boiling until all is dissolved except the insoluble sediment, and the strength becomes 90° Tw., or 1·45 sp. gr. The liquor is now passed into a close leaden vessel, and a vapour is distilled into it containing ammonia obtained from gas ammoniacal liquor, subjected to boiling either by fire or steam injected into the gas-liquor. The quantity of gas-liquor employed is 600 to 900 gallons for every ton of the mineral, according to its richness. When all the ammonia has been distilled into the liquid, it is allowed to settle for a few hours, and the clear solution is run off at a sp. gr. of 1·4, or 80° Tw., into leaden coolers to crystallize in the ordinary way. From a mineral containing 20 per cent. of alumina, Spence obtains a ton and a half of alum for every ton of the mineral used. The mother liquor consists chiefly of a solution of phosphoric acid, and with a small quantity of sulphate of alumina, iron, and sulphate or phosphate of ammonia. This solution may be used directly as a fertilizing agent; or by adding sawdust in sufficient quantity to absorb the whole of the liquor, and then drying it at a low heat, so as not to char the sawdust, an artificial manure may be prepared containing phosphoric acid and ammonia in such quantities and condition as to make it a valuable fertilizer. The phosphoric acid contained in the mother liquor may also be applied to the purposes of producing phosphorus or the commercial phosphates. The insoluble sediment alluded to above may be washed with water, and the washings used for the reduction of the dissolved mineral.

6. *From Cryolite and Bauxite*—Alum may be prepared from the mineral cryolite in the following way (Sauerwein's method):—Very finely ground cryolite is boiled with water and lime, the latter being as pure and as free from iron as possible, in a leaden pan. By this means a solution of aluminate of soda and insoluble fluoride of lime are formed. The latter is allowed to deposit, and the clear liquor is decanted and the residue washed, the first washing being added to the decanted liquor, and the second and third used instead of pure water in the subsequent operations. Excess of finely powdered cryolite is now added to the solution for the purpose of separating the alumina from the aluminate of soda, the result of the decomposition becoming alumina and fluoride of soda. When no more caustic soda can be detected in the liquid, it is allowed to become clear, when the solution of fluoride of soda is run off. The alumina is then dissolved in dilute sulphuric acid, and the solution is treated with potash or ammonia in order to produce the required alum. The fluoride of lime occurring as a bye-product has recently been used in glass-making.

When bauxite is employed as a source of alum, it is first ignited with carbonate of soda in order to disintegrate it, or with a mixture of sulphate of soda and charcoal. In either case, lixiviation of the ignited mass yields aluminate of soda, from which alum may be prepared by processes described in the above paragraph.

7. *The Alum-process for Removing Potash from Saccharine Solutions.*—A process, bearing the above title, has recently been patented by James Duncan, John A. R. Newlands, and Benj. E. R. Newlands, for converting the potash present in saccharine solutions obtained from the beet into alum by treating it with a solution of sulphate of alumina. This process, by which potash alum is produced as a bye-product, is now largely employed in sugar refineries. It consists of two parts:—(1) precipitation of the potash in the form of alum, and (2) neutralization of the residual acid liquor by means of lime.

(1) Precipitation.—This is accomplished by adding to the cold syrup solution of sulphate of alumina, in quantity sufficient to form an alum with the whole of the potash present. It is convenient to work with syrup at a density of 38° B., and solution of sulphate of alumina at 27° B., or thereabouts. If the density of the syrup be much over 38° B., the alum cannot easily separate out. The mixture is well stirred for about fifteen minutes to one hour, and the whole allowed to repose for four or five hours, until the deposit—which consists of small crystals of alum, technically known as "alum flour"—has completely subsided. The tank in which this operation is performed is provided with mechanical stirring gear, and may be called the "alum tank."

The three principal points to be attended to in this part of the process, in order to obtain the best results and to prevent the formation of glucose, are:—(*a*) To work at the lowest attainable temperature, (*b*) to employ solutions as dense as possible, and (*c*) to perform the whole operation as quickly as possible, consistently with due separation of the alum.

The amount of potash present in syrups is generally equal to two-fifths of the ash. The ash is determined in the usual way, by addition of concentrated sulphuric acid, followed by incineration and weighing, one-tenth being deducted from its weight. It is sufficient for most practical purposes to assume that two-fifths of the ash is potash. Every 1 part of potash requires for conversion into alum about 9½ parts of sulphate of alumina, out of which 2⅓ parts are required to convert the potash into sulphate, and the remaining to combine with the sulphate of potash, so as to form alum. If the liquor contain any sulphuric acid, either free or combined, or if the solution of sulphate of alumina contain any free sulphuric acid, the 2½ parts of sulphate of alumina required to convert the potash into sulphate may be partly or entirely dispensed with. For practical purposes, it is sufficient to determine the percentage of ash, to assume two-fifths of this to be potash, then to multiply the percentage of potash by 9·5, which gives the dry sulphate of alumina, and, lastly, to ascertain the amount of solution corresponding to this by means of the following table:—

TABLE SHOWING THE PERCENTAGE OF SULPHATE OF ALUMINA IN SOLUTIONS OF DIFFERENT DENSITIES.

Baumé.	Specific Gravity.	Per cent.	Baumé.	Specific Gravity.	Per cent.
22½	1·184	34	28	1·225	43
24	1·188	35	29	1·235	44
24½	1·190	36	30	1·245	45
25	1·197	37	31	1·256	46
25½	1·201	38	31½	1·261	47
26	1·206	39	32	1·267	48
26½	1·211	40	32½	1·277	49
27	1·216	41	34	1·288	50
27½	1·218	42			

(2) Neutralization.—The alum-tank is provided with several taps, at different heights, and when the alum has well settled down, the clear acid liquor is run off, by means of these taps, into another tank placed on a lower level, and also provided with mechanical stirring-gear. This tank may be called the "limeing-tank." As soon as the acid liquor has been thus decanted into the limeing-tank, a little finely-divided chalk, previously made into a paste with water, is added, so as to produce a slight effervescence. Milk of lime is then added at frequent intervals, until the froth has nearly, but not entirely, disappeared; the gradual abatement of the froth serves to indicate when the neutralization is nearly complete. This operation takes from one to two hours. The point at which the neutralization is practically complete may be known by three simple observations:—(*a*) The absence of any large amount of froth; (*b*) the absence of any taste of aluminous compounds; (*c*) the liquor should give only a dull-red tinge to blue litmus paper (see Sugar).

To wash and dry the precipitated alum, it is convenient to employ a small centrifugal machine. After once machining for a few minutes, a little water being added as usual during the operation, the alum appears white and dry, but still retains a small amount of syrup. It is then mixed up with some cold water, and machined a second time, after which it will be found free from sugar and fit for sale. The advantages of the process are:—(1) The removal of potash and ammonia from syrups without much dilution; (2) the removal of a great deal of the colouring and albuminous matters; (3) a considerable improvement both in taste and odour; (4) the alum produced is nearly equal in value to the sulphate of alumina used, so that the expense of the process is not great; (5) the plant required is of the simplest description, the cost of labour small, and the entire process is of a continuous and rapid character.

This process has now been in constant operation during twelve months at the sugar refinery of Jas. Duncan, of London, where the syrup from many thousands of tons of sugar has been treated with excellent results, several hundred tons of potash alum of good quality being, during the same time, produced, and sold at a fair market price. The process has lately been adopted by many of the principal sugar refiners of the United Kingdom, and it has also been applied successfully in Holland, Belgium, and the United States of America.

For the successful and economical conduct of the manufacture of alum, it is absolutely necessary that by whatever process or from whatever materials it is obtained, the exact composition of the mineral or minerals employed should be carefully ascertained. This can only be effected by actual analysis, which should be extended to several parts of the same bed, and particularly to the upper and lower strata, which frequently differ in composition from each other, and thus require different treatment. The presence of lime in alum ores and shales is most prejudicial, since its affinity for sulphuric acid is greater than that of either alumina or iron. The ores, therefore, which are selected should contain as little as possible of this substance. The presence of magnesia is also objectionable; but in this case the sulphate of magnesia left in the mother liquor is not entirely wasted, as it may be crystallized and sold as Epsom salts; it is the custom in some English alum-works to employ this method of utilizing it.

The salt of potash used for precipitation of the alumina solution is generally either sulphate or chloride, but most often the latter. It is used in the form of waste liquor from soap-works, saltpetre refineries, and glass-works. As we have already stated, the gas-liquor, or crude sulphate of ammonia from the gas-works, is used as the common source of ammonia for precipitation. Salts of soda are rarely, if ever, used for the production of alum, since the resulting alum is very difficult to crystallize. But there is certainly one advantage which soda-alum possesses ; that is, the cost of sulphate of soda is trifling compared with sulphate of ammonia ; and as the consumption of this latter material is gradually increasing, owing to its high value as a fertilizer, and as the agriculturist is now beginning to see the great value of these nitrogenous products, and as their value is lost in alum, it may ultimately, now that the practicability of producing soda alum on the commercial scale has been demonstrated, even with all the difficulty of crystallization, be a more economical way of producing this double salt.

Uses.—The chief use of alum is in the processes of dyeing and calico-printing, as a mordant. This application depends upon the great affinity of the alumina contained in the alum for textile fibres, and especially wool and cotton ; it cannot, however, be employed in the case of aniline dyes. When steeped in a solution of alum, a basic salt of alumina is formed which adheres to the fabric so firmly that it is never removed by washing. The fabric is by this means enabled to combine with larger quantities of the colouring material, and to retain it more tenaciously (see Dyeing). It is used to clarify liquors of various kinds, and especially water ; to harden tallow, fats, and gypsum ; in the "tawing" of leather, along with common salt ; in the preparation of paper, and of bookbinders' paste, which contains one-sixth of alum ; in the preparation of the lakes, and of pyrophorus ; to render wood and paper incombustible ; to remove greasiness from printers' blocks and rollers ; to prepare a paper for whitening silver, and silvering brass in the cold ; in the bottling of fruits for preservation, the preparation of butter from milk, and extensively in the adulteration of bread, beer, gin, and artificial port. A novel and curious application is in the lining of Milner's safes, which is a mixture of alum and sulphate of lime ; owing to the large quantity of water which it contains, which moistens the inner chamber of the safe when heated, and thus prevents the contents from being consumed, and also to the non-conducting properties of the mixture, after expulsion of the water, this substance assists materially in protecting the interior from injury by fire. In medicine, alum is used as a tonic and astringent in doses of 5 to 20 grains ; as a gargle (1 drachm to half a pint of water) ; and as a collyrium and injection (10 to 15 grains to 6 oz. of water). In lead colic, ½ to 1 drachm of alum dissolved in gum-water, and taken every three or four hours, is said to be infallible. Powdered alum is often applied with a camel's-hair brush in cases of sore throat, ulceration of the mouth, &c. According to Dr. Meigs, a teaspoonful is one of the best emetics in cases of croup.

ALUMINA. (Fr., *Alumine ;* Ger., *Alaunerde.*) Formula Al_2O_3.—Alumina, the only oxide of aluminium known, is a very large constituent of the earth's crust. In combination with silica, it enters into the composition of all slatey and clayey earths, and of many rocks, minerals, and shales. It is seldom found in the pure state, except in varieties of the mineral *corundum*, such as ruby, sapphire, &c. Emery is a less pure variety of the same mineral, which, on account of its extreme hardness, has received numerous industrial applications. As the hydrate, alumina occurs in *diaspore*, *hydrargyllite*, *gibbsite*, and other minerals. In *bauxite*, so called from Baux in France, whence it is obtained, alumina exists in proportions varying from 60 to 75 per cent. of the whole substance. The following is the average composition of bauxite :—

Alumina	64·24	Magnesia	0·38
Silica	6·29	Soda	0·20
Oxide of Iron	2·40	Potash	0·46
Lime	0·55	Water	25·74

Alumina is insoluble in water, but soluble in acids and alkalies ; with the former it combines to form the ordinary salts of aluminium, but with the latter it plays the part of an acid, forming the salts called "aluminates." Crystalline alumina has a specific gravity of 3·9, and, next to the diamond, it is the hardest substance known. When pure, it is infusible in all temperatures except that of the oxy-hydrogen flame.

The strong affinity exhibited by alumina for vegetable colouring matter renders it invaluable to the dyer and calico-printer, and upon this property, in conjunction with its powerful attraction for all vegetable fibres, depends its extensive use as a mordant (see Dyeing). By combining, first, with the colouring matter, and then with the fibres of the substance to be dyed, the cloth and the colouring matter are brought into very intimate union with each other. In the form of clays of various kinds, alumina is largely employed in the manufacture of pottery of all descriptions (see Clay). The uses of alumina in the form of emery, alluded to above, are well known.

There are various methods of preparing alumina in a pure state. It may be obtained from common potash alum by heating it with a solution of carbonate of ammonia ; the hydrate of alumina precipitated is well washed, dried, and ignited, the residue consisting of pure alumina. A better method is that of igniting ammonia alum, by which its volatile constituents are driven off, and alumina in a tolerably pure state is left behind.

Clay, or minerals containing alumina, digested with a concentrated solution of potash or soda, yields an alkaline aluminate, from which hydrated alumina may be precipitated by passing a stream of carbonic acid through the solutions, or by heating it with chloride of ammonium or acid carbonate of soda; the hydrate is dried and ignited as in the previous case.

Alumina in a state suitable for the preparation of the pigments known as "lakes" may be produced in the following manner: "Dissolve 1 lb. of alum in ½ gallon of water, and add 75 grains of sulphate of copper, and about ¼ lb. of zinc turnings; leave the mixture for three days in a warm place, renewing the water lost by evaporation. The copper is first deposited upon the zinc, the two metals thus forming a voltaic couple sufficiently strong. Hydrogen is disengaged, sulphate of zinc is formed, and the alumina gradually separates in the state of a very fine powder; the action is allowed to continue until there is no more alumina left in solution, or until ammonia ceases to give a precipitate. If the reaction is prolonged beyond this point, oxide of iron will precipitate if present. The alumina washes easily, and does not contract upon drying."—(*Derniers Progrès de l'Industrie Chimique.*)

Sulphate of Alumina.—This salt is obtained by dissolving alumina in sulphuric acid. It is now largely employed as a substitute for alum under the name of "concentrated alum." When clay is used for the preparation of sulphate of alumina, the iron is removed by adding ferrocyanide of potash to the dilute solution of the sulphate, whereby Prussian blue is precipitated. Sulphate of alumina, owing to its variable composition, may not be always safely used in dyeing and calico-printing instead of alum, but in the majority of cases it is a thoroughly effective substitute (see Alum).

AMALGAMS. (Fr. *Amalgame;* Ger., *Amalgam.*)—Mercury unites with a large number of metals, forming definite chemical compounds called "amalgams." Some of these are solid, while others exist in a fluid state. It is probable, however, that fluid amalgams merely represent a solution in excess of mercury of some fixed compound of mercury with another metal, inasmuch as when a quantity of such fluid amalgam is pressed through the pores of a chamois-leather bag a small portion of mercury passes through, leaving behind the solid amalgam, which, on examination, is generally found to have a fixed chemical constitution. The fluidity of an amalgam seems therefore to depend upon the presence of an excess of mercury over and above the amount theoretically required to enter into combination with the other metal.

The chemical affinity which causes the mercury to combine with other metals is generally of a feeble character. Gentle pressure will drive out a considerable quantity of the combined mercury, leaving a combination in altogether different proportions from the original one. A moderate heat also is sufficient to decompose almost any amalgam. This fact was formerly made use of in the process known as *water-gilding.* The article to be gilded was covered with an amalgam of gold with excess of mercury, and then subjected to a strong heat. The mercury was driven off, leaving the article covered with a fine coating of metallic gold, which, on burnishing, regained its beautiful and characteristic lustre.

The following are some of the most important amalgams:—

Copper Amalgam.—There are several methods of preparing this amalgam, the following being, perhaps, the best. A mixture of finely-divided metallic copper (obtained by precipitating copper sulphate with metallic iron) and mercurous sulphate is triturated under hot water for half an hour. After this the water is repeatedly changed until it is no longer blue. The mass is then dried, kneaded well and allowed to harden, when it consists of an amalgam of seven parts mercury with three parts copper. The peculiarity of this amalgam is its property of softening when kneaded and becoming quite hard again after standing some hours. It has been used by Parisian dentists as a stopping for decayed teeth, though, owing to the poisonous nature of the copper, it is not to be recommended for this purpose.

Gold Amalgam.—This amalgam is formed when mercury is heated with powdered gold or gold-foil. It consists usually of two parts of gold to one of mercury. It has been found native near Mariposa, in California, and in the platinum region of Columbia.

The readiness with which mercury combines with gold is made use of in the extraction of the latter from its ores. The ore is crushed in an iron mortar or battery, as it is termed. This is a simple iron trough, usually 4 or 5 feet long, 12 or 14 inches wide, and 9 inches deep, cast with a solid bottom 9 or 10 inches in thickness. The ends of the battery are lined with amalgamated copper plates, while another plate of the same kind, about 10 or 12 inches wide and as long as the inside of the battery, is so fixed in a frame that it may be set and secured in an inclined position behind the stamps by which the ore is crushed. A similar plate, though narrower, is generally used on the front or discharge side of the battery. Water is introduced into each battery by a number of small pipes. The mercury is placed in the batteries in small quantities, and it unites with the gold as the latter is liberated by the crushing process. The larger portion of the amalgam is afterwards found in the batteries, adhering to the copper plate, the remainder being caught by the inclined plate placed outside the battery for that purpose. This plate is fixed at such an inclination that the stream passes steadily over its surface and allows the amalgam to adhere to it. The plate is grooved at right angles to the line of motion, thereby affording increased facilities for the contact of the two metals and the amalgamation of the gold. Leaving this plate, the stream flows into tanks or basins, carrying with it small quantities of amalgam not retained by the plate, and a little unamalgamated gold. The amalgam formed in the batteries and on the plate is cleaned up at intervals varying in length according to the richness of the ore. The outside plates are cleaned by carefully scraping off the adhering amalgam, first gently with a knife, and finally with a thick piece of hard gum or rubber which scrapes the surface closely without cutting or scratching it. The plates are then washed with water and prepared for use again by sprinkling mercury over them, and spreading the same evenly by means of a cloth, thus forming a freshly amalgamated surface.

Iron Amalgam.—Iron will not unite with mercury under ordinary conditions. Small quantities of an iron amalgam have, however, been formed by immersing sodium-amalgam (containing 1 per cent. of sodium) in a clear, saturated solution of ferrous sulphate.

Silver Amalgam.—This compound is formed by the union of mercury with finely-divided silver. Beautiful crystals of native silver amalgam have been found at Moschellandsberg, in the Palatinate, and in several other places. Mercury is used for silver extracting, in a process somewhat similar to that described above for the extraction of gold.

Sodium Amalgam.—Sodium and mercury combine readily under ordinary conditions by being brought into contact one with another. The union is attended with much hissing and spluttering, and with a considerable evolution of heat.

Tin Amalgam.—Tin and mercury combine readily at ordinary temperatures. If three parts of mercury be brought into contact with one part of tin, six-sided crystals of tin amalgam are formed. Tin amalgam is used for silvering looking-glasses. When pulverized and rubbed on the polishing-stone it forms a kind of mosaic silver. Electric amalgam may be made by melting tin and zinc together in various proportions in a porcelain crucible. The mixture is well stirred up, and when on the point of solidifying, the mercury is added and worked into the mass. The whole is next transferred to a mortar warm enough to keep the amalgam soft while it is well worked together, after which a piece of tallow or lard, not quite equal in bulk to the mass, is kneaded in until the amalgam attains the proper consistency.

Zinc Amalgam is formed by mixing and triturating zinc filings with mercury, at a heat somewhat below the boiling point of the latter. It is usually prepared by pouring mercury into zinc at the temperature at which the latter is just kept in a fused state. Care must be taken to keep the liquid stirred, and to add the mercury slowly and in as fine a stream as possible.

ANGELICA. (FR., *Angélique;* GER., *Angelika.*) *Archangelica officinalis,* or *Angelica archangelica.*—This plant belongs to the genus *Angelica* of the natural order *Umbelliferæ.* It has a long, straight, fluted stem, rising sometimes to a height of 6 ft., and large leaves of a beautiful green, with greenish flowers in almost spherical umbels. Its fruit is ovoid in form and encloses two seeds. If these are not permitted to ripen, the plant, naturally triennial, becomes perennial. Its root is long and fusiform, with irregular rugose radicles.

This plant does not grow abundantly in England, though it is sometimes cultivated in moist districts. It was originally brought from Syria, and is now naturalized in many parts of Europe, including Lapland, where it is much valued as an article of food, and as a medicine, the roasted stalks being supposed to possess great efficacy as a remedy for disorders of the chest.

The angelica of commerce is chiefly prepared at Niort, in France, and at Hamburg, from whence the dried root is imported in casks.

The stem, leaves, seeds, and roots are all aromatic and bitter. The root contains much resin and essential oil (angelica oil). It has long been used as an aromatic stimulant and tonic for nervous disorders, flatulence, and indigestion. So high, indeed, were the medicinal virtues of this plant in the estimation of the ancients that, in recognition of them, they applied to it the name which it now bears.

The root and seeds are used by rectifiers and compounders in the preparation of gin and of liqueurs. The tender stems and the midribs preserved with sugar form an agreeable and wholesome sweet-meat.

ANISEED. (FR., *Anis;* GER., *Anis.*)—The seed of the *Pimpinella anisum,* an annual plant of the natural order *Umbelliferæ.* This plant is characterized by its reticulate fruit and by the short duration of the stem, which is annual. It came originally from Egypt, and is now largely cultivated in France, Spain, and the East. It does not grow in England, though attempts have been made to cultivate it.

Aniseed is very aromatic, and has an agreeable smell. It is universally used as a wholesome and pleasant ingredient in pastry, and as a flavouring for liqueurs. It has also been used medicinally as a stimulant, to relieve flatulence, and sometimes in pulmonary affections. The chief use of aniseed is in the manufacture of a volatile, nearly colourless, oil, called oil of anise (*oleum anisi*). One cwt. of seed distilled with water yields about 2 lb. of oil. At Erfurt, in Germany, one of the principal sources of the oil, it is distilled from the stems and leaves as well as from the seed.

Anise-water—water flavoured with the oil and sweetened with sugar—is made largely at Bordeaux and at Amsterdam. As a cool and pleasant beverage, it is much esteemed.

Star, or Chinese anise is the seed of the *Illicium anisatum*, of the natural order *Magnoliaceæ*. It owes its name to the star-like shape of the seed. It very closely resembles common aniseed, and yields an essential oil called oil of star anise (*oleum badiani*). The Chinese use star anise as a stomachic and as a spice. It has been largely imported into Europe from China and Singapore as a substitute for ordinary aniseed, the qualities both of its seed and of the oil so closely resembling those of common anise, that it may be used instead of the latter for almost every purpose.

AQUA REGIA. (Fr., *Eau régale;* Ger., *Königswasser.*) Literally, *Royal Water.*—The name given by the alchemists to a mixture in certain proportions of nitric and hydrochloric acids, which was found to possess the power of dissolving metals hitherto insoluble in any acid. This power is apparently due to the presence of free chlorine, and not, as has been stated, to a compound of chlorine, oxygen, and nitrogen.

Aqua regia is also called nitro-muriatic, nitro-hydrochloric, or hypochloro-nitric acid. It is made by mixing the two acids in various proportions, of which perhaps the best is one volume of strong nitric to three volumes of strong hydrochloric acid.

Aqua regia is used for dissolving gold, platinum, and other metals.

ARGOL, or ARGAL. (Fr., *Tartre brut;* Ger., *Weinstein.*)—Argol is the crude tartar which, after the fermentation of wine, is deposited on the sides of the cask, along with tartrate of lime, colouring matter, &c., in a thick crust which may be easily detached. It is composed chiefly of bi-tartrate of potash or cream of tartar, but contains also varying proportions of bi-tartrate of lime; it is red or white according to the colour of the wine.

It is from argol obtained in this way that the refined cream of tartar and the tartaric acid of commerce are chiefly prepared (see Tartaric Acid). The neighbourhood of Montpellier, in France, is the chief centre of the manufacture of cream of tartar, which is carried on in the following manner:—The crude tartar, after being reduced to powder, is dissolved in water contained in large vats, and heated to the boiling point. The water is kept at this heat for two or three hours and then allowed to cool and to stand for a day or two, at the end of which time the clear liquor is run off from the impure sediment at the bottom into wide-mouthed earthen vessels. The bi-tartrate, partly freed from colouring matter and other impurities, is then deposited in a thick bed of crystals. In order that these may be further purified they are once more dissolved in boiling water, in which has been placed, for every hundred parts of salt, eight or ten parts of a mixture of clay and animal charcoal. The whole is boiled down until a thin film appears on the surface. It is then run into conical vessels and allowed to stand for eight days, or longer, according to the temperature. The alumina contained in the clay forms, with the remaining colouring matter, an insoluble compound which is deposited along with the animal charcoal at the bottom of the vessel, the sides of which become covered with beautiful, colourless crystals of pure bi-tartrate. These are left for some days on sheets in the open air to be dried and whitened by exposure to the sun.

Cream of tartar is largely used for the manufacture of tartaric acid and the tartrates. The dyer employs it as a mordant for fixing colours on woollen materials. Mixed with whiting, it is much used for cleaning silver. In medicine, it acts as a mild purgative, but when used for this purpose, owing to its very sparing solubility in water, it is usually mixed with a quarter of its weight of powdered boric acid which renders it easily soluble.

AROMATIC VINEGAR. (Fr., *Vinaigre de toilette;* Ger., *Aromatische Essig.*) *Acetum aromaticum.*—This is the name given to various mixtures of aromatic substances with strong, pure acetic acid. They are prepared chiefly in France, and in the following manner:—

A quantity, about 20 lb., of crystals of acetate of copper, or verdigris, is broken up small, and placed in an earthenware retort of about 2 gallons capacity. The mouth of this retort is connected with a series of stoppered globes, each of which is constantly kept cool by a stream of water; the last of these receivers is furnished with a safety tube, the end of which dips into a vessel filled with water. The whole apparatus is carefully tested, and the retort is placed in a reverberatory furnace and heated gently. The acetate of copper is decomposed by the action of the heat into acetic acid, which passes over as a vapour, and is condensed in the receivers, and into metallic copper, which remains in the retort mixed with a little charcoal. When the vapours of acetic acid cease to be given off, the retort is withdrawn from the furnace, and allowed to cool. The 20 lb. of crystals should yield about 10 lb. of crude acetic acid, of specific gravity 1·061; this acid is of a greenish colour, owing to the presence of certain salts of copper, which are formed and carried over during the operation. It is purified by further distillation in a glass retort, heated by a sand-bath, and fitted with a tubulated glass receiver. The moisture contained in the salt renders the first portion of the distillate too weak; it is therefore rejected until the liquid in the receiver has a specific gravity of about 1·07, when the distillate is collected. It then constitutes the purest and strongest acetic acid known. In this acid are dissolved various essential oils, such as oil of cloves, rosemary, thyme, lavender, mint, and rue. Camphor is also frequently added. The following recipe has been given by the Edinburgh Pharmacopœia:—

One pint and a half of acetic acid; one ounce each of dried rosemary and thyme; one half-ounce of lavender; one half-drachm of bruised cloves. This mixture is to be macerated for a week, strained, strongly expressed, and filtered.

The "*Vinaigre des quatre voleurs*" contains the following substances: Camphor dissolved in alcohol; the dried ends of the wormwood plant, rosemary, sage, mint, rue, garlic, dried lavender flowers, the root of the *Acorus calamus*, cinnamon, and nutmeg. It owes its name, it is said, to the fact that four thieves preserved themselves by its use from contagion while plundering the victims of the plague of Marseilles.

Aromatic vinegars are antiseptic and disinfectant; they are largely employed as articles of toilet.

ARSENIC. (Fr., *Arsenic;* Ger., *Arsenik.*) Symbol, As. Combining weight, 75.—Arsenic is an iron-grey, brittle substance, possessing metallic lustre. It occurs native, in veins, in crystalline rocks, and the older schists. It is found in this country as the oxide and sulphides, in association with ores of tin and copper, and on the continent, with those of cobalt and nickel. Arsenic itself is a substance of no commercial importance, but some of its compounds, as the oxide, commonly called "white arsenic," or "arsenious acid," and the sulphides, orpiment and realgar, are largely used for various industrial purposes.

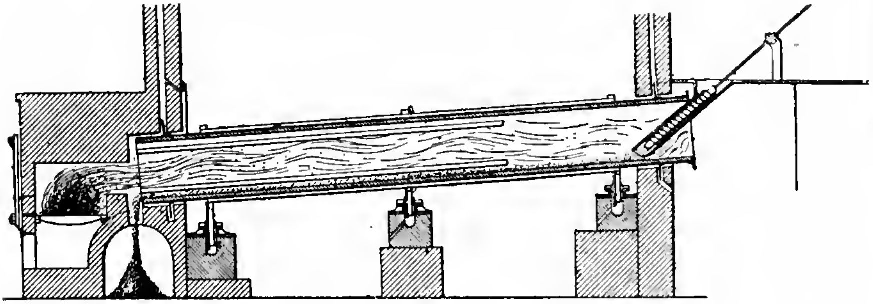
White Arsenic.—The nature of white arsenic, or arsenic, has been fully treated of under the head of Arsenious Acid (see Acids); but it remains to describe here the processes by which it is obtained in this country and abroad. As already stated in the article referred to, the sources employed in England are chiefly the arsenical pyrites, or *mispickel*, which is smelted solely for the arsenic which it contains, and the ores of tin and copper, from which arsenic is obtained as a bye-product from the various smelting processes. The manufacture in this country is confined to Cornwall, Devon, and South Wales. In the former county, the Botallack and South Wheal Crofty tin mines, and the East Pool and West Wheal Seton copper mines produce large quantities of arsenic annually. In Devonshire, the Devon Great Consols, Wheal Friendship, and Maria and Fortescue copper mines, yield still larger quantities; the produce of the former mine is well known as the very best refined arsenic ("D.G.C." brand).

Arsenic sublimes at 218° (424° F.); but in order to effect the thorough roasting of the ore, the temperature must be raised to low redness, but not beyond, since any increase of temperature above that which is absolutely necessary for sublimation, must be compensated for by a greater length of flue, in order that the vapours may be sufficiently cooled in their progress to be entirely deposited. This, of course, applies only to the ores (as mispickel) which are roasted solely for the sake of the arsenic which they contain. When tin and copper ores are employed, and arsenic is yielded merely as a bye-product, a much greater heat is required, and consequently the series of flues and condensing chambers must be longer in proportion, in order that the requisite space may be afforded for the cooling of the superheated vapours.

The furnace in which the arsenical ores are most largely roasted is known as Oxland and Hocking's calciner, and is shown in Figs. 273, 274, and 275. It consists of a long wrought-iron cylinder, lined with firebrick, 3 ft. inside diameter and 32 ft. long, placed at an inclination of 1 in 16 to 1 in 24, according to the nature of the stuff to be treated, and supported upon rollers, upon which it is made to revolve at a very slow speed of six or eight revolutions per hour. The ore is supplied into the higher end of the cylinder, through a hopper fitted with a feeding-screw, and gradually traverses the length of the cylinder to the lower end, where it falls into a chamber, from which it is removed for further treatment. The heating furnace opens into the lower end of the cylinder and the volatilized arsenic and sulphur, &c., are carried off by a flue from the upper end; this flue is extended to a considerable distance, and divided by baffle walls into a succession of chambers, in which the arsenic is deposited and periodically collected. The time taken for the ore to pass through the calciner is from three to six hours. The firebrick lining of the calciner is constructed with four longitudinal ribs, projecting internally, as shown in the transverse section, Fig. 275, and extending two-thirds of the length from the lower end, as shown in Fig. 273; in the revolutions these have the effect of continuously stirring the stuff and exposing the whole of it to the heat. In this calciner, the stuff being supplied at the upper end, farthest from the heating furnace, is exposed first to the lowest heat, and afterwards to a gradually increasing heat, as it works its way along to the hotter end of the calciner; by this means the most advantageous effect is obtained from the fuel consumed in the furnace.

An older calciner, known as Brunton's, consists of a horizontal revolving table, about 12 ft. in diameter, enclosed in a shallow reverberatory furnace; the table is slightly conical in shape, its surface sloping downwards from the centre to the circumference. The ore delivered on the centre of the table, through a hopper in the roof of the furnace, is exposed to the flame passing through the furnace, and is continuously stirred by a set of scrapers fixed in the roof, whilst the table rotates very slowly below them, making only about six revolutions per hour. The scrapers being set obliquely, shift the stuff gradually from the centre to the circumference of the table, where it falls off, and is collected in a chamber beneath.

273.



274.

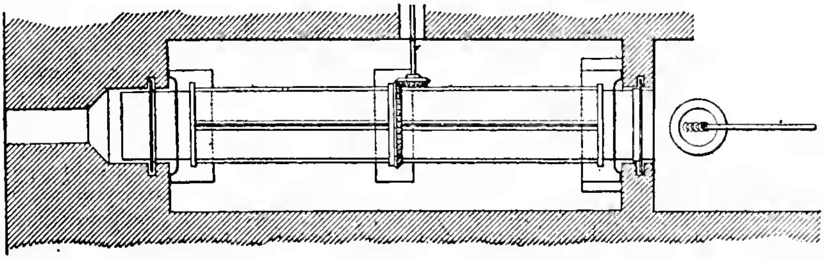
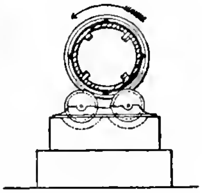


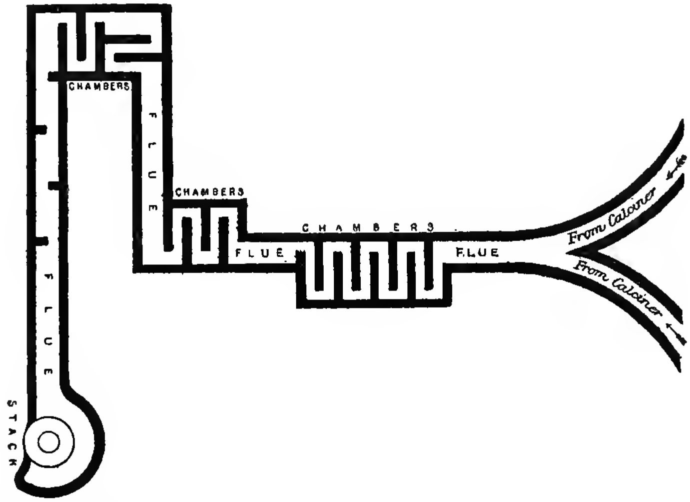
Fig. 276 represents the system of flues and condensing chambers employed at a large arsenic works in Cornwall. The flues are built of bricks, and are from three to four feet in width; they are built underground, and covered with iron plates, which may be removed in order to gain access to the interior; in some cases they are lined inside with slate. The chambers, which consist of a series of brick baffle-walls, are wider and higher than the ordinary flues. At stated periods, called "clearing-up days," the calciners are laid off, the iron plates removed, and the flues entered by workmen, who sweep the deposited arsenic into heaps, and shovel it out. In some cases, there are two sets of flues from the calciners to the chimney, in order that while one set is being cleared out, the vapours from the calciner may be turned into the other, so as to avoid a stoppage of work. The flowers of arsenic, or rough white arsenic, of the smelters (the *giftmehl*, or poison-flour, of the Germans), obtained in this way, is next purified by re-sublimation in suitable iron pots, or other iron vessels, before it is fit for the market. It then forms a semi-transparent, vitreous cake, which gradually becomes opaque, and of snowy whiteness, by exposure to the air, and at length acquires a more or less pulverulent state on the surface.

275.



The chief seats of the arsenic manufacture on the Continent are Altenberg, in Saxony, and Reichenstein, in Silesia. In these places the *modus operandi* is somewhat different from that pursued in England. After being crushed moderately small, the arsenical ores are roasted in a muffle furnace, in charges of about 10 cwt., spread carefully over the bed of the furnace in an even layer two or three inches deep. A fire is lighted beneath and the charge slowly raised to a full red heat; the heat should afterwards be slightly lowered, care being taken to maintain it at the same level throughout the operation. The charge must be constantly agitated, and air freely admitted during the whole process by allowing the furnace door to remain open. Twelve hours is sufficient to volatilize the whole of the arsenic, when the old charge is withdrawn and a new one introduced. The muffle furnace in common use is about 10 ft. long by 6 ft. wide, and has a fire under its whole length; its bed should be slightly inclined. The raw ore is poured into the furnace by means of a funnel, and the vapours of arsenic and sulphur are conducted through a channel into a condensing arrangement placed above, and called the "poison tower." This arrangement consists of a system of chambers placed one above the other, and numbering usually six in all. In their course through these chambers, the vapours are condensed and fall in a light powder on the floor; that found in the first two is the purest, the rest being contaminated with more or less sulphur. After the withdrawal of each charge, the arsenic deposited in the upper chamber is raked into the lower ones, which are emptied about once every six weeks. The rake is inserted through small doors in the sides of the tower, and communication is effected between the upper and lower chambers by means of trap-doors. Owing to the poisonous nature of the arsenic fumes the greatest caution is necessary in effecting the removal of the sublimed acid. The workmen should have their mouths and nostrils protected by moist linen, and should be covered from head to foot with a leathern dress and helmet, the latter being furnished with glass eyes.

276.



The further purification of the crude arsenic obtained in the above manner is carried on in an arrangement consisting of a series of iron pots, upon which are fitted cylinders of sheet iron, each terminating in an iron pipe connected with a condensing chamber. The pots, being open at the top, are charged with 3 cwt. of the crude acid, and the cylinders are fitted on by means of handles, the connections being carefully luted together. A fire is lighted beneath each pot, and heat is applied, at first moderately, but, after the lapse of half an hour, more strongly. The volatilized arsenic is carried upwards, and condenses in the sides of the pipe, and on the floor of the chamber, from which it is afterwards detached in a thick, transparent crust, which becomes opaque on exposure. Great care is necessary in regulating the fire; if the heat be either too strong or too feeble, the quality of the product is much impaired. It is customary to regulate the fire by the warmth of the upper part of the cylinder, as felt by the hand. The end of the operation is ascertained by inserting a metal rod into the cylinder; if the process be complete, no arsenic will be sublimed upon it when withdrawn. The sulphur always contained in the crude arsenic is converted by the heat into sulphurous acid, and is conducted away by means of a chimney.

At Rebas, in Catalonia, arsenic is obtained as a bye-product from the smelting of ores containing small quantities of mispickel, by passing the gaseous products through a series of flues connected with the smelting furnace. The process is carried on in much the same manner as in Cornwall and Devon, except that the furnace is somewhat different in construction. It is made so as to allow the flame to enter the furnace, and to play upon the charge in the interior, being shut off by means of a damper when required. The furnace bed is supported upon cross-walls of brickwork, through which the flame is allowed to pass when the damper is open; when it is closed, the flame passes through a flue into the chimney. There is another damper, also, which is closed when the flame is required inside the furnace, in which case the products of combustion are conducted away through a second flue. The process of refining or re-sublimation is precisely the same in Spain as that employed in Saxony and Silesia.

Arsenic is extensively used in the manufacture of the sulphides, orpiment, and realgar, and of various pigments, such as arsenite of copper, or *Scheele's green*, *Schweinfurth green*, and others. In glass-making, it is employed to combine with the iron contained in the sand, and thus to prevent it from imparting an objectionable tinge to the glass; it also enhances the lustre and brilliancy of the better kinds of glass. Dyeing and calico-printing consume large quantities of arsenic, and it has lately received a new application in the manufacture of aniline dyes. Owing to the power possessed by arsenic of arresting putrefaction, it is employed by naturalists in the form of a soap for the preservation of stuffed birds and other organic specimens. In agriculture, it is used in solution as an anti-smut for seed wheat, and as an anti-vermin lotion for sheep and cattle, but its use is not free from danger, especially to the shepherds or dippers. In Spain and Germany, it is largely used in the preparation of fly-poison, vermin-killers, &c. Taken in minute doses, it is much valued as a powerful homœopathic remedy.

The quality of commercial arsenic depends upon its purity. The best quality is perfectly white, but the presence of sulphur, due to its deposition with the arsenic in the condensing flues or chambers, imparts to the latter a highly objectionable yellow tinge. This is especially characteristic of the German article, which is often called "yellow arsenic." The arsenic from Swansea is also yellowish in colour, while that from the works in Cornwall and Devon is entirely free from sulphur. Refined arsenic should be in compact, vitreous lumps, and perfectly free from particles of metallic arsenic; when of bad quality, it is in loose masses, more or less soft and friable, due to re-subliming the crude acid under too feeble a temperature.

The manufacture of arsenious acid is carried on chiefly in the neighbourhoods where the mines containing arsenical ores are worked. Although arsenic is almost as widely distributed as any known metal, yet, with one or two exceptions, it is found only in such minute quantities as to be worthless for the purpose of extraction. Consequently the seats of this industry are few in number. In England, the most important works are scattered about in Cornwall and Devon. There are one or two also situated in the neighbourhood of Swansea, in Glamorganshire. The arsenic districts on the Continent are Altenberg and Freiberg, in Saxony; Reichenstein, in Silesia; and the province of Catalonia, in Spain. The works at Altenberg and Reichenstein are supplied by two mines of arsenical pyrites in Silesia.

Arsenic has been manufactured in small quantities for a large number of years, but during the last twenty years it has undergone very considerable development. Although the production is confined to a small number of works—there being only about ten manufacturers in this country—these works have been extended from time to time in order to meet the rapidly increasing demand. The amount of capital needed to carry on the manufacture depends upon the manner in which the arsenic is obtained. If the arsenical ores are treated directly for this article, the plant required may consist of an ordinary reverberatory furnace, with flues and chimney of greater or less length; but if the arsenic be obtained as a bye-product from the smelting of tin or copper ores, the only extra cost lies in the erection of flues and chambers in connection with the calciner. In either case, another reverberatory furnace and set of condensing chambers are required for the re-subliming operations. The most expensive item in the erection of the flues is the slate with which they are occasionally lined.

The price of arsenic is constantly varying, between the limits of 7*l.* and 15*l.* per ton. It is ruled to a great extent by "rings," which consist almost entirely of merchants. This is illustrated by the course of prices during the first six months of the year 1878. A combination of merchants drove up the price from 7*l.* to 12*l.* in three weeks, all surplus stocks being got rid of by consignment to the United States. The combination, however, broke down, and the price of arsenic fell, almost as rapidly as it had previously risen, to 8*l.* per ton. Such manipulations are readily carried through, because the make is small—only about 8000 tons per annum, and, as pointed out above, in very few hands (see Acids).

Orpiment. (Fr., *Orpiment*; Ger., *Auripigment.*) Formula, As_2S_3.—Orpiment, or trisulphide of arsenic, is a lemon or orange-yellow coloured substance, found native in Hungary, the Hartz, and other places; the finest samples used by artists (golden orpiment) come from Persia. The commercial article is artificially prepared for use as a pigment in the following way:—

A mixture of arsenious acid and sulphur is placed in an iron subliming-pot, similar to those used in the preparation of crude white arsenic. The mixture is then heated until the sublimate which immediately forms upon the rings fixed above the pot begins to melt. The proportions of the two ingredients used vary largely; the best colours being probably produced when the mixture contains from one-third to one-fifth of sulphur; for the lighter colours, a smaller proportion of sulphur is employed. Orpiment made in this manner consists of a mechanical mixture of sulphide and oxide of arsenic.

As stated above, the chief use of orpiment is as a pigment; but it is also employed as a dye; in the preparation of fireworks, and in some depilatories. The native sulphide is preferred to the artificial variety by artists and dyers by reason of its richer colour (see Pigments).

Realgar. (Fr., *Réalgar;* Ger., *Rothes Schwefelarsenik*). Formula, As_2S_2.—Realgar, or disulphide of arsenic, is a deep orange-red substance, soluble in water, and highly volatile and poisonous. It is found native in some volcanic districts, especially in the neighbourhood of Naples; but the commercial article is made by distilling in earthenware retorts, arsenical pyrites, or a mixture of sulphur and arsenic, or of orpiment and sulphur, or of arsenious acid, sulphur, and charcoal, in the proper proportions; it has not the brilliant colour of the native mineral, and is much more poisonous.

On a large scale, the manufacture is carried on in the following way:—The ingredients are mixed together in such proportions that the mixture shall contain 15 per cent. of arsenic, and from 26 to 28 per cent. of sulphur, in order to make allowance for the volatilization of a portion of the latter substance. The mixture is then placed in a series of earthenware retorts, which are charged every twelve hours with about 60 lb.; this quantity should fill them three parts full. These are then gradually heated to redness for from eight to twelve hours, during which time the realgar distils off, and is collected in earthen receivers, similar to the retorts, but perforated with small holes to permit the escape of these gases. After the operation, the receivers are emptied, and the crude product is remelted. This is performed in cast-iron pots, the contents being well agitated, and the slag carefully removed. The requisite amount of sulphur or arsenic is then added, according to the colour of the mixture, or else a proper quantity of realgar containing an excess of the required constituent, and the mass is again stirred. When, on cooling, it exhibits the correct colour and compactness, it is run off into conical moulds of sheet iron, cooled, and broken up; it is sometimes refined by re-sublimation. The chief use of realgar is as a pigment; and in pyrotechny, in the preparation of white fires (see Pigments).

ASBESTOS. (Fr., *Asbeste;* Ger., *Asbest.*)—This name, which is derived from the Greek word *ἄσβεστος*, incombustible, is given to several varieties of amphibolic and augitic minerals. The commonest form occurs in masses of coarse, white, flexible, crystalline fibres, varying considerably in texture, and being sometimes so fine as to resemble silk, when it is termed "*amianthus*." The fibres are found lying in parallel masses in extreme regularity, and may be easily separated one from another; the individual fibres are flexible and elastic, of a white or greenish-white colour, and a fine silky lustre. Its chief peculiarity is that from which it derives its name, viz. almost complete incombustibility. A single fibre, exposed to a strong heat, fuses to a white enamel, but when woven together into a kind of coarse cloth it is capable of resisting the highest known temperatures; it is also quite indestructible by acids.

Asbestos has been known upwards of two thousand years. According to Pliny, it was used in his time for weaving shrouds in which to wrap the bodies of important personages before submitting them to the flames of the funeral pile; or it was spun into cloths and napkins to be used at feasts or on state occasions. In those districts where it is found plentifully it has been used by the peasantry from time immemorial for making the wicks of lamps; its power of capillary attraction renders it particularly applicable to this latter purpose. The art of weaving asbestos or amianthus into cloth seems to have consisted in interweaving fibres of flax with those of the mineral, and then subjecting the cloth to a strong heat in a furnace. The flax was thereby consumed, and a fireproof cloth, composed entirely of asbestos, obtained. The Chevalier Aldini, of Milan, has invented a much stronger cloth woven without the intermixture of any foreign substance; the cloth is made loose in texture, and the fibres are prevented from breaking by the action of steam. The Chevalier has also contrived a fireproof dress, made of the same material, for the use of firemen. Some years ago, the Société d'Encouragement offered a prize for the improvement of asbestos cloth; and the use of it was publicly shown in London in 1858.

The chief use of asbestos is for packing for steam pistons and pump-rods, stuffing-boxes and manhole plates, and to form a non-conducting covering for steam boilers and pipes: for all of these purposes it is specially adapted, owing to its power of resisting moisture, friction, high temperatures, and even flame itself. In Great Britain, the chief centre of the asbestos manufacture is in Glasgow, where experiments made with this substance have of late resulted in the production of many articles of utility, one of the most important of which is the covering for boilers and steam-pipes, mentioned above. This covering is applied like ordinary cement or plaster, and is easily manipulated. A single layer, 1 in. in thickness, is amply sufficient. Its own adhesive properties render the assistance of other cementing material superfluous. The cylinders of some steamers have been covered with this material with complete success. The price of this covering is the same as that of the ordinary kinds. An asbestos jointing in the form of a paste or cement, is also manufactured at Glasgow. On account of its impervious resistance to acids, oils, high-pressure steam, hot water and sugar liquors, this substance claims to be far more durable than those applications which have been formerly restricted to white and red lead or indiarubber. A mill-board jointing made of asbestos is also becoming an article of considerable importance as an economiser of labour in machine shops; it can be effectively and reliably used on a rougher face than any other; and thus the tedious and lengthy processes of "getting up" or "facing" are obviated.

In America, where asbestos is becoming an article of extensive manufacture, it is employed in preparing a kind of lining, or sheathing paper, for ceilings, walls, and floors. These papers are made in rolls of any length or thickness, and can be printed with any pattern; not only do they render the building safer in case of fire, but they also have the desirable effect of keeping it cooler in summer and warmer in winter. Audesley, who owned considerable deposits of asbestos near Baltimore, introduced asbestos paper into the States with much success. Owing to the friability of paper made from asbestos, it can only be applied to coarse purposes, although it is not impossible that its peculiar property of resisting heat might be of use under some circumstances. In 1853, a patent was taken out for the preparation and use of asbestos for this purpose. The pulp was mixed with alum, and an indestructible paper produced; this paper burns with a flame, leaving a white residue, which retains the shape of the paper if carefully handled. Any writing in common ink is perceptible even after the organic substance of the paper is consumed.

The common forms of asbestos found in lumps have been lately largely used in some kinds of gas-stoves for heating purposes.

Common asbestos is not indigenous to any particular part of the globe, but occurs in abundance in most countries. It is found in the veins and seams of the serpentine formation of rocks, which are blasted to procure the fibre. The long, strong, fibrous quality, which is found in sufficient quantity for commercial purposes, is taken from the Italian Alps at elevations of several thousand feet; in this district alone at least one hundred different varieties are found, and no two localities seem to yield precisely the same fibre. In Great Britain it occurs in Cornwall, Inverness, Aberdeenshire, and in some islands in the north of Scotland. It also occurs in France, Italy, Hungary, Silesia, and very abundantly in Corsica, where it has been employed for packing minerals. In Greenland it is also found abundantly, and the fibres are still used by the inhabitants of this country for twisting into lamp wicks. The United States of America yield it in considerable quantities.

The price of asbestos ranges between 10*l.* and 100*l.* per ton, according to the quality of the fibre. Owing to the many uses to which it is being put, it is likely to rise very much higher in price. It is only recently that asbestos, formerly nothing more than a mineral curiosity, has become an important article of commerce; but there is every reason to believe that this substance will yet receive a much wider application, and that it will ultimately become a staple manufacture of this and other lands.

There are three other varieties of asbestos, besides the common one, called respectively *mountain leather*, *mountain wood*, and *mountain cork*. In these three varieties the fibres are not parallel as in the common one, but are interwoven. Mountain leather is yellowish-white and tough, as its name implies; it is chiefly found at Wanlock Head in Lanarkshire. Mountain wood occurs in soft, tough masses; it has a brown colour, much resembling wood, and is found in Scotland, France, and the Tyrol. Mountain cork, or elastic asbestos, varies in colour from white to brown; it is elastic and opaque, much resembling cork in appearance.

ASPHALT. (Fr., *Asphalte;* Ger., *Asphalt.*)—Asphalt, or native bitumen, is believed to be produced by the decomposition of organic, and probably vegetable, matter, under the earth's surface, in places where water is present, but air is almost entirely excluded. These organic remains being deposited in the beds of seas, rivers, and lakes, have been gradually enclosed in sand or clay, and have then undergone a process of decomposition, by which asphalt, petroleum, naphtha, pit-coal, and other substances of a similar nature are formed. The true varieties of bitumen have probably been formed from coal or lignite by subterraneous heat.

When pure, asphalt is a black, or brownish-black solid, possessing a bright, conchoidal fracture. It fuses at 100°, emitting a strong smell of pitch, and burns with a bright flame. It dissolves in five times its weight of naphtha, but is insoluble in water and alcohol. It has a specific gravity of from 1·0 to 1·2.

Asphalt was formerly found in considerable quantities and in a very pure state on the shores of the Dead Sea, or *Lacus Asphaltites*, whence it derives its name. Only a small quantity is now derived from this source. There are also beds of pure asphalt at Altona, in Albania; at Coxitambo, in South America; in the Island of Barbadoes; and in the great Tar Lake of Trinidad. This wonderful lake, or rather plain, is circular in form, about a mile and a half in diameter, and consists of bituminous scoriæ, vitrified sand, and earth, cemented together. From its colour and smoothness it resembles a lake of water, and in hot weather its surface to a depth of some inches is covered with a thick, cohesive liquid, which emits a powerful sulphurous or bituminous odour. When dry, the surface is covered with little cracks or fissures, which when filled with water are almost invisible. The edges of the lake are almost always hard and cold, but the bitumen gradually becomes warm and softer as the centre is approached, where it is at last found to be boiling. According to Sir Charles Lyell, this lake is probably formed from the woody and vegetable matter carried by the River Orinoco into the surrounding seas, where, by the influence of currents, it is accumulated in particular spots. The decomposition of these beds of vegetable matter is then effected by subterranean volcanic action, and the bitumen so formed is by the same agency forced to the surface, where it becomes indurated by exposure to the air, thus giving rise to the different varieties of pure and earthy pitch so abundant on the island.

The substance now commonly called asphalt is a perfectly pure carbonate of lime (containing sometimes slight traces of silica), impregnated naturally with bitumen; this impregnation has been effected by geological agencies, of the precise date and particulars of which we know but little. It is in the proportion of about 7 or 8 parts of bitumen to 93 or 94 parts of the limestone. This mineral, which is found in layers interposed between beds of ordinary limestone, especially in the upper Jurassic formation, presents the following physical characteristics:—

Its colour is a deep chocolate, almost black. Its fracture also resembles chocolate in appearance and colour; it is granular and irregular, without any plane of cleavage; its colour is deeper according as it is worked in the direction of the stratification or perpendicularly to that direction; it is deeper and more floury in the first case, and drier and clearer in the second. Each individual mine has its own particular shade, which is always that of chocolate.

In consistence, it varies with the temperature; it is very hard and sonorous when cold, but softens when heated; until at 50° or 60° it falls to powder. In winter, it may be broken easily with a hammer, like ordinary limestone; in summer, it is softened by blows into a kind of paste. Its average specific gravity is 2·235.

Its structure varies in different samples, the produce of each mine being somewhat different from that of the others.

Asphalt of the best quality may be known by the following conditions:—The grain is fine and homogeneous, and does not exhibit a particle of ordinary or white limestone. The rock is often lined with streaks of a darker colour than the rest, which give it very much the appearance of a tiger's skin. Other samples contain crystals of carbonate of lime, impregnated with bitumen like the rest; these crystals are sometimes of a considerable size. All these varieties are perfectly good so long as they are completely penetrated by the bitumen. Bad qualities may be recognized as follows;—Sometimes the rock is regularly impregnated, but the proportion of bitumen is as low as 6 per cent., when it can be worked only with much difficulty. Sometimes the limestone is very hard and much cracked, the cracks being filled with bitumen, so that, when broken, the fracture appears brownish black, like the good samples, but when examined with the microscope, the impregnation is seen to be very incomplete. Samples of this kind are frequently met with in Auvergne. Sometimes the limestone, while it appears rich in bitumen, contains clay, which, being impenetrable, spoils the homogeneity, and causes the fissures so often seen in streets paved with the material; the presence of clay in the sample is easily recognized. Some bituminous limestones, that of Lobsann, for instance, contain an oily principle beside the bitumen, which renders them greasy and spoils the consistence of the mastic made from it; this oil may be removed by distillation, after which the asphalt is fit for use. When asphaltic rock has been long exposed to the air, the bitumen on the surface dries up, to a depth of about 0·01 of an inch. This desiccation, which is due to the slow evaporation of the bitumen, is sufficient to discolour the asphalt so much that it becomes similar in appearance to ordinary limestone: blocks of this kind, which are suspected to contain bitumen, must be broken up to ascertain the colour of the interior. This evaporation rarely extends farther into the rock than $\frac{1}{32}$ of an inch. By means of these indications, it is easy to distinguish between good and bad asphalt, and they will be found very useful to those who have occasion to seek for this valuable mineral. To such also the following hints may be of use: (1) To search only in calcareous districts; (2) not to be content with the exterior colour of samples, but to break into them and inspect the interior; (3) to examine the character of the mineral, and to determine the proportion of bitumen it contains by a process to be described hereafter.

The discovery and application of asphalt to industrial purposes dates from the remotest ages. Many ancient Egyptian buildings bear traces of its use as a cement. D'Eyrinis, the discoverer of the Val-de-Travers mine, and author of a work on the subject published in 1721, affirmed that Noah's ark was coated with this material, and also that the Tower of Babel was probably cemented with it, basing these assertions upon the proximity of the mine of Siddim. These statements are not, however, worthy of credence, since asphalt cannot properly be used as a cement, especially in a warm climate, except for the foundations of buildings. At any rate it is certain that it was much used by the ancients for a variety of purposes, examples of its use being frequently found in Eastern countries. After this time, it was lost sight of, and does not appear to have been employed at all throughout the Roman era. In fact, it did not reappear until the eighteenth century, when D'Eyrinis, a professor of Greek, while making a geological excursion in the Val-de-Travers, in the canton of Neuchâtel, discovered in 1710 a deposit of asphalt, which seemed to him to be identical in character with that found in the East. On making experiments, he found that the deposit consisted of limestone impregnated with bitumen, and that, by boiling, it afforded a mastic which closely resembled the Babylonian cement. The enthusiasm of D'Eyrinis passed all bounds, and from the pamphlet which he wrote some years afterwards, it would be supposed that there could be no possible purpose for which the mineral was unfitted. The pamphlet, however, hinted obscurely at some of the applications which have since been made, though certainly not that which has since proved the greatest success, viz. its use for paving purposes. The Val-de-Travers mine was, for nearly a century, the only known source of asphalt. The first asphalt pavements were constructed in Paris in 1838, and about this time another mine, that of Seyssel, on the Rhone, entered into rivalry with it; both were worked for a long time, and enjoyed a period of very great prosperity. But as often happens to new industrial schemes carried on on so gigantic a scale, it fell into the hands of speculators, whose main object was not the successful working of the mine, but immediate pecuniary gain. "A ring" was formed which, in a few months, raised the price of the shares from 500 francs to 13,000 francs. It is scarcely necessary to say that this did not last, and in a short time the 13,000 franc shares were being offered at 25 francs each! Asphalt, however, was destined to overcome these difficulties, and although it remained for some time in the hands of speculators, it eventually took its proper place as an important and profitable industry. At the present time, many of the streets of the principal towns of Europe are paved with it. Paris notably has been paved almost exclusively with it, and it has been laid down in many of the finest streets and squares in London.

The chemical composition of asphalt is variable, as regards, at least, the relative proportions of limestone and bitumen. The purest varieties, such as those of Seyssel and Val-de-Travers, contain nothing but these two substances, in about the proportions already indicated. Those which are less pure, as, for example, the bituminous limestones of Auvergne, have been impregnated by volcanic agency, and contain, besides these, clay, silica, magnesia, salts of iron, &c. The Auvergne samples contain also traces of arsenic. As a general rule, it may be stated that samples of asphalt are valuable in proportion as they are free from these foreign matters. It is seldom necessary to make a qualitative analysis of asphalt, the constituents of each separate variety being perfectly well known. But it is often required to determine the proportion of bitumen entering into their composition. This determination, moreover, has constantly to be made by persons unfamiliar with the processes of chemical analysis, and it is therefore deemed desirable to describe here a process recommended by Malo, which applies equally to all bituminous substances. A quantity (about 200 grm.) of the substance is reduced to a fine powder, and dried by exposing it in a current of air heated to a temperature higher than 110°, but not above 150°, since above this temperature the bitumen may be altered by the vaporization of certain essential oils. After well mixing this powder, about 100 grm. is taken and placed in a beaker. About 100 grm. of pure carbon disulphide is then poured upon it, and the mixture is well stirred with a glass rod. After resting a moment, it is poured into a weighed filter, having another beaker placed beneath. More carbon disulphide is poured upon the limestone remaining in the first beaker, well stirred, allowed to stand, and the clear portion again added to the filter; this is continued until the powdered limestone is perfectly white, and the last portions of carbon disulphide added exhibit no tinge of brown. The limestone is then dried whilst the liquid in the filter is running through. When perfectly dry, the limestone and the filter are weighed together, and after deducting the weight of the filter, the weight of the washed limestone is obtained, and, by difference, the weight of the bitumen removed by the carbon disulphide. The following is an example of such a test:—

Before the operation.

Weight of bituminous limestone taken	100·00	grm.
Weight of the filter	3·15	„
	103·15	„

After the operation.

Weight of the filter and washed limestone	92·17	grm.
Weight of the filter alone	3·15	„
	89·02	„

From which it will be seen, by a simple calculation, that the proportion of bitumen contained in the limestone was 8·90 per cent. The correctness of the result may be confirmed by evaporating in a water-bath, at 70°, the carbon disulphide. This is volatilized at 48°; the bitumen remains as a residue, and may be collected and weighed, the percentage being thus determined directly.

Bituminous limestones are now found in many different localities. It has been discovered in all the countries of Europe, and, indeed, in nearly all parts of the world. In what manner these rocks originally became impregnated with bitumen is still a mystery which geology cannot explain. In an exceedingly interesting pamphlet published by the Montrotier Asphalt and Cement Concrete Paving Company, the following explanation is advanced:—"Gigantic masses of vegetable matter became, in the course of geological epochs, embedded in successive strata in the neighbourhood of the primitive rocks. Then, during incalculable periods, these masses were exposed to intense rays of heat penetrating from the inner fires through the crust of the earth, which had not yet grown cool. Under the action of this heat, slow combustion took place, till at length, consequent upon a disruption of the earth's crust, a fissure, or a series of fissures, let out the imprisoned vapour, and this vapour of the consuming vegetable accumulations, escaping with a violence in proportion to the power by which it had been held back, came forth charged with the boiling bituminous substance, which it left, in passing, in the limestone strata, and the hot limestone was then impregnated with bitumen, forming this singular example of a mixture of vegetable and mineral elements."

Very few of these beds of bituminous limestone have been worked; some on account of the difficulty of gaining access to them, and others on account of the presence in the rock of certain foreign substances which render the asphalt useless for industrial purposes. Of the former class, there are several mines in Spain, rich in bitumen, but placed in such inaccessible situations that they do not pay the expense of working and transporting. Of the second class, are the limestones of Auvergne, which contain so much sand and other impurities as to be quite useless. Of the mines which are worked successfully, the most important is that of Seyssel. In the neighbourhood of this town, and situate on the banks of the Rhone, there is a hill composed entirely of limestone, about 400 yards in breadth at the base. The presence of bitumen in certain portions of this hill has been known from time immemorial, as will be seen from the fact that it has been known for ages as Pyrimont, or the mount of fire. The right of working this limestone, and of extracting the bitumen, was first granted by the French Government to a man named Secretan, in the fifth year of the Republic. Secretan established a factory on the banks of the Rhone for the manufacture of asphaltic mastic, which for some years produced only small quantities, until, in the year 1838, the establishment in Paris of the first asphalt pavements gave an unexpected impetus to the manufacture, and from that time it rose to a position of importance which it has maintained ever since. In the year 1855, the output from this mine was 1500 tons; in 1863 it reached the large amount of 10,000 tons. As regards production, this mine is still the most important, sending annually into the market, either in the rough state or in the form of mastic, from 9000 to 10,000 tons of asphalt. The factory close by the mine transforms annually from 7000 to 8000 tons of the mineral into mastic. The chief characteristics of the Seyssel limestone is the extreme variableness of the appearance of the mineral, and of its richness in bitumen, the constituents, pure limestone and bitumen, remaining always the same.

The Val-de-Travers mine is very different from that of Seyssel. It is much richer in bitumen, but of considerably less extent. The bed of asphalt is covered with a thin layer of soil, underneath which is another layer of earthy asphalt, varying in thickness from 2 ft. 6 in. to 3 ft. The bed itself is circular in form, about 22 ft. thick and 160 yards in diameter. It contains 12 or 13 per cent. of bitumen, and it was the first kind ever employed in the construction of pavements.

These two mines are by far the most important sources of asphalt; but there are several smaller ones from which an equally good product is obtained. Among these are those of Challouge, Chavaroche, Manosque, Lobsann, Dallet, and Pont du Chateau, all of which are still being worked profitably. There is also a large mine at Maestu, near Vittoria, in Spain, the product of which is of a very fine quality. Unfortunately, access to this mine can only be gained by means of mules and oxen, which is a serious drawback to its successful working.

The processes by which the rock is prepared for the market are four in number, viz.: (1) Extraction from the mine; (2) Preparation (powdering, sifting, &c.); (3) Boiling, and (4) Casting into blocks. The details of these processes are as follows:—

Extraction.—Asphalt is ordinarily obtained from the mine by blasting, like other rocks. This is sometimes carried on in the open air, as at Seyssel and Val-de-Travers, and sometimes in underground workings, as at Challonge and Chavaroche. In winter, owing to the hardness of the rock, the work is much easier than in summer, when it is more or less soft and sticky. It happens sometimes that the elasticity of the mineral cannot be overcome by gunpowder, in which case it must be hewn out with the pick. In the very hot weather, the miners work for only a few hours in the morning, before the rock has had time to soften under the influence of the sun. These remarks do not, of course, apply to the extraction of the rock from underground workings, where these obstacles are avoided by the unvarying low temperature of such workings. The blocks of mineral should never be piled up in high heaps, as in such a case, an elevation of temperature would cause the undermost blocks to crumble to pieces, when, should the fragments become mixed with rain-water, the subsequent operations are much impeded.

Preparation.—The preparation of the mineral consists in breaking it up, reducing it to powder, and passing it through sieves. The blocks of asphalt are generally reduced to the required size by passing them through a species of crushing-mill, constructed of two large metal rollers, placed at any required distance from each other, and furnished with steel teeth. During the summer, the asphalt is mostly broken by hand, the operation being much impeded by the softness of the rock, which almost resembles lead in consistence. The cost of breaking varies in winter and summer in the proportion of 3 to 5.

The pulverization of the broken asphalt is effected in one of two ways, each of which admits of two different processes. If it be powdered by *decrepitation*, the rock may either be heated by means of a stove or by means of steam. If it be reduced to powder by *crushing*, either metal rollers or an ordinary crushing-mill may be employed.

The first of these methods, viz. decrepitation, is now practically abandoned, owing to its high cost, as compared with the other. It will not therefore be necessary to describe the two processes here.

The second of these methods, that of crushing the asphalt, is performed by means of two pairs of metal cylinders, one of which serves to break the stone roughly, and the other to complete the pulverization. This method is always employed with the more homogeneous rocks, which do not enclose particles of ordinary limestone. The cylinders of the first set are armed with spikes about 5 or 6 centimetres in length, which overlap one another; they are placed at such a distance from each other, that the rock is broken to about the size of an egg. After passing between these rollers, the crushed rock is passed by means of a hopper through the second pair. These are perfectly smooth, and placed only about half an inch apart; their effect is to crush the fragments into a thick cake or paste, in which state the asphalt is ready for conversion into mastic.

When the rock contained but little bitumen and a large proportion of oily matter, it was formerly crushed between mill-stones, but this plan has also been abandoned, and a kind of mill resembling a large coffee-mill is now exclusively employed to pulverize these asphalts. In spite of many defects it is the most expeditious and economical method yet devised.

The sifting of the powdered rock is a very simple operation. When it leaves the mill, the powder falls into cylindrical sieves, which are made to revolve twenty-five times in a minute. The sieve is made either of wire or of perforated sheet-iron; in either case, the aperture is about $\frac{1}{12}$ in. in width.

Boiling.—The powder which is collected from the sieve is taken immediately to the boilers in which the conversion into mastic is effected. These boilers are made of sheet iron, and are semi-cylindrical; they are usually 6 ft. in length and 3 ft. in diameter, and are built over an ordinary brick furnace. Each boiler is fitted with suitable agitating gear, worked by steam, and with a metal hood, which is also semi-cylindrical, and furnished with door, through which the material is introduced. At the top of this hood, there is a pipe to convey away the vapours of steam which are disengaged abundantly throughout the operation. The bottom of the boiler is generally made of two sheets, one above the other, and fitting closely together; the bottom one is much thicker than the other, and may be removed, in case of any damage done to the boiler, without necessitating the removal of the contents.

The process is conducted as follows:—About 3 cwt. of *pure bitumen* are thrown into the boiler, where it immediately begins to melt. When it has become sufficiently liquid, the agitator is set in motion, and the powdered asphalt is then added, little by little, each separate addition being made when the last has become well mixed with the liquid bitumen. This is continued until the mixture becomes thick and pasty, and begins to adhere to the arm of the agitator, when it is ready to be cast into blocks. At this time, about 2 tons of the asphalt will have been added, and about 3 cwt. of essential oils will have been disengaged; 2 tons of mastic therefore remain in the boiler.

Casting into Blocks.—The mastic is ladled out in vessels, containing about 56 lb., into iron cylinders of about 6 in. in height, and 14 in. in diameter. These moulds are soaped in the interior in order to prevent the adherence of the mastic to the iron. In about four or five hours' time, the moulds become cool, and the mastic solidifies; this is hastened by sprinkling cold water upon them. The blocks may be easily detached by striking a light blow upon the side of the mould, when it instantly becomes detached, and may be turned out whole. Each block weighs about 56 lb.

Besides its use for paving purposes, asphaltic mastic has numerous other applications. A patent was taken out in 1837 by Claridge, who applied it to paving roads and terraces, kitchens and stables, and to preserving buildings from damp. He also published a pamphlet, entitled 'Instructions for the Use of Seyssel Asphaltic Mastic,' in which he gives a very full and complete description of the various applications for which this substance is fitted.

If the mastic be required for roofing or other cement, it is reduced to powder and mixed with mineral pitch; but if required for paving purposes, it is necessary to mix with it clean gravel or sea-grit. The ingredients are strongly heated for some hours in large cauldrons, and stirred by machinery. The mastic is afterwards run into moulds and formed into blocks weighing about 1 cwt. In this state, it may be easily transported from place to place, and melted down when required for use.

Asphaltic mastic is ductile and elastic, and consequently very durable. It is used in France as a lining for the walls of stables; for, owing to the toughness and elasticity of the surface, no injury is sustained by the horses from kicking, nor is any damage done to the wall. An asphaltic surface is easily laid down, and easily repaired; weather has no effect upon it whatever.

ASSAYING. (Fr., *Docimasie;* Ger., *Probirkunst.*)—The term "*assaying,*" in its strictest sense, means the process by which the precious metals are separated from their alloys, or extracted from their ores, and subsequently purified. Of late, however, the word has come to be used in a much wider sense, namely, the examination of ores and minerals, by any method whatever, with a view to ascertaining, first, what metal or metals they contain; and secondly, with as much accuracy as possible, how much of these metals. We wish, at the outset, to make a very broad distinction between the province of the assayer and that of the analytical chemist. The assay of a mineral is a mere mechanical process, depending to a very large extent upon manipulation and practice, by which the operator can quickly and easily estimate the character and value of the mineral brought under his observation; whereas in order to conduct an exact chemical analysis, it is requisite that the operator should have much elaborate and costly apparatus, as well as a complete knowledge of chemistry, at his disposal. Having made this distinction, we shall endeavour as far as possible to avoid the use of all technical expressions which are familiar only to the professional analyst, and to confine ourselves to such information as will be of use to the miner, the mechanic, or the explorer, and to those methods which admit of being easily understood and employed with only a slight previous knowledge of chemistry, and which do not require any apparatus that cannot be easily made or readily procured by the assayer. Although the assayer who knows little or nothing of chemistry may attain a degree of accuracy hardly surpassed by an experienced analyst, at the same time we must remind the reader that so-called "rule-of-thumb" methods are not by any means to be recommended in preference to the more accurate methods of chemical analysis, and we must impress upon all who are engaged in mining or metallurgical operations the inestimable advantages to be derived from a thorough knowledge of chemical science, and the help afforded by understanding the chemical nature of the ores dealt with, and the various changes undergone by these in the process of assaying.

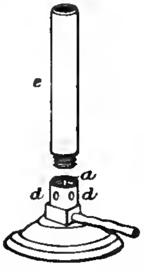
The assay of a mineral may be divided into two parts: the qualitative assay, by which the *composition* of the mineral, or the nature of the metals which it contains, is ascertained; and the quantitative assay, by which we determine the *amount* of valuable matter contained therein. In dealing with the former part of the subject, we shall describe the methods usually employed to estimate the character of the most commonly occurring ores. A practised assayer can frequently judge of the nature of different minerals by a mere inspection of them—by the colour, weight, fracture, &c., which they possess or exhibit; but as it takes years of experience to do this with certainty, it is indispensable that those who have not gained this experience should possess some rough but sure means of discovering whether any ore brought under their notice is valuable for smelting purposes, and if so, how much metal they may expect to extract from it.

The system of examining minerals by means of what is termed "blowpipe analysis" is extremely valuable to the mineralogist, since it is readily performed and gives sufficiently reliable results. Though not, of course, so accurate as the system known as "analysis by wet methods," blowpipe analysis occupies far less time, and necessitates the use of very few reagents. Indeed, the operator can pack up all that he is likely to need in a small box or case, to be carried in his pocket, so that he may examine on the spot any mineral met with in the course of his explorations.

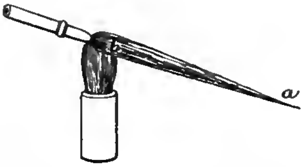
Blowpipe Analysis.—A brief description of the blowpipe, and its auxiliary apparatus and reagents, will here be of use. The best form of blowpipe is that shown in Fig. 277. It consists of a tube made of brass or German silver, and having a horn mouthpiece; a second tube fitted with a platinum point is fixed into the end at right angles. The air-chamber serves to partially regulate the blast, and to contain the condensed moisture, thereby preventing the narrow air-passage from becoming obstructed. The whole is made to unscrew into three pieces, for the purpose of cleaning. In using the blowpipe, the lips are pressed against the mouthpiece, and the stem is firmly held; the cheeks are inflated with air, which is expelled from the mouth through the pipe by contracting the muscles of the cheeks, care being taken to inhale only through the nostrils; by this means a continuous blast is kept up. When gas can be had, the best flame for the blowpipe is that of the Bunsen lamp, Figs. 278 and 279. In this lamp, the gas issues from a small central burner *a*, and passing unburnt up the tube *e*, draws air up with it through the holes *d*; the blowpipe flame, Fig. 279, may be divided into two distinct parts: the oxidizing flame *a*, where there is excess of oxygen, and the reducing flame *b*, where there is excess of carbon. The flame of an ordinary small oil lamp is, however, sufficient for ordinary purposes; this lamp should have a flat wick, and refined rapeseed or olive oil should be used. When a flame is propelled by a current of air blown into or upon it, the flame produced may be divided into two parts, possessing respectively the properties of reduction and oxidation. The reducing flame is produced by a weak current of air acting upon the flame of a lamp or candle; the carbon contained in the flame is thus brought into contact with the substance to be examined, which is reduced. The oxidizing flame is formed by blowing strongly into the interior of the flame. Combustion is thus thoroughly effected; and if a small piece of an oxidizable substance be held at the point of the flame, the former speedily acquires an intense heat, and combines freely with the oxygen of the surrounding air. The substance to be analyzed should, when exposed to the flame of the blowpipe, be supported on some infusible, and in many cases, incombustible, material. Other articles commonly used in assaying are crucible tongs, agate mortars, platinum wire and foil, forceps, test-tubes, &c.; and for the preliminary examination of minerals, a strong pocket lens will often be found of use. The reagents most commonly employed are the following;—Carbonate of soda, which must be anhydrous and perfectly pure, is used to reduce metallic oxides and sulphides, and to flux silicates; borax and microcosmic salt are largely used for dissolving metallic oxides, in a manner to be described hereafter; nitrate and cyanide of potash, nitrate of cobalt, and strong solutions of hydrochloric, sulphuric, and nitric acids are also used by the assayer, together with a variety of other reagents. These should all be kept in stoppered bottles.

277.

278.



279.



The mineral to be examined, after being carefully separated from all foreign matter, is broken up small and finely powdered in an agate or steel mortar. Small portions of it may then be subjected to various simple tests, the results being carefully noted. If mercury, sulphur, or arsenic be present, they are readily detected by the formation of a sublimate when the substance is heated in a clean, dry test-tube, and by the odour of the vapours which are evolved. A number of metals, such as lead, copper, iron, antimony, lithium, &c., may be recognized by the characteristic colours which they impart to the flame, when a small portion is held in it on the end of a platinum wire. Others, such as iron, cobalt, manganese, chromium, &c., are detected by the power they possess of colouring a bead of borax or microcosmic salt. This is effected by forming a loop at the end of a platinum wire, and heating a fragment of borax in it until it runs to a clear glass; a minute quantity of the substance under examination is then added to the fused bead, which is again heated before the blowpipe, when the metallic oxide is dissolved; the following results must be observed:—the colour of the bead in the reducing and oxidizing flames respectively; and whether the colour so imparted be altered when the bead has become cool. Care must be taken only to add enough of the substance to give a slight tinge to the bead, or the colour may be too intense to be distinguishable. When microcosmic salt, which is a combination of phosphate of soda and ammonia, is used, it should be fused upon platinum foil to expel the water and the excess of ammonia contained in it; it is then used upon platinum wire in the same way as borax. The assayer should also make himself familiar with the incrustations formed by different metals when heated upon charcoal. To obtain these, a small hollow is cut in a block of close-grained pine-wood charcoal; a small portion of the powdered mineral is placed in the hollow and heated in the reducing flame, with a mixture of carbonate of soda and cyanide of potash; lead, antimony, bismuth, zinc, and cadmium are indicated in this way. He should be able also to distinguish between the beads of metal obtained by heating many metallic salts on charcoal with reducing agents.

We have now to point out the most characteristic tests for the more commonly occurring metals.

Detection of Antimony.—When reduced on charcoal with carbonate of soda, it yields a brittle bead of metal, the charcoal at the same time being coated with a white incrustation of oxide. On continued heating, the bead volatilizes completely. A further test may be made by acting upon the metal bead with a small quantity of nitric acid, by which it is converted into the oxide; this substance is insoluble in pure hydrochloric acid, but dissolves readily if a few drops of nitric acid be added; on diluting the solution with water, a white precipitate is formed, which redissolves on addition of excess of hydrochloric acid. If a stream of sulphuretted hydrogen (formed by the action of sulphuric acid upon fragments of iron pyrites) be passed through the solution of the bead in hydrochloric acid, a brick-red precipitate of sulphide of antimony is thrown down. This precipitate dissolves readily on treatment with sulphide of ammonia, but is reprecipitated on addition of an acid.

Detection of Bismuth.—Native bismuth fuses readily in either the oxidizing or reducing blowpipe flame, coating the charcoal with a yellowish-brown incrustation, which is somewhat darker in colour than that obtained from lead. The following is the most delicate test for the presence of bismuth:—A small quantity of the powdered mineral is heated in the reducing flame on charcoal, with pure carbonate of soda; the metallic bead thus obtained will be observed to be of a reddish-white lustre, and, when cold, exceedingly brittle. It is dissolved in a little warm, dilute nitric acid. To the solution is then added a few drops of a liquid obtained by adding caustic soda to a solution of stannous chloride (the "*tin-salts*" of commerce), until the precipitate formed at first is redissolved. The presence of bismuth is shown by a black precipitate of oxide of bismuth. Fused in a borax bead on platinum wire, bismuth imparts to the bead a yellow colour while hot, which disappears on cooling. With microcosmic salt, used in precisely the same manner, only adding slightly more of the assay, bismuth gives a yellow bead which is also colourless, or sometimes enamel-white, when cool. The borax test for bismuth ought never to be relied on by itself, but only employed as confirmatory of the above method in the wet way.

Detection of Cadmium.—When heated on charcoal with reducing agents, cadmium compounds give a brownish-yellow incrustation of oxide, which appears the moment the heat is applied; this serves to distinguish it from that obtained from zinc compounds, which takes a much longer time to form. With borax or microcosmic salt cadmium compounds form a yellow bead, becoming colourless when cool. On passing a stream of sulphuretted hydrogen through an acid solution of cadmium, a bright yellow precipitate of sulphide is formed, which, on standing, darkens a little in colour. This sulphide may be distinguished from other yellow sulphides, thrown down by sulphuretted hydrogen, by its complete insolubility in sulphide of ammonia.

Detection of Chromium.—The presence of this metal is generally determined by means of the blowpipe. All the salts, when fused with borax in either blowpipe flame, yield a beautiful emerald-green bead. The production of this bead in both flames serves to distinguish chromium from the metals vanadium and uranium, which yield a green bead only when heated in the reducing flame. All compounds of chromium, ignited with a mixture of nitre and an alkaline carbonate, form a chromate of that alkali; if this be dissolved out with water and neutralized with acetic acid, the solution will give with lead salts a splendid, yellow precipitate of chromate of lead. The mineral known as chrome-iron ore, which is the commonest source of the metal, is generally recognized by its brownish-black appearance.

Detection of Cobalt.—Compounds of cobalt reduced on charcoal with carbonate of soda, or other reducing agent, give a grey, magnetic powder of metallic cobalt. Fused with borax in either flame of the blowpipe, cobalt gives a splendid blue bead; this is a very characteristic test, and serves to detect the most minute quantities. If iron be present in large quantity, the bead will be tinged with green. Only a minute trace of the assay should be employed, or the colour will be so intense as to appear black.

Detection of Copper.—All compounds of copper tinge the flame green. Fused with borax in the oxidizing flame of the blowpipe, copper-salts impart a bright green colour to the bead while hot, turning to a beautiful blue when cold. Reduced on charcoal, before the blowpipe, with carbonate of soda or cyanide of potash, a bright red bead of metallic copper is obtained. The oxides and carbonates are reduced to metal without the aid of reducing agents. The metallic bead, thus obtained, should be dissolved in a small quantity of dilute, warm nitric acid, in a test-tube, and the solution, which is of a bluish colour, diluted with water until perfectly colourless. The addition of ammonia in excess now produces a deep blue coloration, which is obtained if the slightest trace of copper be present.

Detection of Gold.—Gold compounds heated on charcoal with borax, in the inner flame, yield a yellow, very malleable bead of metallic gold, which may be readily recognized. Native gold is generally known by its colour and weight; it is soluble in aqua regia, the dilute solution affording a purple precipitate (purple of cassius) on treatment with chloride of tin; this reaction will indicate the presence of one part of gold in 64,000 parts of liquid, by a faint tinge of the purple colour.

Detection of Iron.—When a very minute quantity of a powdered iron ore is heated with borax in the outer blowpipe flame, a yellow bead is produced, which becomes colourless on cooling; if a little more iron be added to the bead, it becomes red, turning yellow when cool. In the inner flame, the bead is of a greenish colour. The presence of cobalt, chromium, and other metals interferes materially with these reactions; when the presence of iron is doubtful, it is advisable therefore to have recourse to the wet methods of analysis. The principal ores of iron are, however, so well known, that it is seldom necessary to submit the mineral to any test for this metal previous to its *quantitative* determination.

Detection of Lead.—When heated on charcoal with reducing agents in the inner flame, lead compounds give a bluish-white, very malleable bead of metallic lead; around the bead is formed a yellow coating of oxide of lead, which becomes lighter in colour on cooling. The bead of metal is readily soluble in nitric acid, but with difficulty in sulphuric and hydrochloric acids, unless strong and boiling; sulphuretted hydrogen passed through the solution produces a black precipitate of sulphide of lead, insoluble in weak, cold acids. Sulphuric acid produces a white, heavy precipitate of sulphate of lead, soluble in hot, concentrated nitric acid, and in solutions of salts of ammonia.

Detection of Manganese.—The presence of manganese may readily be detected by the borax method. In the outer flame of the blowpipe, a bead is obtained of a beautiful and very characteristic amethyst colour, which, when heated in the inner flame, becomes colourless. Only a trace of the powdered mineral should be introduced into the bead or the colour will be too intense. Another test, which is more delicate still, may be made by heating a mixture of the powdered mineral with twice its weight of carbonate of soda and a little nitre on platinum foil in the blowpipe flame, which is preferably directed upon the foil from beneath. If the least trace of manganese be present, it is at once converted into manganate of soda, which may readily be recognized by its bright green colour.

Detection of Mercury.—Native mercury is, of course, recognized at once by its appearance, and cinnabar may also be known by its weight and colour. If a mineral containing mercury, powdered and quite dry, be placed in a narrow tube open at one end, and heated gently, it is decomposed with sublimation of metallic mercury in the upper part of the tube. When only a small quantity of mercury is present, the sublimate is not easily distinguished from those of antimony and arsenic without the aid of a lens; examined in this way, the sublimate will be seen to consist of minute globules of metallic mercury.

Detection of Nickel.—It is difficult to detect the presence of nickel in its ores by the borax method, owing to the deep blue colour imparted by cobalt, which is almost invariably present also. When heated on charcoal with carbonate of soda in the reducing flame of the blowpipe, a grey, metallic powder is produced, which is highly magnetic. The fused mass should be powdered under water and stirred up with a magnet, or with a magnetized pen-knife; the powder is attracted and may be withdrawn from the water adhering to the magnet, and then scraped off with a knife. When free from cobalt, nickel compounds heated with borax in the oxidizing flame yield a reddish bead which turns yellow on cooling.

Detection of Potassium.—The estimation of the alkalies, potash and soda, is described separately in the article on Alkalimetry.

Detection of Silver.—When mixed with carbonate of soda and heated on charcoal in the reducing flame, silver compounds are reduced to a bright white bead of metallic silver. This bead may be dissolved in pure, warm, dilute nitric acid. Hydrochloric acid added to this solution produces a white, curdy precipitate of chloride of silver, by which the least trace of silver may readily be detected. This precipitate gradually turns violet on exposure to daylight, ultimately becoming black; it is easily soluble in solution of ammonia.

Detection of Tin.—Heated on charcoal with carbonate of soda, tin ores yield a bright, malleable, metallic bead, no coating being formed around it. This bead is soluble in hydrochloric acid; the solution, when treated with mercuric chloride, gives a white precipitate of mercurous chloride; this precipitate becomes grey on heating, from reduction of metallic mercury.

Detection of Tungsten.—When heated with borax in the inner flame, tungsten compounds yield a yellow bead, if sufficient quantity has been added; if not, the bead is colourless. With microcosmic salt, in place of borax, the bead is blue, unless iron be present, the latter turning it blood-red. The addition of a small quantity of metallic tin to the bead reproduces the blue colour immediately.

Detection of Zinc.—Heated with carbonate of soda on charcoal in the inner flame, all zinc compounds give a yellow incrustation of oxide, which turns white on cooling, and does not disappear when heated in the outer flame. With borax, they form a yellowish bead, turning white when cool, and opaque if much zinc be present. If the white incrustation or the white bead be moistened with a dilute solution of cobalt nitrate and then heated strongly in the outer flame, a rich green colour is produced.

Valuation of Ores and Minerals.—Having ascertained by examination the nature of the mineral, the assayer now proceeds to examine it further with a view to determining its value for smelting or other extracting purposes. The methods employed to effect this are very numerous. In many cases, the whole of the metal contained in a weighed quantity of the powdered ore may be obtained by subjecting the sample to a strong heat in a furnace with the aid of reducing agents, or fluxes. In others, it is necessary to employ the longer and more tedious operations of analysis by the wet way. Only the simplest and readiest methods will, however, be described here. It will be assumed that the operator understands the use of the balance, and is, to some extent, accustomed to the manipulation of apparatus, reagents, &c.

For the operations which have to be performed on a large scale in the dry way, the following apparatus is usually required:—

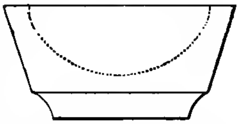
Crucibles.—These are of different kinds, according to the use for which they are intended. A full description of each will be found in the article on Crucibles. It is sufficient to say that the most useful to the assayer are those made of a mixture of fireclay and sand, commonly called Hessian crucibles. Those made of plumbago, porcelain, and platinum are also sometimes indispensable.

Furnaces.—A description in full of the ordinary forms will be found in the article on Furnaces, but those of special construction, used exclusively for assaying purposes, will be described under the metal for the extraction of which they are employed.

Cupels.—These are small, round dishes, made generally of bone-ash or other porous material, which is capable of resisting high temperatures. They are made in the form shown in Fig. 280, and vary from ½ in. to 2½ in. in diameter.

Balance.—Two balances will be found sufficient for ordinary purposes, one for rough, and one for delicate work. The former should carry 3 or 4 lb. in each pan, and should turn easily with a quarter of a grain. The other should carry 100 grains in each pan, but should turn quickly and distinctly with $\frac{1}{1000}$ of a grain.

280.



Other necessary implements are crucible-tongs of all sizes, stirrers, a sand-bath, drying-oven, iron mortars, &c., &c.

Assay of Antimony.—There are two methods of assaying the ores of antimony in the dry way, one being employed when the ore contains sulphur, as is generally the case, and the other when no sulphur is present; these will be described in turn. Owing to the ease with which antimony is vaporized, its assay must rather be considered as a commercial approximation than as being rigorously exact. When the pure sulphide is operated upon, its examination will be of but little value, since every 100 parts of that mineral correspond to 72·8 of antimony. According to Mitchell, the best method of assaying the crude sulphide, which is by far the most important ore, is to mix it intimately with 4 parts of cyanide of potash, and then to heat the mixture gently in an earthen crucible. Only a low heat should be employed in order to avoid as far as possible sublimation of the metal. A bead of pure metallic antimony is found at the bottom of the crucible after the operation.

The assay of antimonial ores containing sulphur may be performed by roasting them, and then fusing the oxidized residue with black flux, a substance formed by deflagrating 1 part of saltpetre with 2 or 3 or more parts of argol (crude bi-tartrate of potash); generally 1 part of saltpetre and 2½ parts of argol are taken. Or the assay may be performed by directly fusing the crude mineral with the addition of black flux and finely divided metallic iron or with iron scale. Owing to its fusibility, and the readiness with which it is sublimed, sulphide of antimony must be roasted with much care. The operation should be conducted at a very low heat, and the assay should be constantly stirred with a thin iron rod until all the sulphur is burnt off. The residue being then fused with 3 parts of black flux, yields a bead of metallic antimony.

Ores of antimony which do not contain sulphur, such as the oxides and native antimony, are not commercially of much importance. When freed from earthy matters, they are readily reduced to the metallic state by being gently heated with powdered charcoal. The assay may be conducted in an earthenware crucible lined with charcoal, without the addition of any flux. If, however, the ore contain much siliceous impurity, it is necessary to use a flux. For this purpose, the ore may either be intimately mixed with 2 parts of black flux, or with 1 part of carbonate of soda and 0·25 of finely powdered charcoal. In this case, lining the crucible is unnecessary, and after it has remained in the fire until its contents are in a state of tranquil fusion, it should, on being withdrawn, be tapped gently against some hard body, to collect the fused metal into a compact button. When the crucible has become cold, it is broken, and the button extracted and weighed. Care is required in detaching it from adhering slag, since from its brittleness it would otherwise be liable to become broken, and a portion consequently lost. This method is inapplicable to ores containing sulphur in any quantity, as the sulphide when heated with black flux yields only one-half of its metal, the rest being retained in the slag.

Assay of Bismuth.—When the ores of bismuth to be assayed consist of bismuth in the metallic state, or of oxides or sulphides free from admixture with other ores, the operation is a simple one. The powdered ore is mixed with the most fusible flux that can be obtained, and fused at a low heat in an ordinary fireclay crucible. A good flux consists of a mixture of 2 parts of carbonate of potash or soda, and 1 part of common salt, with a little red argol or cyanide of potash.

But when, as is generally the case, the ore contains a large proportion of copper, the above method cannot be adopted, because the copper is reduced also; and the necessity for a good method of separating the two metals has long been felt. A very simple means of effecting this has been devised by Hugo Tamm. The ores containing both bismuth and copper are the bismuth-copper pyrites, or the sulphides of the two metals, and their double oxides or carbonates. The method employed in each case is varied slightly. It depends upon the fact that in presence of alkaline fluxes, carbonaceous reagents or carbon itself reduce sulphide of bismuth to the metallic state, leaving the sulphide of copper unaltered. In the case of the sulphides, all that is required is to flux the ore with a mixture of carbonate of soda or potash and common salt, to which a little flowers of sulphur and powdered charcoal have been added. In this operation, metallic bismuth is extracted easily and is tolerably free from copper. When the mixed metals consist of oxides or carbonates, the only difference to be observed is in the proportion of sulphur employed. Three parts of ore should be mixed with from 2 to 3 parts of a flux composed of:—

Carbonate of soda	5 parts	Flowers of sulphur	2 parts
Common salt	2 „	Powdered charcoal	1 „

Iron stirrers must not on any account be used in this operation. There is an unavoidable loss of about 8 per cent. of bismuth which should invariably be allowed for in the result. The composition of the flux and the amount employed may be varied to suit each particular case; the operator will, after a few trials, be able to judge for himself of the most suitable proportions.

A good method in the wet way is to dissolve 100 grains of the powdered ore in strong nitric acid. Evaporate the solution to dryness and add a little sulphuric acid. Evaporate again to dryness, and then add a little water acidulated with sulphuric acid. Filter; add carbonate of ammonia in excess; filter, wash and dry the precipitate, and then ignite it in a porcelain crucible, and weigh it. Every 100 parts correspond to 90 parts of bismuth.

Assay of Cadmium.—Owing to its extreme volatility, cadmium cannot be assayed in the dry way. Except in the case of the mineral greenockite, it is always found in ores of zinc. It may be separated from the latter by dissolving the powdered ore in hydrochloric acid, and passing a stream of sulphuretted hydrogen through the solution. The cadmium is thrown down as sulphide, which must be dissolved by boiling with concentrated hydrochloric acid; the chloride is thus formed, and this is converted into the carbonate by treating with an excess of ammonia. Finally, the carbonate is converted by ignition into the oxide, which, when mixed with one-tenth of its weight of powdered coal and distilled in a glass or porcelain retort at a low red heat, yields a button of metallic cadmium.

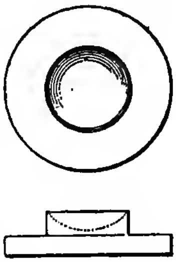
Assay of Cobalt and Nickel.—These two metals are almost invariably found associated together, and the operation of separating them from other metals with which they are found, and from each other, is one of the most useful, and also one of the most difficult that the assayer may have to perform. The following methods, for which we are indebted to Oliver North's 'Practical Assayer,' are quite accurate enough for ordinary purposes. Fifty grains of the finely powdered ore are calcined in a clay crucible until quite free from sulphur. The calcined residue is mixed with an equal weight of metallic arsenic, and heated in a small French crucible, at a low heat, for ten or twelve minutes. A pellet of clay should be inserted in the tapering crucible, in order to prevent the rapid disengagement of arsenical vapours. The residue is detached, broken up, and mixed with a flux of the following composition:—

Carbonate of soda	150 grains.
Borax	50 „
Argol	50 „

The mixture is fused in a larger crucible of the same kind. The metallic bead obtained, containing both the metals, is poured out in the ordinary way and weighed, when cold. If iron be not present in the ore, about 5 grains of fine iron wire must be added as an indispensable condition.

For commercial purposes, the following method is by far the best in use; after a little practice, it yields very accurate results. Take 100 grains of the powdered ore and dissolve them in *aqua regia.* Dilute the solution with distilled water, and filter. Now pass a stream of sulphuretted hydrogen through the solution for half an hour. Filter again, and wash the filter with the sulphuretted hydrogen water. Boil the filtrate and peroxidize the solution with a few drops of nitric acid. If the filtrate be not oxidized, a drop of nitric acid will produce a dark colour, which appears only instantaneously, and must be closely watched. Add barium carbonate until alkaline; boil, filter, and wash the precipitate; then dry and ignite it in a crucible. The residue so obtained must now be fused with an equal weight of arsenic, as in the operation previously described. The button of metal reduced, however, need not be weighed. If it be not much larger than a pea, the whole may be taken for the next operation, but if it be much larger, it must be broken up and a weighed quantity taken. During this time, the smallest and strongest muffle furnace procurable must have been urged to its utmost heat; the back of the muffle should be difficult to see on account of the high temperature. Some small clay cups similar to those shown in Fig. 281, are now placed in the muffle to heat, and the operator proceeds as follows:—

281.



Remove the door of the muffle, and place a little borax glass in one of the cups, and push it back to the far end of the muffle, and shut the door again. When the clay and borax are at the same heat as the furnace, wrap up the weighed piece of speiss in a piece of paper, and with the tongs drop it into the melted borax. The furnace should be hot enough to instantly melt the button, this being one of the indispensable conditions of the assay. There must only be sufficient borax to allow the melted button to revolve in, and not enough to *drown* the button. The button immediately begins to rotate, like a silver-lead bead in a cupel, and after a few moments the cup must be seized with the tongs and drawn quickly out, and plunged, head and all, as quickly as possible, into a basin of water. When cold, examine the borax, and if iron be still coming off, only the characteristic tinge of iron will be observed ; but if the very smallest trace of cobalt has come off, the borax will be tinged blue. Directly this occurs, the operator knows that only cobalt, nickel, and perhaps copper remain. Supposing that no blue tinge appears in the borax, a fresh little cup is placed at the back of the muffle, the button again dropped in and cooled as before, until the blue tinge appears. The operation is proceeded with till all the iron is gone, when the button is taken and placed in a small crucible and covered over with charcoal ; it is melted till no more arsenic fumes are given off, and is then treated exactly as before, occasionally testing the button to see when the cobalt is exhausted. When this point is gained, the button will stop revolving for a time, and the operator must be on the watch for this sign. The cup is now drawn out again, cooled, and borax examined for the characteristic reddish-brown colour of nickel. Any copper which may be present will come off last. In conducting this process the requisite heat is the only difficulty, but by adding some extra iron piping to the chimney of a Plumbago Crucible Company's muffle furnace, placing some anthracites at the bottom of the fire, and carefully choosing the coke, a very high temperature may be got, as long as the muffle itself is a small one. The estimation of the metals by this process is as follows:—

Product, after removal of the iron and excess of arsenic = $Ni_4As + Co_4As$, in varying proportions. Remove the Co_4As, and Ni_4As is left. But when the weight of each is known, it is easy to calculate the relative amounts of nickel and cobalt. For instance, suppose the weight of the speiss of $Ni_4As + Co_4As$ = 20 grains, and the weight of the Ni_4As, *after* the removal of the Co_4As = 10. The amount of Co_4As = 10 grains by difference. Then

$$\overset{Ni_4As}{193} : 10 \text{ grains} :: \overset{Ni_4}{118} : x.$$

The answer is the amount of nickel in weight of speiss (Ni_4As) which has been found in a given weight of ore.

$$\overset{Co_4As}{193} : 10 \text{ grains} :: \overset{Co_4}{118} : x.$$

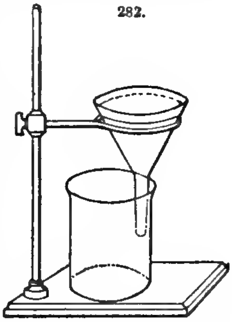
The answer is the amount of *metallic* cobalt in weight of speiss (Co_4As) which has been found in a given weight of ore. As, however, cobalt is usually returned as *protoxide*, then we have—

$$\overset{Co}{29\cdot5} : \overset{Co}{\text{found}} :: \overset{CoO.}{37\cdot5} : x.$$

The answer is the weight of protoxide of cobalt.

Assay of Copper.—The assay of copper ores is conducted in many different ways. Those methods which are performed in the dry way are uncertain and inaccurate, and will therefore not be described. The best method, and the one which is exclusively employed in the laboratories at the mines in Chili, consists in dissolving a weighed quantity of the powdered ore in hydrochloric acid, and precipitating the copper in the metallic state by means of iron wire. It is performed in the following way:—

The sample, carefully taken, is powdered roughly in a clean iron mortar, and afterwards very finely in an agate or steel mortar. 100 grm. are then weighed out (if the ore be very rich, 50 grm. will be sufficient), and washed with as little water as possible into a flask of Bohemian glass, of about 8 oz. capacity. A small quantity, say two or three teaspoonfuls, of pure nitric acid is next poured in in order to set free the sulphur which the ore contains, and which must be entirely got rid of. When the action of the acid has almost ceased, the flask must be placed upon a warm sand-bath, and heated gently. The sulphur, if any be present, will now be observed floating upon the surface; if it be not perfectly yellow in colour, a few drops more nitric acid must be added, and the liquid heated again until the globule of sulphur, previously quite black, has become bright yellow. The liquid in the flask must then be allowed to stand on the bath till perfectly dry.



282.

This done, a little pure hydrochloric acid, slightly warm and about equal in quantity to the nitric acid previously added, is run in, and the contents are once more dried off by the heat of the bath, the object of this being to expel the traces of nitric acid remaining. After driving out the acid fumes from the flask by blowing in gently through a glass tube, a little boiling water containing hydrochloric acid is poured in, and the contents are boiled gently until the yellow paste adhering to the sides of the flask is completely detached. This done, the liquid in the flask must be filtered into a large beaker in the following way:—Pour into the filter (shown in Fig. 282) about half the contents, and when it has run through, wash it down with a little boiling water; now pour in the rest, taking care not to lose a single drop, and leaving as much as possible of the undissolved residue behind in the flask. Wash this residue with boiling water several times, pouring the washings into the filter, and finally wash in the residue; then work the filter down from the top with a jet of boiling water from the wash-bottle. In order to be sure that no copper has been left in the flask, add a few drops of dilute nitric acid, and then a little solution of ammonia; the presence of copper is shown by a deep-blue coloration. When the filter has been thoroughly washed, the beaker containing the filtrate is heated gently in the bath. A piece of pure iron wire, perfectly clean, and about 4 in. in length, must now be heated on the sand-bath, and carefully introduced into the beaker, the contents of which must be nearly boiling. After standing some little time, the copper is precipitated, and forms a thick coating on the wire; this coating is easily detached by gently shaking the flask, so as to expose a fresh surface. When the copper appears to be all deposited, a few drops of hydrochloric acid may be added, and the solution boiled again for a minute in order to extract the last particles. This done, the clear liquid is carefully decanted into a clean evaporating dish, and, if no copper has been poured out with it, rejected. Boiling water is added to the flask, and again poured carefully away. The iron and copper are now to be washed into a porcelain capsule fitted with a lid and handle, and of about one pint capacity. In this the wire is rubbed gently with the fingers, so as to detach the whole of the copper, which should come off readily in thin cakes; the wire is then thrown away. The copper must be washed in the capsule by adding and decanting boiling water, taking care not to pour away the least particle. After two or three washings, a little hydrochloric acid must be added to dissolve any iron which may be present; and, as it is important that none should be left, the addition of hydrochloric acid, with subsequent washing, must be continued until no blue colour is produced by the addition of a drop or two of a weak solution of ferrocyanide of potassium to the acidified liquid. Finally, the copper is washed again with hot water, and drained off as dry as possible. Nothing now remains but to dry and weigh it. Five minutes' gentle heating on the sand-bath in the covered capsule suffices to dry the copper, and it is then brushed carefully into the pan of the balance with a camel's hair brush, and accurately weighed; the weight gives, of course, the exact percentage if 100 grm. were originally taken.

After some practice, assays of copper ores can be made by this method in a little over an hour, with great accuracy. It is well to have two assays of the same sample going on at the same time, and to take the mean of the results as to the correct one. Until the operator has had considerable practice, he will find that his results are generally too low, owing to a slight loss occurring in the washing. In using the above method, the assayer will do well to remember the following rules:—To be careful, in attacking the ore, to use enough nitric acid to free the whole of the sulphur; if it contain only a small quantity, very little will be needed, but in the case of copper or iron pyrites, which contain a large percentage of sulphur, considerably more must be employed. The contents to be *completely* dried in the flask, for the purpose of rendering the silica insoluble and of driving off every trace of nitric acid. In washing the filter, not to use more water than is necessary, as the copper is more easily precipitated from a concentrated solution than from a dilute one. The washing should cease as soon as the ammonia test shows that all the copper has been washed down. To use only the best wire for precipitation, and to heat it to about the same heat as the solution before introducing it. As soon as all the copper is precipitated, to remove the wire, or an excess of iron-salts may be formed which is very difficult to get rid of. It is unnecessary to remind the operator to avoid any loss of the copper in the washing processes; the washings should be examined carefully before being rejected.

This method has been proved by long-continued use to be reliable and accurate, and at the same time expeditious enough for all ordinary purposes; it is, therefore, deemed unnecessary to describe other and more elaborate processes.

Assay of Gold.—Gold is usually found in the native state enclosed in other minerals. A rough assay may be performed by pounding and washing the ore, and collecting and weighing the separated gold; but such an assay would be very inaccurate, because a large proportion of the fine gold would be washed away. The best method, in all cases, is to assay the ore by the process of smelting. As gold ores are usually poor, it is useless to smelt a small quantity; five ounces are little enough in any case for the production of a reliable assay. The ore is finely powdered and sifted, after which, at least an equal weight of litharge is added to it. In most cases, as when the ore is very siliceous or sulphurous, twice or three times its weight is required. The litharge must be pure, and is best obtained by drying acetate of lead at a strong heat, constantly stirring it, meanwhile, to prevent fusion. To the mixture of ore and litharge add a little black flux. Half an ounce of the latter will reduce metallic lead from the litharge in sufficient quantity to absorb all the gold contained in the five ounces of ore taken, which is the object of the process. If sulphides be present in the ore, a little nitre must be added; but if there be none, carbonate of soda or borax may be used instead. The assay is performed in a crucible made of pure clay, or, better still, in an iron pot. When the latter is used, the contents must be poured out into a mould while still hot, or if left till cold they will adhere firmly to the pot. They should be covered with a layer of common salt to facilitate smelting, and the separation of the gold. The melted lead thus obtained contains all the gold and silver derivable from the ore. The gold is obtained in the pure state by destroying the lead and any other metals which may be present by means of a process called *cupellation*, now to be described. The process is founded upon the feeble affinity which gold and silver have for oxygen. The oxides of lead, &c., formed during the process, melt and sink into the pores of the cupel, leaving the precious metals behind perfectly pure and unoxidized. A cupel containing the lead to be refined is placed at the mouth of a muffle furnace, so as to receive the heat very slowly. When all moisture is expelled, the cupel is pushed farther into the muffle, and a stronger heat applied. The heat is now gradually increased, but if the lead becomes too lively, and particularly if there is a considerable evaporation, it must be reduced, or the vapours of the lead will carry away particles of the gold and silver. The best heat is that which just keeps the lead in the liquid state and allows the oxide formed to sink into the cupel and not form a cold, black ring around the hot lead. When nearly the whole of the oxide has been absorbed, the heat is increased to bright whiteness in order to melt the gold and silver into a round globule. When all the lead has disappeared, and the cupel contains only a bright, shining, metallic globule, it is removed from the muffle and cooled. When cool, the globule is detached, cleansed from dirt, and weighed; the yield from an assay of this description is always a little too small. Gold and silver are almost invariably found alloyed together in all assays made immediately from the ore, and the separation of these two from one another, after cupellation, is an operation of much importance. To effect this in the dry way, the alloy should be mixed and melted with three times its weight of crude sulphide of antimony. The melted mass is run into a mould and cooled, and the button obtained is melted in a fresh crucible and treated as before. If, after the pot has been cooled and broken, the button is found to be brittle and hard, it should be subjected to the same process again, with the addition of a little saltpetre and common salt. If the button of gold still remains impure, more antimony must be melted with it, and the refining process repeated until a perfectly pure metal is obtained. When this is the case, the button represents the amount of gold contained in the five ounces of ore taken, and the difference between this weight and the weight of metal received from the cupel represents the amount of silver.

One of the principal conditions of success in the process of cupellation is an accurate proportionment of the ore and the flux. Black flux is preferable to charcoal, but soap is better than either, as it penetrates every ramification of the mass, and its carbon is brought into close contact with every particle of the ore. Alkaline fluxes are objectionable, so far as they cause an ebullition of the mass; and if sulphur be present, it will retain a portion of the gold.

When the gold is in fine grains, such as wash-gold or amalgam, it may be purified by mixing it with a little calomel or corrosive sublimate, heating it at first gently, and then raising the heat until it melts the gold. This operation should be performed in a new crucible; the silver and other metals are then lost by evaporation. The separation of gold from some metals, such as platinum, iridium, and copper, cannot be effected by the above method of cupellation. Indeed, it is useless to attempt to separate them by a dry method; the alloy must be subjected to an elaborate chemical analysis, which it is out of our province to describe.

Assay of Iron.—The assay of iron ores by the dry method is not reliable, and, moreover, requires a much greater heat than is usually at the command of the explorer. We shall describe here a method by the wet way, known as the bichromate of potash method, which for accuracy, simplicity, and quickness leaves nothing to be desired.

The standard solution of bichromate of potash is made by dissolving about 305 grains of the pure salt in 4 pints of distilled water. The operator now takes 10 grains of pure iron wire and dissolves it in pure, weak hydrochloric acid. He then dissolves 3 or 4 grains of red prussiate of potash in half a pint of distilled water, to form the test solution. The remaining apparatus required is an ordinary grain burette, and a square white porcelain slab. He next dissolves in strong, boiling hydrochloric acid in a flask 10 grains, or, if it be poor, 20 grains, of the iron ore to be assayed. The solution of pure wire is then placed in a porcelain basin and diluted with water. A small quantity of the bichromate solution is run into it from the burette, and the contents of the basin are stirred meanwhile with a glass rod; the test is made as follows:—Dip a glass rod in the solution of prussiate, and make several small drops with the adhering liquid upon the slab, which must be perfectly clean and dry. Wipe the rod, and, after each addition of solution from the burette, stir up the contents of the basin, and take up a single drop upon the end of the rod, letting it mix with one of the drops of test solution on the slab. When not the faintest trace of a blue coloration appears when the two drops come into contact with one another, the test is finished. Read off the number on the burette showing the number of grains of solution used, and note it down carefully. The solution of the ore is now diluted with water, and about 30 grains of crystallized sulphite of soda are added to it. It is next heated gently until quite colourless, and then well boiled to expel the sulphurous fumes. The remainder of the process is precisely the same as in the case of the solution of the wire; the liquid is transferred to a porcelain basin, and the standard solution is run in until a drop of the contents mixed with a drop of the prussiate solution produces no blue coloration. It is at first rather difficult to see the last few tints of blue on the slab, but after a few trials it becomes perfectly easy. The calculation is simple in the extreme. If 10 grains of pure iron required the number of grains of the bichromate solution, previously noted down, then a simple proportion sum will give the amount of iron represented by the number of grains of bichromate solution just employed to neutralize the assay solution. When the strength of the standard solution is correctly known, any number of tests may be made with it in an hour, and the degree of accuracy attained after a little experience with this method is surprising.

Assay of Lead.—The assay of lead ores is not a very difficult operation, but it requires care, inasmuch as the metal is very volatile, and if the heat employed in smelting be raised too high, a considerable quantity may be lost by evaporation. It is always conducted in the dry way. The commonest and best method is that recommended at the School of Mines. The ore is finely powdered and a sample carefully taken. A weighed quantity is then mixed with its own weight of carbonate of soda, one-fourth of its weight of borax, and a small quantity of argol; most of the borax and a portion of the carbonate should be reserved to place on the top of the mixture in the crucible. The latter should be an iron pot, of convenient size, and shaped like an ordinary crucible. Having heated it first to a low red heat in the furnace, the above mixture is carefully introduced, and after a short time the heat is raised, keeping the top of the furnace closed. When the contents of the pot are in a state of complete fusion, the heat must be raised as high as possible for a few seconds, in order to cause all the reduced lead to run together in a globule. This done, it is allowed to cool for a moment and then poured out. The bottom, when cool, is carefully cleansed from adhering impurity and then weighed. There is always a certain amount of lead lost by volatilization, but with careful work the loss is less by this method than by any other.

The following is a good rough method of assaying galena. Two hundred grains of the ore are finely powdered and mixed with 200 grains of carbonate of soda and 50 grains of argol in an ordinary crucible, which has been well black-leaded in the interior. Add a few bits of hoop-iron or a few nails, and then cover the mixture with 200 grains of common salt and 200 grains of anhydrous borax. Now place the crucible in the furnace and heat to bright redness. At this point, the cover of the furnace should be partially removed for a few minutes. Cover up again and heat once more to bright redness. When completely melted, the metal may be poured out in the ordinary way, after washing the pieces of iron. In employing this method, care must be taken to keep the top of the crucible as hot as its contents, by covering it completely with bits of coke.

Assay of Manganese.—Manganese ores are valuable in proportion as they possess the power of evolving chlorine, and as it is not the metal itself which possesses this power, but the peroxide, all assays of manganese ores have for their object the determination of the available quantity of this substance present in them. Many methods are employed for this purpose, of which the following are the best.

1. Fifty grains of the ore (which must be powdered very finely in an agate mortar) are placed in a small flask filled with a drying-tube containing chloride of calcium. Then add 1½ oz. of water and 1¼ oz. of strong sulphuric acid, and weigh the whole accurately. This done, remove the stopper and drying-tube and introduce 100 grains of pure oxalic acid, replacing the stopper immediately. Carbonic acid gas is now evolved with considerable effervescence, and is thoroughly dried as it passes through the drying-tube. When the action begins to slacken, the flask may be *gently* heated until no more gas comes off. When this is the case, and the flask has become perfectly cool, it is again weighed. The loss in weight represents the amount of carbonic acid gas disengaged, and therefore the amount of peroxide contained in 50 grains of the ore.

2. Another method devised by Will and Fresenius is very commonly employed and gives capital

results. Fig. 3 represents the apparatus used, consisting merely of two Bohemian glass flasks and three pieces of tubing. Fifty grains of the finely powdered ore are introduced into the flask A with 150 grains of neutral oxalate of potash. Into flask B is poured concentrated sulphuric acid until it is about one-third full. The flasks are then corked up and connected in the manner shown in the figure, and then accurately weighed. The tube *b* is then closed with a pellet of wax, and a little of the acid in the flask B is caused to flow over into A by sucking at the end of the tube *d*. Carbonic acid gas is then formed by the action of the oxygen contained in the peroxide of manganese, upon the oxalic acid, and it passes over into B, being deprived of any moisture which it may carry with it by the sulphuric acid in the flask; through *d* it escapes into the air. This is repeated until no more gas is evolved. The plug is then removed from *b* and air is drawn through the apparatus by sucking at *d*. When quite cold, the whole is again weighed, the loss in weight, as in the former case, representing the quantity of peroxide of manganese in the ore taken.

3. A more accurate method than either of the preceding, though a longer one, consists in combining the ore with iron and then estimating, by means of a standard solution of bichromate of potash, as in the case of iron ores, the excess of iron. The process is as follows:—Dissolve in pure dilute sulphuric acid (1 part of acid to 3 parts of water) about 30 grains (carefully weighed) of pure, clean iron wire, in a large flask, having a tightly-fitting stopper in which is fixed a tube, bent so that the end of it dips into a small beaker containing water. Heat the flask until all the wire is dissolved. Now remove the stopper and tube, and add to the contents of the flask a quantity of the powdered ore equal to the iron previously taken; then replace the stopper and let the flask simmer gently on a sand-bath until the manganese is all dissolved, or the only residue is a small quantity of white sand. The apparatus is then removed from the bath, and, as it cools, the water contained in the small beaker is allowed to flow into the flask, in order to thoroughly rinse out the tube. The contents of the flask are next diluted and allowed to become quite cool. Now, estimate the excess of iron unoxidized by the manganese, by means of the bichromate solution, of which 1000 grains = 10 grains of iron; this is done exactly in the same way as described under Iron (p. 354). The difference between the weight of wire originally taken and the weight indicated by the bichromate solution, represents the amount of iron which has been converted into peroxide by the action of the manganese ore, and from this we can calculate the amount of peroxide in the 50 grains of ore taken for the assay. Supposing that we find 7 grains of iron remain unoxidized, then 50 − 7 = 43 grains of iron oxidized by the manganese. Now, 43 grains of iron correspond to 33·07 grains of peroxide of manganese, therefore, as 50 grains of the ore were originally taken, the percentage of peroxide in the ore is 76·9.

Assay of Mercury.—The only ore of mercury likely to come under the assayer's notice is cinnabar, which is always assayed by distillation. The ore is finely powdered and mixed with half its weight of iron filings and some slaked lime or soda in an iron retort. The retort is then raised slowly to a strong red heat; in its neck is placed an iron pipe about 2 ft. long and ¾ of an in. wide; this pipe is surrounded by another pipe, made of tin, so as to leave a space between the two. In this space flows a current of cold water, entering at the lower end of the pipe and passing out at the other. As the retort is heated, the mercury in the ore is volatilized, and condenses as it passes through the cooled tube; it is then collected under water contained in an iron and porcelain basin. The retort should never be more than one-third full of ore, and great care must be taken to keep it entirely covered with fire, so as to prevent the fumes of mercury from condensing at the top. The iron pipe should be quite smooth on the inside in order that the metal may not adhere to it. Failing an iron retort, a stoneware bottle, or an earthenware jug may be employed. The mercury collected in the basin is put into a tared bottle and weighed; it is not always perfectly pure, but sufficiently so to be depended upon, the amount of impurity never being very large.

Assay of Silver.—Silver ores are assayed in very much the same way as gold ores, differing, however, in the degree of heat used, silver requiring a higher temperature to smelt than gold does. If the ore be rich in silver, a quantity of litharge should be added to it; the quantity may be optional, but should always be inversely proportional to the amount of lead already contained in the ore. One ounce may be considered enough in all cases for a good assay. Half an ounce of black flux, or, better still, of powdered hard-wood charcoal, is added to this, together with ½ oz. to 1 oz. of dried borax. The mixture is thrown loosely into a dry crucible, which should not be more than one-third full. A layer of common salt is spread on the top and the crucible is covered and exposed to a strong and rapid heat.

If the ore contain nothing but sulphides, the smelting is comparatively easy. It is finely pulverized, mixed with an equal weight of litharge and nearly half its weight of saltpetre. If it contain much iron or copper pyrites, the amount of litharge and saltpetre must be proportionately increased. Iron pyrites needs four times, and copper pyrites three times, the above weight of saltpetre. The result of the smelting is an alloy of lead and silver which is afterwards submitted to the process of *cupellation*, in the manner described under the assay of gold.

Assay of Tin.—The assay of tin ores is a difficult and rather unreliable process. An absolutely correct assay can be made only by the wet methods, or, as some prefer, by a partially wet and dry operation. The safest method of ascertaining the exact amount of tin in any ore is to submit it to a chemical analysis, made by an experienced chemist. We shall describe here a rough and practical method employed at the mines in Swansea. Take 100 grains of the ore, which must be very carefully sampled, and mix it with twice its weight of powdered anthracite in a large blue pot, or black-lead crucible, covering the mixture with a thin layer of the powdered coal. Place the crucible in a furnace, in the most intense white heat that can possibly be produced, for a period of fifteen or twenty minutes, or until the mass has ceased to boil, and has settled quietly down in the crucible. Then remove; stir the crucible well with an iron rod, and heat again for the space of five or six minutes, after which the crucible may be removed from the furnace, and the contents poured into a metal mould. The slag should be scraped out into a basin as carefully as possible, pounded, and washed; by this operation much tin may be saved and added to the ingot. In this way the ore will yield nearly all the tin that it contains, but not quite. The metallic tin made by this assay is never pure; it often contains 20 per cent. or more of other metals, which must be subtracted from the actual yield of the ore. In pure ores, this loss is found to be only 8 or 10 per cent. If powdered anthracite cannot be obtained, dry sawdust may be used instead.

In employing the above method, great care must be taken to have the ore very finely powdered, the furnace at a strong white heat, and to pour the molten metal very carefully. The best way to perform this is to push back the slag from the surface with a piece of wood, to place the mould across the mouth of a large iron mortar, and then to pour out as much as possible. All that does not go into the mould falls into the mortar.

The following method is proposed by Domeyko:—Treat 100 grains of the ore with *aqua regia*. Wash and calcine the residue, and mix with 20 grains of charcoal of white sugar. Put the mixture in a small porcelain crucible, and cover over with 100 grains of the same charcoal. Heat in a good muffle furnace for a quarter of an hour. Remove the crucible, and treat the residue when cool with *aqua regia* and precipitate the tin from the solution by means of pure zinc.

Assay of Zinc.—This metal is far too volatile to admit of its being assayed in the usual way. The best plan, if the ore be blende, is to roast it thoroughly with powdered charcoal. The oxides do not require roasting, but must be heated in order to drive off the water and carbonic acid contained in them. This done, the ore must be powdered finely, mixed intimately with 15 or 20 per cent. of charcoal powder, and exposed to a strong heat in a black-lead crucible. It should be perfectly dry, and packed tightly into the crucible, which must be covered over with another, inverted. The zinc is entirely volatilized if the heat has been sufficient, and the remaining matter is scraped out of the crucible, and calcined in an open dish to remove the carbon. The weight of the residue from this operation, deducted from the weight of ore originally taken, gives the amount of oxide of zinc contained in the roasted ore, of which every 100 parts correspond to 81 parts of metallic zinc. Small quantities of other metals are always volatilized along with the zinc in this operation, so that it can only serve as a very rough guide.

There are a few other substances besides the above metallic ores, which have now become of so much importance as articles of commerce that it has been thought desirable to incorporate into this article the methods employed to ascertain their respective commercial values. Some of these assays, such as those of fuel, sulphur, or limestone, enter as largely into the everyday work of the professional analyst as do those of copper, tin, or iron ores. The methods given are, in all cases, the simplest and readiest.

Assay of Arsenic.—If it be required to determine the amount of pure arsenious acid in a sample of the crude article, the assay is best performed in the dry way. If no other volatile matters be present, the powder is sublimed in an earthenware retort, and the sublimate collected and weighed. In the other case, the acid must be dissolved out by means of boiling water, and the *residue* is weighed, the difference giving the amount of pure arsenious acid in the sample.

The following method of assaying arsenical ores by the wet way is given in Crookes' 'Practical Assaying':—"Digest the ore in strong nitric acid, adding occasionally a crystal or two of chlorate of potash until no more is dissolved, and there is no further action on adding fresh acid. Dilute with water, and filter; add to the filtrate nitrate of lead; wash the precipitate formed well on a filter, and digest it in dilute nitric acid; this dissolves the precipitated arseniate of lead, leaving the sulphate. Filter, and saturate the filtrate with soda, which precipitates the arseniate; this is collected, washed, dried, and weighed. Every 100 parts correspond to 22·2 parts of metallic arsenic, or to 29 parts of commercial arsenious acid."

Arsenical ores may be assayed in the dry way by heating them slowly to redness in an earthenware retort or cylinder. If they be sulphides, they must be previously mixed with potash or quicklime. A considerable portion of the sublimed arsenic is collected upon a thin iron plate, rolled up, and inserted in the neck of the retort, and the remainder in a cone, made of copper foil, and luted upon the neck; the cone has a small opening at the top for the free escape of gas. The sublimate is afterwards carefully detached and weighed. Commercial arsenic may be assayed in the same way by mixing it with 16 to 20 per cent. of charcoal.

Assay of Coal.—The assay of coal is frequently an operation of much importance; it consists generally in determining the moisture, the volatile and combustible matters, the fixed carbon (coke), and the sulphur contained in it.

(1) Moisture.—Powder the coal finely, and heat 1 or 2 grains of it in a covered platinum or porcelain crucible, placed in an air-bath at from 100° to 115° for fifteen minutes. Then allow the crucible to cool, and weigh it carefully, afterwards replacing in the air-bath, until its weight is constant, or begins to rise. The loss of weight indicates the amount of moisture in the quantity employed.

(2) Volatile and Combustible Matters.—Heat the same crucible and its contents to bright redness over an ordinary Bunsen lamp for three and a half minutes, and then for the same space of time over a foot blowpipe flame. Allow it to cool and weigh it; the loss from the previous weighing represents the volatile and combustible matters present, and includes half of the sulphur of any sulphide of iron which may be present in the coal.

(3) Fixed Carbon.—Heat the same crucible over the Bunsen lamp until its contents are perfectly white, and its weight is constant; the loss represents the carbon present in the coal, together with half the sulphur contained in the sulphide of iron.

(4) Sulphur.—Weigh out 15 to 20 grains of the finely powdered sample, and treat it with a little nitric acid and chlorate of potash in a flask until there is no further action; then wash the whole carefully through a filter. If the residue in the filter contain any particles of unoxidized sulphur, dry and weigh it, and then ignite and weigh it; the difference indicates the amount of sulphur unoxidized. Now add to the filtrate a little pure hydrochloric acid; boil, and add solutions of chloride of barium until the precipitate ceases to form. Boil well, and allow the precipitate to settle. Filter carefully, washing with hydrochloric acid, and finally with boiling water. Dry, ignite, and weigh the precipitate; this weight, less that of the filter ash, multiplied by 16 and divided by 116·5, gives the amount of sulphur in the weight of coal taken. The weight of *unoxidized* sulphur, previously determined, must, of course, be added in.

The following is another good method of determining the sulphur in a sample of coal:—Make a mixture of 1 part of the finely powdered coal, 8 parts of nitre, 16 parts of common salt, and 4 parts of carbonate of potash, all of which should be pure. Place the mixture in a platinum crucible, and heat it gently; after a time the contents will take fire and burn. Then raise the heat until the mass fuses, and maintain the temperature until it becomes quite white. Allow it to cool, and dissolve it in water. Filter, add hydrochloric acid and chloride of barium, and proceed as in the above case.

Assay of Guano.—(1) Moisture.—Weigh out 5 grm. in a platinum or porcelain crucible, and dry in a water-bath until the weight is constant.

(2) Total Fixed Constituents.—The dried residue from the above operation is to be ignited at a low red heat till all organic matter is consumed, when the residue will be greyish white in colour; the weight gives the percentage of fixed constituents, and acts as a check upon the subsequent results.

(3) Insoluble Matter.—The residue from the above operation is to be boiled with dilute hydrochloric acid until all the soluble matter is dissolved; the residue is then to be filtered, washed, dried, ignited, and weighed; the weight gives the amount of insoluble matter in the sample.

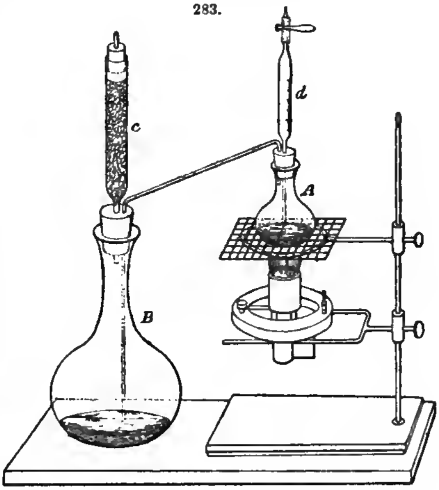
(4) Phosphoric Acid.—Dilute the filtrate from the above operation to 500 c.c. Take 250 c.c. and add ammonia in excess, to precipitate phosphate of lime and magnesia; redissolve in acetic acid and divide the solution in half. One portion is to be tested for phosphoric acid by what is termed the "uranium method." Three solutions are required for this process:—

1. Standard uranium solution, prepared by dissolving about 35 grm. of crystallized uranium acetate or nitrate in 900 c.c. of water, and adding 25 cc. of glacial acetic acid. 2. Sodium acetate solution, made by dissolving 100 grm. in 900 c.c. of water, and making up to 1 litre with strong acetic acid. 3. Standard calcium phosphate, made by dissolving 4·336 grm. of that salt in a small quantity of nitric acid, and making up to 1 litre with water. The solution must be standardized by determining the amount of phosphoric acid present with molybdic acid, as described in the handbooks of analysis. The uranium solution is now diluted with water until 20 c.c. are exactly precipitated by 50 c.c. of the phosphate solution. Fifty c.c. of the latter are placed in a beaker; 5 c.c. of acetate solution are then run in, and afterwards about 10 c.c. of the uranium solution, with constant stirring. After this it is added more slowly, in quantities of about 1 c.c., or 0·5 c.c. at a time, testing the liquid as follows, after each addition. A few drops of the liquid in the beaker are

brought upon a porcelain slab, and brought into contact with a small crystal of ferrocyanide of potassium; a reddish-brown coloration shows that excess of the uranium solution has been added. If there is no coloration, the addition of test-solution is continued until a drop of the liquid, when tested with ferrocyanide of potassium, shows that a slight excess has been run in. The requisite quantity of water is now added to the solution in order that 21 c.c. shall exactly correspond to 50 c.c. of the phosphate solution. Every cubic centimetre of the uranium solution of this strength corresponds to 0·05 grm. of phosphoric acid.

Having made these solutions, and brought the uranium solution to the correct strength, it is easy to apply the process to the estimation of the phosphoric acid in the sample of guano, 50 c.c. of the acetic acid solution being treated exactly as described above. The uranium solution should be checked with the standard phosphate solution every time before using, and two or more estimations of the same sample should be made. About the same quantity of sodium acetate must be used in each test.

283.



The other half of the acetic acid solution may, if it be required, be tested for lime, magnesia, and alkalies.

(5) Ammonia.—One grain of the guano is carefully weighed out and placed with a little water in the small flask A, Fig. 283; the tube *d* is filled with a strong solution of caustic magnesia; the larger flask B contains an accurately measured quantity of standard sulphuric acid which has been poured through broken glass contained in the tube *c*. The apparatus being made quite air-tight, a portion of the magnesia is caused to flow into the flask A by opening the clip; it is then heated by a Bunsen lamp until the contents are brought to gentle ebullition. Great care must here be taken, by regulating the heat, to prevent any tendency to boiling over or frothing, to which the contents of the flask are very liable. The lower end of the distilling tube reaches to the surface of the acid in the flask B. The ammonia contained in the sample is now evolved in the gaseous state and passes over into the standard acid, which must of course be in more than sufficient quantity to neutralize the whole of it. Ebullition is kept up for ten or fifteen minutes, and the apparatus is then left to stand for the same period in order to allow all the ammonia to be absorbed; the flask is then boiled again for a minute and allowed to become cool. When cool, the clip is opened and air is blown through to force any remaining gas to pass into the acid; the tube *c* is then washed down with distilled water, and the contents of the flask B are titrated with standard alkali (see Alkalimetry) to determine the excess of acid. This excess, deducted from the quantity previously introduced, gives the amount of acid which has been neutralized by the ammonia given off. This method, of course, gives only the ammonia contained ready formed in the guano.

(6) Total Nitrogen.—In order to estimate the total amount of nitrogen in the sample by converting it into ammonia, 0·5 to 1 grm. is dried in a water-bath and mixed with soda lime in a combustion tube, closed at one end, about 14 in. long and ½ in. in diameter. A small quantity of a dried mixture of oxalic acid and soda lime is placed in the closed end of the tube, and then the mixture of guano and soda lime is introduced, leaving a space of about 2 in. at the open end to be filled with more soda lime; the end is finally closed with a stopper having a Varrentrap and Will's nitrogen bulb arrangement fixed in it; these bulbs contain a sufficient quantity of standard sulphuric acid. The tube is then heated in a combustion furnace; a strong heat is applied to the end containing the oxalic acid, by which means a current of carbonic acid is produced, which drives the ammonia evolved through the tube into the bulbs. When this current slackens, and before the acid in the bulbs has time to run back into the hot tube, the stopper is withdrawn, and the acid solution is washed from the bulbs into a beaker and the excess of acid determined, as in the previous case, by titrating with standard alkali.

Assay of Gunpowder.—An assay of gunpowder comprises the determination of moisture, nitre, sulphur, and charcoal, and is performed in the following manner:—

(1) Moisture.—Weigh out about 75 or 80 grains of the powder, and dry them over concentrated sulphuric acid, or in an air-bath at 40°, until the weight is constant. The loss in weight represents the moisture.

(2) Nitre.—Weigh out about the same quantity and moisten it with a little water, triturate in

ATOMIC WEIGHTS.—The following are the atomic or combining weights of all the elementary bodies yet discovered:—

Name.	Atomic Weight.	Symbol.	Name.	Atomic Weight.	Symbol.
Aluminium	27·4	Al	Molybdenum	96	Mo
Antimony	122	Sb	Nickel	59	Ni
Arsenic	75	As	Niobium	94	Nb
Barium	137	Ba	Nitrogen	14	N
Bismuth	210	Bi	Osmium	199·2	Os
Borax	11	B	Oxygen	16	O
Bromine	80	Br	Palladium	106·5	Pd
Cadmium	112	Cd	Phosphorus	31	P
Cæsium	133	Cs	Platinum	197·1	Pt
Calcium	40	Ca	Potassium	39	K
Carbon	12	C	Rhodium	104·4	Rh
Cerium	138	Ce	Rubidium	85·4	Rb
Chlorine	35·5	Cl	Ruthenium	104·4	Ru
Chromium	52·4	Cr	Selenium	80	Se
Cobalt	59·8	Co	Silicon	28·5	Si
Copper	63·4	Cu	Silver	108	Ag
Didymium	95	Di	Sodium	23	Na
Erbium	168·9	Eb	Strontium	88	Sr
Fluorine	19	F	Sulphur	32	S
Glucinium	9·4	G	Tantalum	182	Ta
Gold	197	Au	Tellurium	128	Te
Hydrogen	1	H	Thallium	204	Tl
Indium	113·4	In	Thorium	231·5	Th
Iodine	127	I	Tin	118	Sn
Iridium	198	Ir	Titanium	50	Ti
Iron	56	Fe	Tungsten	184	W
Lanthanum	93·6	La	Uranium	240	U
Lead	207	Pb	Vanadium	51·3	V
Lithium	7	Li	Yttrium	92	Y
Magnesium	24	Mg	Zinc	65	Zn
Manganese	55	Mn	Zirconium	89·5	Zr
Mercury	200	Hg			

BARYTA.—This name is given to the oxide of the metal barium, BaO, one of the alkaline earths. It has been already described under the above heading in the article on Alkalies, (p. 232); but some of the salts of this earth, such as the carbonate, nitrate, and sulphate, have become of sufficient commercial importance to demand separate treatment.

Carbonate of Baryta. (Fr., *Carbonate de baryte;* Ger., *Kohlensaures Baryt.*) Formula, $BaCO_3$.—Carbonate of baryta occurs abundantly in the natural state as the mineral *Witherite*, in Shropshire, Westmoreland, Cumberland, and Northumberland. It is obtained in an absolutely pure state by adding an alkaline carbonate to a solution of chloride of barium, or by saturating the hydrate with carbonic acid gas; in either case, the heavy, white precipitate formed is well washed and dried. It is almost insoluble in water, and is decomposed by acids; it is also highly poisonous. In the arts, carbonate of baryta is employed as the base of certain delicate colours, and as an ingredient in plate-glass Wedgwood ware. In France, it is largely used in the preparation of beetroot sugar. The native carbonate is used in pharmacy for preparing some of the other salts of barium, for which purpose it is sufficiently pure. Only a small quantity is now produced in England.

Nitrate of Baryta. (Fr., *Nitrate de baryte;* Ger., *Barytsalpeter.*) Formula, $Ba(NO_3)_2$.—Nitrate of barium is made by neutralizing a hot, dilute solution of nitric acid with carbonate of baryta, and evaporating the solution until crystals are obtained. These are transparent, colourless octahedra, anhydrous, insoluble in alcohol, and requiring about eight parts of cold and three parts of hot water for solution. Its chief use is in pyrotechny, in the preparation of green fires. It has also been lately employed in the manufacture of explosive agents, as a substitute for nitrate of potassium. (See Explosive Agents.)

Sulphate of Baryta. (Fr., *Sulphate de baryte;* Ger., *Schwefelsaures Baryt.*)—This salt, the most important of the salts of barium, is found native in large quantities, forming the species of mineral termed *barites* or *barytes*, and commonly known as *heavy-spar*, on account of its weight (sp. gr. from 4·3 to 4·7). It is found in Derbyshire and Shropshire, and often occurs in fine tabular crystals. The massive variety found in the mountain limestone of the above counties is sometimes called "cawk"; it is more frequently found in white or reddish-white masses. In Saxony, it occurs as the mineral *stangen-spath*, in a columnar form; and at Bologna, a nodular variety is found, called Bologna stone, which is notable for its phosphorescent powers when heated.

The pure salt may be prepared artificially for use as a pigment, by adding dilute sulphuric acid to a solution of chloride of baryta, when a white precipitate is formed; this is well washed and dried. It is a heavy, white powder, insoluble in water and nearly insoluble in all other menstrua. It may also be prepared by heating the native mineral, grinding it to powder, and well washing it, first in dilute sulphuric acid, in order to remove any traces of iron, and afterwards in water; the white powder is afterwards thoroughly dried. This process is employed at several works in the neighbourhood of Matlock Bath, in Derbyshire, but much larger quantities could be produced in different parts of the country, if the demand for the article rendered its production more profitable. The principal use of sulphate of baryta is to adulterate white lead, and to form the pigment known as *blanc fixe*, or permanent white. For these purposes, the native mineral, ground and washed, as described above, is commonly employed. It is also used in paper-making, and as a substitute for the more expensive nitrate in some of the processes of pyrotechny. Sulphide of barium is prepared from the sulphate by heating it to redness in a covered crucible with charcoal.

BEVERAGES.—By the term "beverages" are here understood those common drinks which are not the products of distillation. Those which have been produced by that process have already been treated of as Alcoholic Liquors. Many of these beverages, however, as beer and wine, contain alcohol as a product of their fermentation.

Aerated Water. (Fr., *Eau gaseuse;* Ger., *Gashaltige Wasser.*)—This name is given to a variety of natural and artificial drinks, consisting of water impregnated with carbonic acid gas. The consumption of these drinks is, at the present time, very great, and it is, moreover, rapidly increasing. Thirty years ago, two hundred thousand bottles were consumed annually in France; now, two hundred million bottles are scarcely sufficient to satisfy the demand in that country. In America, aerated waters have come still more rapidly into favour. In our colonies, these refreshing beverages are largely drunk, and in these countries, as well as in our own land, the consumption is daily increasing. Hence, their manufacture has become a staple industry of rising importance.

The sparkling and refreshing qualities of aerated beverages, and in some measure their taste and hygienic properties, are due to the presence of carbonic acid gas (see Carbonic Acid). All natural mineral waters contain it in greater or less quantity, owing to the action of certain subterranean forces. In wine and ale it is formed during fermentation. And it is introduced into artificially aerated drinks by the help of various chemical and mechanical operations, to be described hereafter. In all these beverages, the *rôle* played by the gas is threefold: to give them a sparkling effervescence, thereby rendering them far more refreshing than they were before aeration; to afford them an agreeable, piquant flavour; and, as in the case of natural waters especially, to render them capable of holding in solution certain mineral salts which possess valuable medicinal properties.

The physiological effects of this gas upon the human organism are well known. It exerts a peculiar action upon the nervous system, and especially upon the brain; but these effects are dangerous only when long continued, or when the gas is respired in large quantities, and unmixed with air. Generally, it has a pleasant, exhilarating influence, a notable instance of which is seen in the effect of champagne, a wine containing a large proportion of carbonic acid gas. This gas has also a favourable action upon the organs of digestion. Its presence in wines and ales renders them digestive, as well as agreeably pungent; when the gas has been allowed to escape, they lose the former property, becoming at the same time unpleasantly insipid and flat-tasted. For this reason, all beverages which contain carbonic acid gas are more wholesome when drunk immediately after the bottles are opened.

At ordinary temperatures, water dissolves naturally its own volume of carbonic acid, and alcohol nearly three times as much. By pressure, and with the help of agitation, it may be made to take up a quantity directly proportional to the pressure exerted; that is, by doubling the pressure, we double the quantity of gas absorbed by the water. Hence, the weight of the atmosphere being 15 lb. to the square inch, by applying a pressure of 15 lb. to the inch, we force the water to take up twice the quantity of gas it is capable of absorbing when not subjected to pressure; when, however, the pressure is removed, the gas which has been absorbed in consequence of its application escapes rapidly, causing the phenomenon known as effervescence.

In beer and wine, as remarked above, the presence of carbonic acid gas is due to fermentation. During this process, the sugar contained in the wort or lees from which the beer or wine is made, is decomposed, alcohol and carbonic acid gas being formed. A portion of the latter remains in the liquor after fermentation, and thus imparts to it the sparkling and refreshing qualities which are so highly valued in these beverages.

The presence of an elastic, gaseous body in the water yielded by many springs was well known to the ancients, and was mentioned in the writings of Pliny, Galen, Celsus, and others. In later times, Van Helmont, Boyle, and Bergmann discovered that the gaseous substance was of the same nature as that produced by the combustion of carbon and the decomposition of marble. The investigations of science have since shown that this gas is a compound of carbon and oxygen, and to it was given the name of carbon dioxide, or carbonic acid. In these mineral waters, it is contained either in the free state, or as carbonates, in combination with lime, soda, magnesia, ammonia, potash, iron, manganese, cobalt, nickel, strontium, copper, lithium, &c. In most of these springs, the gas holds in solution certain salts which are precipitated when it is removed by evaporation. The beverages which are made in imitation of these natural waters are, as already stated, impregnated artificially with the gas. For this purpose, it is usually obtained by the action of an acid upon refuse marble, whiting, and other forms of carbonate of lime.

Natural Waters.—We shall consider, first, those few natural aerated waters which have become, or are likely to become, of commercial importance.

Apollinaris Water.—This favourite beverage is obtained from the Apollinaris Brunnen, a German mineral spring, situate in the valley of the Ahr, not far from Neuenahr. According to an analysis made by Professor G. Bischof, of Bonn, it contains in 10,000 parts by weight :—

Fixed Constituents.

Carbonate of soda	12·57	Carbonate of lime	0·59
Chloride „	4·66	Oxide of iron and alumina	0·20
Sulphate „	3·00	Silicic acid	0·08
Phosphate „	trace		
Salts of potash	trace		25·52
Carbonate of magnesia	4·42		

Volatile Constituents.

Free and semi-combined carbonic acid	27·76
Combined carbonic acid	8·07
	35·83

In the Apollinaris spring, there is a high proportion of carbonic acid, especially in the form of carbonates of soda and magnesia ; while the proportion of chloride of sodium is much less than that contained by most other natural waters, and hence its power of quenching thirst is correspondingly greater. The first qualities desired in aerated beverages, namely, a pleasant flavour and a brisk effervescence when mixed with wine and sugar or fruit syrups, are possessed by the Apollinaris water in a high degree, and it has therefore met with general approval since its introduction into this country. The artificial mineral waters, especially soda water, have until lately had the advantage of being strongly effervescent, by reason of the large amount of carbonic acid which they contained, and were therefore preferred by many to the natural mineral waters. But since the year 1863, the gases which escape from the Apollinaris Brunnen, containing more than 99 per cent. of carbonic acid, have been recondensed into the water by the aid of machinery specially erected at the spring for the purpose. By these means it has been rendered possible to export it strongly impregnated with its own gases, and hence it has been made to possess not only the characters of a natural mineral water, but also the high proportion of carbonic acid gas belonging to the artificial aerated waters, and thus to combine the advantages of both.

The Apollinaris spring furnishes a regular supply of water, amounting to 6000 quart bottles per hour, equal to more than 40,000,000 bottles per annum. The bottles and jars are filled and sealed on the spot, as the water issues from the rock, under a pressure of six atmospheres. The arrangements for bottling and export give employment to more than two hundred workmen.

Carlsbad Water.—At Carlsbad, in Bohemia, there are several springs of alkaline and saline composition. An analysis made by Ragsky in 1862 gave the following result:—

Sixteen ounces (7680 grains) contain :—

Sulphate of potash	1·2564 grains.	Carbonate of manganese ..	0·0046 grains.
Sulphate of soda	18·2160 „	Phosphate of alumina ..	0·0030 „
Chloride „	7·9165 „	Phosphate of lime	0·0015 „
Carbonate „	10·4593 „	Fluoride „	0·0276 „
Carbonate of lime	2·2870 „	Silica	0·5590 „
„ magnesia ..	0·9523 „		
„ strontia ..	0·0061 „	Total of fixed constituents	41·700
Alumina and oxide of iron	0·0215 „		

The amount of carbonic acid set free, entirely or in part .. .. 5·8670 grains.

Valuable medicinal effects are attributed to the use of these waters, principally in cases of diabetes, gout, and biliary diseases ; these are said to be due to the large proportion of sulphate, carbonate, and chloride of sodium which the waters contain, together with the temperature at which they are drunk, the temperature of the water from the various springs ranging between 40° and 70°. All the springs have the same specific gravity, viz. 1·004 at 18°; the taste is slightly saline. The water is now largely imported into this country; it should be warmed to the natural temperature before drinking.

Friedrichshall Bitter Water.—The bitter water of Friedrichshall, near Coburg, contains, according to Bauer and Liebig, in 16 ounces, about:—

Sulphate of soda	44·12 grains.	Sulphate of lime	10·79 grains.
„ magnesia ..	39·55 „	Carbonate of lime	0·11 „
Chloride of sodium ..	64·23 „	„ magnesia ..	2·34 „
„ magnesium ..	30·66 „	Silica of magnesia	0·27 „
Bromide of magnesium ..	0·19 „		193·03
Sulphate of potash ..	0·77 „		

Carbonic acid gas .. .. .. 5·32 cubic inches.

This water is much valued, and often prescribed by medical men as an aperient and diuretic. It is taken in only small doses of a few table-spoonfuls, or at the most of half a tumblerful. It should be warmed to about 12° or 15° before using; the slightly bitter taste may be disguised by a few drops of lemon juice or by drinking it with wine. The water will keep in bottles for a long period without losing its characteristic properties.

Rosbach Water.—The water from the Rosbach springs, famed for their purity, has been from time immemorial consumed by the peasantry of the Wetterau, where they are situate. Among these peasants it has gained a high reputation for medicinal virtues as a palliative and preventive of gout, rheumatism, and dyspepsia. This reputation has lately extended to our own and other lands, where it is valued as an agreeable table beverage. Large quantities are now annually bottled at the source and exported. The water has been made the subject of a special analysis by Professor Wanklyn, who found it to contain, in one gallon (70,000 grains):—

Chloride of sodium	83·0 grains.
Carbonate of lime	25·7 „
„ magnesia	12·6 „
	121·3 „

The rate of overflow is about 6 gallons a minute, equal to about 18,000,000 quart bottles full in the year. The Rosbach water issues from the spring super-saturated with carbonic acid, and is therefore effervescent. The escaping gas is recondensed into the water under two separate pressures, of two and four atmospheres respectively. Like the Apollinaris water, it is remarkably free from organic impurities, each of several samples tested by Wanklyn showing only 0·03 or 0·01 parts of albuminoid ammonia per million parts of water. Copper and lead are entirely absent, and there is only a minute trace of iron. The peculiar features presented by its mineral constituents are the almost entire absence of sulphates, the comparatively slight alkalinity of the water, and the presence of the carbonate of magnesia.

Seltzer Water.—The mineral waters of Seltz, or Selters, are derived from a spring of that name situate in the duchy of Nassau, near Mayence. It was discovered in the year 1525, and has since been the ordinary beverage of the inhabitants of the neighbouring country. The numerous cures attributed to the use of these waters attracted the attention of many physicians during the last century, and they are still highly valued both for their refreshing and for their medicinal properties. Since 1803, the spring has been the property of the duke of Nassau, who permits the peasantry of the village to visit it for an hour at mid-day, for the purpose of carrying away the water to their homes. Between the hours of one and seven, the water is bottled for export, more than a million bottles being sent annually to all parts of the world. From this source he derives the larger part of his revenues.

According to an analysis made by Henry, a litre of the water contains:—

Bicarbonate of soda	0·979 grm.	Chloride of potassium	0·001 grm.
„ lime	0·551 „	Sulphate of sodium	0·150 „
„ magnesia ..	0·209 „	Phosphate „	0·040 „
Bromide of iron	0·030 „	Silica and alumina	0·050 „
Chloride of sodium	2·040 „	Free carbonic acid	1·035 „

The water is limpid and transparent, and possesses an agreeable acidity. When mixed with wine, and especially with champagne, it constitutes a favourite beverage. Mixed with goats' or asses' milk, it is frequently recommended by doctors to persons suffering from bilious fevers. It is often prescribed with success as an aperient and diuretic, and in many cases of disordered digestive organs.

Vichy Water.—The natural springs of Vichy, which are the property of the French state, are nine in number. They have a common origin, all issuing from the fresh-water calcareous deposit which forms the bottom of the valley of the Allier. The waters are extremely alkaline and very limpid; they are charged with carbonic acid gas in large quantity. In some of the springs, the water has a sharp, acid taste, and occasionally it emits a slight odour of sulphuretted hydrogen. The chemical composition of the most important of the waters is given in the following table, in which the solid ingredients are expressed in grammes per litre, and the free carbonic acid gas in fractions of the litre:—

	Grande-Grille.	Petit-Puits Carré.	Grand-Puits Carré.	Hôpital.	Acacias.	Lucas.	Célestins.
Carbonate of soda	4·9814	4·9814	4·9814	5·0513	5·0513	5·0863	5·3240
„ lime	0·3498	0·3488	0·3429	0·5223	0·5668	0·5005	0·6103
„ magnesia	0·0849	0·0852	0·0867	0·0952	0·0972	0·0970	0·0725
Chloride of sodium	0·5700	0·5700	0·5700	0·5426	0·5426	0·5463	0·5790
Sulphate of soda	0·4725	0·4725	0·4725	0·4202	0·4202	0·3933	0·2754
Oxide of iron	0·0029	0·0031	0·0066	0·0070	0·0170	0·0029	0·0059
Silica	0·0736	0·0721	0·0726	0·0478	0·0510	0·0415	0·1131
Carbonic acid, per litre ..	0·475	0·499	0·534	0·491	0·619	0·540	0·562

The springs have different degrees of temperature, and observations made at different periods have shown in that respect notable variations. In general, the most abundant springs are the hottest, and those which yield only a small thread of water are the coldest; thus the Puits-Carré and the Grande-Grille, which yield respectively 52,800 and 21,000 gallons a day, have a temperature of 44° and 40° respectively, and that of the Grande-Grille has risen 10° since the erection of the works, which have increased the volume of water tenfold. The Célestins spring, which gives about 5500 gallons a day, is almost cold, and marks from 15° to 16°.

The greater part of the Vichy water, bottled and exported to the different countries of Europe, is furnished by the Grande-Grille spring. The water of this spring, which derives its name from the iron railing by which it is surrounded, is employed only as a beverage.

Wilhelm's Quelle Water.—The natural spring which bears this name is situate at Kronthal, in the Taunus Hills, near Frankfort-on-the-Maine. It was known in the sixteenth century as "the old Sauerborn," and is, therefore, no new discovery. It yields a bright and sparkling water, having an agreeable, saline flavour. It has risen rapidly in favour in this country, although it has only lately been introduced. It is also highly esteemed in Germany, where the consumption has reached the amount of several hundred thousand bottles a month. The medicinal virtues of the water were published as long ago as the year 1584, by Tabernae Montanus, a physician of Worms, in a work entitled the 'Water Treasury.' It has always been the exclusive beverage of the inhabitants of Kronthal. The aerating and bottling works were erected in 1877, and the water is now impregnated with its own gases under a high pressure. It is often prescribed by medical practitioners to persons suffering from gout, rheumatism, and diseases of the bladder. According to an analysis lately made by Fresenius, and since verified by Professor Attfield, the water contains in one thousand parts by weight:—

Chloride of sodium	1·69096	Carbonate of magnesia	0·09647
„ potassium	0·03658	„ iron	0·02967
Sulphate of potassium	0·02363	„ manganese	0·00237
Bromide of sodium	0·00064	Silica	0·10109
Iodide „	0·00001		
Phosphate „	0·00095		2·45769
Carbonate „	0·05104		
Carbonate of lithium	0·00354	Carbonic acid (combined) ..	0·27072
„ barium	0·00038	„ (free) ..	2·24974
„ strontium	0·00202		
„ lime	0·41834		4·97815

ARTIFICIAL WATERS.—On account of the high reputation gained by the waters from various natural springs, and the many wonderful cures which they were supposed to have effected, it is not surprising that a desire should have been manifested to reproduce them artificially, and thus to enable suffering humanity to procure readily and cheaply the benefits which hitherto could only be obtained at the price of a long journey.

We find that as far back as 1560, a study of natural mineral waters, their composition and virtues, was made by Thurniesser, and that he succeeded in making very close imitations of them. He was followed by Hoffman, Geoffroy, and Venel; by Priestley, who in the year 1772 published a paper on the subject; and by Bergmann, who wrote in 1774, to prove the value of the carbonic acid gas held in solution by the waters of Selters, Pyrmont, and other places. The first apparatus for aerating water artificially by means of a pump was made by Paul, in Paris, in the year 1799, who seems to have had a very complete plant. Suave also had a similar establishment in Dresden, in the early part of this century, and he made many important observations on the constitution of different natural waters.

Those natural springs which had received particular attention on account of their beneficial action upon the human system, have, in many cases, been credited with producing results to which they only partially contributed. They were visited by numbers of people who believed implicitly in their curative properties, and added the potent influence of faith to the restorative effects of the journey to the springs, the change of air, scenery, society, and mode of living.

Provided they be carefully made, artificial aerated waters have certain distinct advantages over the natural waters. The most important is obviously that the various constituents of the latter, determined by analysis, can be varied in the artificial drinks, in order to suit particular requirements and cases; and further, waters which are brought from a natural source at a distance cannot be so fresh as those prepared artificially, and certainly are not supposed, like wine, to gain in virtue by keeping. They have also, in many cases, a very unpleasant and even nauseous taste, which can, of course, be avoided in making artificial imitations. It is now generally recognized that the artificial waters are wholesome and pleasant beverages; and they can be produced so cheaply that they are within the reach of all classes of society. The demand for them is fully established, and since the withdrawal of the duty of three-halfpence a bottle, levied some forty years since, the trade has developed, under free competition, with rapid strides. The great drawback to the general consumption has been the high prices charged by the retailers, especially in hotels, sixpence per bottle being often charged for water that has cost them less than twopence.

The first attempts to produce artificially aerated waters resulted in pure water impregnated solely with carbonic acid gas, and containing no other ingredients. Shortly after this, the water was made to still further resemble the natural waters by the addition, in different proportions, of certain salts, to which the medicinal properties of the water had been attributed. Subsequently, beverages of agreeable flavour were prepared by the addition of syrups to the aerated water. Hence we have three classes of artificial water: (1) Simple aerated waters; (2) Aerated saline waters; and (3) Aerated saccharine waters.

Plain Aerated Water.—In the preparation of waters of the first class, the only materials used are pure water, carbonate of lime, and a mineral acid. The water, to ensure purity, must either be distilled, or filtered through such substances as will remove both suspended and dissolved impurities. The carbonate used for the production of the carbonic acid gas is generally in the form of marble or whiting, and the acid most commonly employed is oil of vitriol or concentrated sulphuric acid. The quality of the product depends largely upon the perfection of the apparatus used, and upon the choice of the materials; but the manner in which the operation of impregnating the water with gas is conducted exercises even more influence upon it. The gas, previously carefully washed and purified, is pumped into the water until the latter contains as much as five times its own volume, when it is bottled in strong bottles or siphons, which are constructed to bear a very high pressure. This beverage is commonly called soda water in this country, and Seltzer water in France.

Aerated Saline Water.—In the preparation of waters of the second class, namely, those which contain carbonic acid gas and different saline ingredients in solution, it is necessary only to imitate as carefully as possible the composition of the natural waters. By so doing, artificial waters may be produced which far more closely resemble these than by adopting any of the numerous recipes and formulæ which are published for the purpose. The mixtures of the salts, as determined by analysis, may generally be made directly, especially if they are all soluble; but if they are insoluble, they may often be dissolved by carbonic acid. Some makers obtain by *double decomposition* certain salts which they require the water to possess. Distilled or filtered rain water should be used in preparing these saline waters; and for the chalybeate waters, it should be boiled and allowed to cool out of contact with the air. Solutions are generally made and stored in slate tanks, in which the drawing-off pipe is carried up a few inches from the bottom to allow room for the sediment. When small quantities only are required, the bottles are dosed with the exact amount before the carbonated water is let in. Those who wish to avoid the trouble of preparing them, and require only small quantities, can purchase the concentrated solutions ready made.

Many natural waters contain minute traces of bromides and iodides, of manganese, and of phosphoric and fluoric acids. It may be well to remark that it is the opinion of many high authorities that the medicinal virtues of these waters are due rather to the presence of the above substances, and to the high state of dilution in which they are held, than to those salts which are present in far more abundant quantities.

There are also a few saline waters which are not made in imitation of any of the natural springs, but which, nevertheless, have many valuable properties, and are widely consumed. The common recipes for beverages of this kind are given below.

Carrara Water.—Lime water, made from lime made by calcining Carrara marble, supersaturated with carbonic acid under a strong pressure, so that the carbonate of lime at first precipitated is redissolved. It should contain 8 or 10 grm. of carbonate of lime per half-pint bottle.

Chalybeate Water.—Ferrous sulphate, 3 grm.; bicarbonate of potash, 61 grm.; cold rain or distilled water, 1 quart; mixed and agitated in a corked bottle. This water is equal in tonic properties to that of the springs, and may be rendered refreshing by aeration at a low pressure.

Lithia Water.—A solution of carbonate of lithia, of any required strength, in aerated water; or 3 to 5 grains may be placed in the bottle and filled up with highly charged water, and well shaken. Lithia water and potass water are often mixed together.

Magnesia Water.—About 1 oz. of fluid magnesia to a bottle of water; or carbonate of magnesia may be dissolved in aerated water, under a slight continued pressure, in about the proportion of 1 oz. to 10 quarts of water.

Potass Water.—About ½ oz. of bicarbonate of potash to the gallon is the usual quantity, proceeding as described below for soda water.

Seidlitz Water.—Nearly ½ oz. of tasteless salts of Rochelle, dissolved in warm water, per gallon of spring water.

Soda Water.—The amount of soda varies with the purpose for which it is required. If it is for medicinal use, as much as 15 grains to the bottle is sometimes employed, or about ½ oz. of bicarbonate of soda per gallon. If sold as a refreshing beverage instead of plain carbonated water, which is often erroneously called soda water, 2 grains, or less, to the bottle is sufficient, or about 1 oz. of bicarbonate of soda to 12 gallons. After mixing, the solution is allowed to settle, and the clear portion filtered through lawn before being passed through the machine.

Aerated Saccharine Waters.—The third class, or saccharine aerated waters, consist, as we have remarked, simply of gaseous water sweetened, flavoured, and sometimes coloured with various ingredients; they are consumed only as refreshing and pleasant drinks. The sugar and flavouring matter are mixed together and dissolved in water, constituting what are called *syrups;* of these there are many varieties; their general preparation and a few recipes for the most common, are given below.

Syrups are formed by making concentrated solutions of sugar in pure water, or in water containing the principles of various flavouring substances; the former are called simple, and the latter compound syrups.

There are many precautions to be taken in order to ensure the production of good syrups, the most important being, perhaps, the selection of the sugar. Cane-sugar only should be used, and that should be perfectly refined. The least shade of colour in the sugar is due to the presence of impurities, and syrup prepared from such sugar not only has an unpleasant flavour, but is also very difficult to keep. The use of common or brown sugar may be regarded, in many cases, as an adulteration.

Syrups are very easily prepared. A hemispherical copper basin, not tinned, but well polished, and kept scrupulously clean, is the apparatus employed. This basin stands on three legs, and is furnished with a false bottom, which is also hemispherical. The two hemispheres are surrounded by a copper cylinder, fitted with a lid; the three parts of the apparatus are fixed together by means of two circular iron rings, which are fitted to the circumference of the hemispheres and to the bottom of the cylinder, the whole being well pinned or bolted together. A stop-cock in the outer hemisphere communicates by means of a short pipe with the inner one, and serves to withdraw the contents. Another cock, placed almost at the top, serves for the admission of steam between the two bottoms; and the condensed water is drawn off by means of a third cock communicating only with the outer bottom, and placed at a short distance from the first. The whole apparatus may be of any convenient size. Its chief advantage is that the syrup can be heated to the required degree with the utmost nicety; the steam is admitted until this degree is reached, and the supply may then be stopped in a moment, thus ensuring perfect regularity of working.

There are many circumstances which tend to produce changes in syrups when made, and to cause them to degenerate and become worthless; these must be carefully guarded against. The most common is fermentation; this may be either the result of too short or too long-continued boiling; or of the presence of an excess of mucilaginous substances; or an imperfect clarification of the syrup will also produce it in the course of time. But the most frequent cause of fermentation is found in leaving the syrup in a warm place, or in vessels which are not completely filled, and especially if they happen to have been wet when the syrup was introduced. In order to guard against under or over-boiling of simple syrups, it should be laid down as a rule that they stand at 32° B. when boiling, and when cold at 34° in winter and 35° in summer. They should then be bottled, and stored in a cool cellar.

Lemonade.—The manufacture of lemonade is one of the most extensive and profitable branches of the aerated water trade, and is at the same time extremely simple. The addition of syrups and flavouring ingredients to gaseous water not only does not affect the hygienic properties of the water itself, but frequently enhances them by rendering the water tonic, as well as pleasant to the taste. Lemon or lime-juice mixed with simple syrup and aerated water constitutes an agreeable acid and most refreshing beverage. Tartaric and citric acids are also added to lemonade, either separately or together. Their qualities are similar, but not identical, and they are best when mixed together. Citric acid possesses, when diluted with water, a fresh bitter flavour which is very agreeable. Tartaric acid has not so fine a flavour, but it is less costly, and it has also the valuable property of assisting to preserve syrups and lemonades.

The lemon is not the only fruit that is used to flavour aerated waters. Oranges, raspberries, vanilla, and several others are largely employed, each producing a distinct and pleasantly flavoured beverage. The three saccharine aerated drinks most commonly prepared are lemonade, orangeade, and ginger ale. To make the first of these, about half an ounce of essence of lemons is mixed with 1 quart of simple syrup; orangeade is made by mixing the same quantity of essence of oranges with 1 quart of syrup; and for ginger ale about the same quantity of essence of ginger is added to the syrup. Another favourite beverage is made by flavouring the syrup with ½ oz. of essence of vanilla. The flavoured syrups thus prepared, are placed in bottles, the quantity added varying in different places, and the bottles are then filled and corked at the machine in the ordinary way. The regular dose of syrup is from 2 oz. to 2½ oz. per bottle.

All the essences used by aerated water makers are usually purchased by the makers ready made, though in many cases it is found desirable to prepare them at the factory. Below are given a few recipes for those most commonly used:—

For essence of lemons, remove the outer rinds of 40 lemons, without a particle of pulp, and macerate them with 6 quarts of perfectly pure alcohol at 85°. After two or three days, distil to dryness in a water-bath; add 2 quarts of water and rectify to obtain 5 quarts of the essence. The essences of oranges and cedrats are made in precisely the same way.

For essence of strawberries and raspberries, take 56 lb. of the fresh fruit, free from stalks and leaves, and place them in 45 quarts of pure alcohol at 80°. Macerate for twenty-four hours in a vessel closed in a water-bath; add 20 quarts of water, and distil to obtain 44 quarts, each containing 17½ oz. of essence.

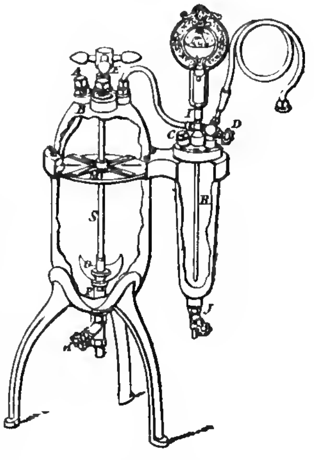
Many manufacturers prepare the essences of lemons and oranges by a process of simple infusion without distillation, which is much more readily performed. The outer rinds of twenty lemons are allowed to macerate for eight or ten days in 3½ pints of pure alcohol at 56°, which should be perfectly tasteless and odourless. Filter the product, and add 1½ oz. to each quart of syrup. The aroma obtained by this method is more concentrated than that obtained by distillation. The essences should be kept in air-tight bottles, and preserved at an ordinary temperature. They improve much by keeping.

The following is the common method for preparing fruit syrups for use at counter fountains in conjunction with aerated water. The fresh fruit, freed from stalks and leaves, is mashed by means of a wooden instrument, and about a fiftieth part in weight of crushed loaf sugar is added. It is then left to stand at an even temperature for a few days until fermentation has taken place. The juice is next expressed, and left to settle in a cool place. When clear, it is simmered for a few moments with nearly double its weight of best loaf sugar, the scum being removed as it forms. If not intended for immediate use, a little spirit should be added. The vessels in which the syrups are placed should be perfectly air-tight; and in order to prevent the ill effects of variation of temperature they are often stowed away in ashes.

Manufacture.—The apparatus employed in the manufacture of aerated water consists essentially of four parts: namely, the generator, a vessel in which the carbonic acid gas is generated by the action of an acid upon a carbonate; the purifier, another vessel partially filled with water, through which the gas is made to pass for the purpose of removing impurities carried over; the gas-holder, a reservoir in which the gas is expanded and stored; the mixing machine, consisting of a cylinder containing an agitator, into which the water and gas are pumped, and stirred up to cause absorption of the latter by the former; and the bottling machine, by means of which the aerated liquid may be transferred into bottles or siphons, and securely closed without allowing any of the contained gas to escape during the operation. In all large manufactories of aerated water, other auxiliary machines are used to cleanse the bottles returned from the consumer to be refilled. It now remains to describe in detail each of these several parts of the apparatus.

The Generator.—This vessel, which is shown partly in section in Fig. 293, consists of a vertical cylinder, made either of lead, wood, or copper. The body is well and substantially supported, under its top flange, on a cast-iron ring attached to the framework, and also at the bottom part on four iron brackets, which are secured by bolts to the legs. The bottom part is joined to the body by a circle of bolts and nuts; and these may be easily removed to give access to the agitator, which is the only part liable to derangement. The frictional or working part of the spindle which carries the fans, is a stout silver tube, worked in the stuffing boxes, so that it is not affected by the acid. The top of the cylinder is covered with a lid, which is fastened down and made to fit tightly by means of asbestos jointing. At one side, and close to the top, is a curved leaden pipe, connected with an acid box, for supplying the acid. In the interior of the vessel, and at the bottom, is a metal agitator, or fan, worked by a handle, which is turned by hand from the outside. At the bottom of the vessel is an aperture through which the waste products are withdrawn when necessary; this aperture is securely closed by means of a tightly-fitting lid, working on a hinge. The carbonate, which is generally made into a semi-fluid state, in order to facilitate the action of the acid, is introduced through the opening at the top of the vessel; whiting, or any other cheap and perfectly pure form of carbonate of lime, may be used. With pure materials, 50 parts of whiting will neutralize 49 parts of oil of vitriol, liberating 22 parts of carbonic acid gas, and forming 77 parts of hydrated sulphate of lime; from these figures may be calculated approximately the amount of both carbonate and vitriol required to produce a given quantity of gas. The vitriol is introduced by means of the leaden pipe connected with the top of the vessel. The evolution of the gas may be regulated by the speed with which the agitator is made to revolve. Sometimes the vitriol chamber is connected by a swing joint, and, if fixed above, when working under pressure, has an equalizing pipe. The outlet is closed by a lever or screw, which is locked to prevent leakage, or automatically closed by the pressure of the gas. In some places, it is enclosed in the body of the generator, and manipulated from the outside; in other places, the plan is reversed, and the acid solution is placed in the body of the generator, the carbonate, which is held on plates with revolving discs, being allowed to fall in as desired; some carbonates, however, are apt to cake, and instead of a steady delivery, fall in in lumps; this arrangement is shown in Fig. 284. In other places, again, it is customary to suspend the carbonate above the acid, and to dip it in when required, but care must be taken to see that there is no waste by the formation of an insoluble crust. In many cases, the apparatus is self-acting, the carbonate being lowered into the acid as the pressure is lessened in the generator. In those systems in which the gas is retained under pressure, the gauge is usually fixed on the purifier, and the generator is provided with a safety-cap in which a disc is ruptured when the pressure becomes excessive. Some safety-valves have an alarm whistle which can be set to blow off at various pressures.

284.



The generator shown in Fig. 293 is made usually in two sizes, holding respectively 36 gallons and 26 gallons. The former kind is 3 ft. 6 in. long and 1 ft. 11 in. in diameter; the latter is 2 ft. 2 in. long and 1 ft. 6 in. in diameter. The whole is placed on a strong iron stand, at a convenient height for a pail or gutter to be placed directly underneath it.

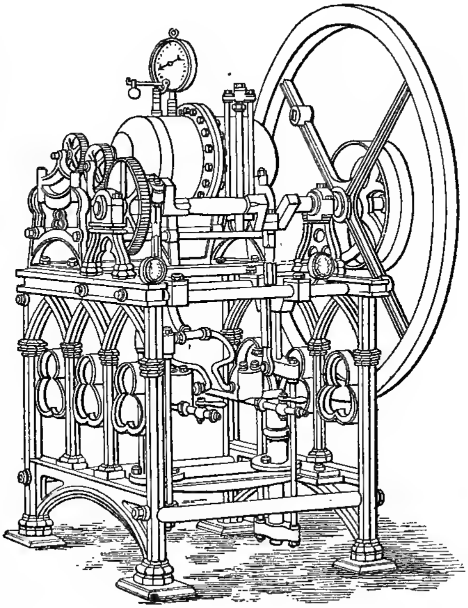
As soon as the action of the acid has ceased, and the required quantity of the gas has been evolved, the aperture at the bottom of the generator is opened, and the waste sulphate of lime allowed to fall out into vessels placed beneath; the generator must then be thoroughly cleansed by pouring in water at the top and running it out from below. The sulphate of lime has hitherto been rejected as useless, and is often a source of much annoyance to manufacturers; there is, however, a possibility of its being utilized for the preparation of plaster of Paris, or as a manure.

The Purifier.—The gas, as evolved, passes directly from the generator through a pipe into another vessel called the purifier, in which it is washed. This vessel is exactly similar in shape to the gas-holder, shown in Fig. 293, but is smaller, and has, of course, no rising bell. The pipe which conducts the gas into this vessel reaches nearly to the bottom, and another pipe, for the exit of the gas, reaches to within a few inches of the surface of the water. The object of the purifier is not so much to *wash* the gas as to act as a catch-box, to retain any whiting or vitriol that may be blown over by the force of the escaping gas. A few pieces of marble or other limestone should be introduced into it, in order that any acid carried over may not be wasted. Various arrangements of pipes in the purifier are adopted by different manufacturers to cleanse the gas as thoroughly as possible. As it is difficult, however, to effect a thorough purification of the gas in this vessel, it is again washed in its passage through the gas-holder, which will now be described.

The Gas-holder.—As it leaves the purifier, the gas is conducted by a leaden pipe into the gas-holder, a vessel consisting simply of a wooden tub, containing a rising bell, as shown in Fig. 293. The tub is filled with water up to the dotted line, the bent tube from the purifier dipping well underneath the surface. The other, or drawing-off pipe, stands above the water, and at such a height, that it is impossible for the latter to be drawn into it. If it be suspected that this is the case, the pipe should at once be examined for a crack or split. The water must be changed when it has become too impure for the purpose; generally the holder is cleaned out once a month. The copper holder, or bell, is steadied by means of counter-weights. To commence the process, the top cock is opened to allow the air to escape as the bell descends; the latter should not touch the bottom, but remain within a few inches of it. The drawing-off pipe, by which the gas is conducted from the gas-holder to the filling machine, is bent in the shape shown in the figure.

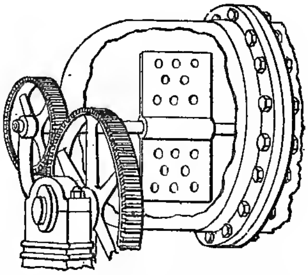
The Mixing Machine.—This machine, in which the gas and water are mixed together, consists essentially of a cylinder containing an agitator. The gas and water are forced in, and the mixture is effected by the aid of the agitation, the gas being, of course, under a high pressure. To force in the gas and water, a pump is attached to the machine, having connection with the gas-holder and with a vessel containing water placed at the side. There are two arrangements of the pump in common use; in the first of these, each stroke of the piston drives in the gas first and then the water; in the second this order is reversed, the water going in first and the gas following. When the water is ejected from the pump-barrel before the gas, all the passages of the valve-box are filled with the latter under compression, which must expand before the pump can draw a new supply; this expansion is equal to a loss of fully one-third of the labour employed, since the plunger is half-way up the barrel before it begins to draw. But with the other arrangement of the pump, in which the valve-box is at the top and the plunger underneath, the gas is ejected before the water, and all the passages being empty, the pump begins to draw from the commencement of the descent of the plunger.

285.



In Fig. 285 is shown what is termed a *double pump* machine, having one cylinder and two pumps, of the first of the two classes mentioned above. If *two* cylinders are affixed to this machine, it will produce two kinds of aerated waters at the same time; or it may be arranged to yield a water doubly charged with gas. The cylinder, which is shown partly in section in Fig. 286, is made of copper thickly lined with tin, and is in two parts, firmly bolted together. The advantage of this is that if anything goes wrong in the interior, it may be readily discovered by taking the cylinder to pieces; machines which have the cylinder soldered up often occasion a good deal of trouble. The agitator should have a bracket support outside the cylinder, in order that it may work in leather instead of metal, since the latter imparts a metallic taint to the water in the interior. The cylinder in the figure is provided with a water gauge, dial indicator, and safety-valve; the necessity for these will be obvious. As will be seen, the pumps are placed beneath the cylinder; they are connected by means of tinned pipes, with the gas-holder placed alongside the machine, and with the water or solution pan, which is also placed at the side or behind the machine on a stand, as shown in the figure. Another pipe made of pure tin connects the cylinder with the bottling machine, to be described later. The agitator should be driven by toothed wheels, not by belts or bands. Belts are always liable to run off or to slip, occurrences which seriously interfere with the regular working.

286.

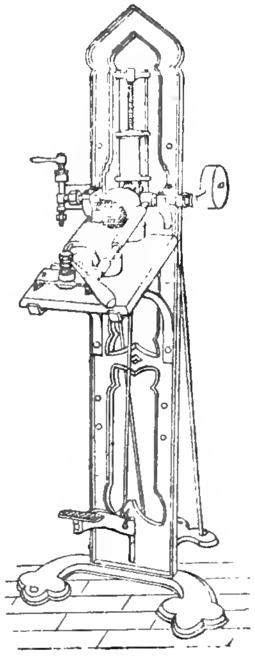


Before setting to work, the machine should be turned round a few times, and all the parts of the machine carefully examined to see that the water and pressure gauges are in working order, index cocks properly set, the bolts of bearings at proper tension, and the valves free from grit. If it has been standing some time, the machine will probably leak, on account of the washers being dry, in which case, time should be allowed for them to soak thoroughly before tightening up; this, when necessary, is done gradually and evenly all round. As the cylinder should not be more than about half-full of water during working, the gas cock is turned on full, and the water cock half way. The earthenware pan at the side of the machine, which supplies the solution or water, should be kept cool and covered over.

When the machine is working, the pump draws at the same time the gas from the gas-holder, and the water or solution from the pan at the side, generally called the solution pan. The gas and water are forced up through the valves into the cylinder, the gas entering first, and the water last, and both being thoroughly mixed by the agitator. The variations of pressure in the cylinder are shown by the dial indicator, and the lever safety-valve is set to blow off at any required pressure.

The Bottling Machine.—The aerated water made in the cylinder of the mixing machine, is passed through the tin pipe to an apparatus called the bottling machine, which stands near. This machine has now reached such a degree of perfection that it is made to perform three distinct operations, viz. filling, syruping, and stoppering the bottles, which operations are carried on almost simultaneously; the machine may be efficiently worked by any unskilled person. All these improvements have been effected within the last few years. As the soda water trade developed, the necessity for a bottling machine which could be easily worked made itself seriously felt. The old-fashioned method of bottling by hand and knee, directly from the nose of the machine, had many disadvantages, the principal being that it required much practice to get rid of the air in the bottle, and to retain the gas; and also that much trouble and expense was occasioned by having to compress the end of the cork, and to fit it to the mouth of the bottle before finally stoppering. The methods which have been used to force in the cork by machinery are various. Simple and compound levers, racks and pinions, screws, besides many other forms, have each their advocates. Machines having arrangements to expel the air in the bottle, and different sizes of nozzle cones to suit different corks, were patented more than fifty years ago; and self-supplying and corking machines about twenty-five years ago. The treadle which works the cup in which the bottom of the bottle is put before forcing its mouth against the filling nozzle, has been worked in several different ways, such as by a foot lever, by a hand rack, and by a lever connected with a saddle upon which the bottler sits, and in other ways. Machines filling very large quantities and worked by steam power have lately come into use; these are made self-syruping and corking, a slight variation in the form being made for internally stoppered bottles.

287.

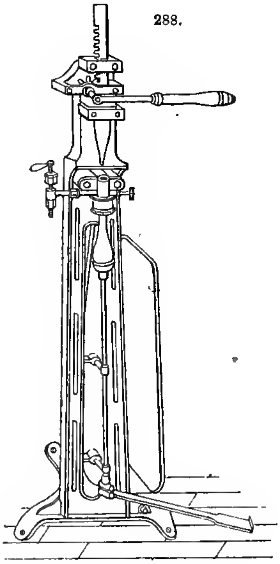


The bottling machines now in use are of two kinds, viz. those made to fill the self-stoppering bottles, and those made to fill the ordinary bottles. Codd's filling machine is shown in Fig. 287. The bottle is laid on the table in the two hollows, the indented side being always kept uppermost. The guard and excentric motion containing the cup are then brought down over the bottle by means of the handle, which is lowered. forcing the cup to rise and so bringing the bottle up to the rubber nipple: by keeping the hand firmly upon the handle, the bottle is kept tightly against it. At the same time, the handle of the supply valve is turned, and the bottle filled up to the required height, that is to about the shoulder, which can be seen by looking through the holes in the bottle guard. The hand is then removed from the supply valve and the guard quickly raised, the mouth being still kept pressed against the nipple, until it is sufficiently high to allow the ball in the neck of the bottle to roll into its collar. The bottle may now be released into the left hand by simply pressing the handle up, and the machine is left ready for a fresh bottle.

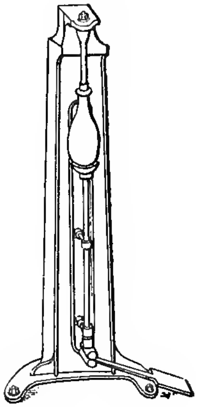
The foregoing method is that adopted for bottling plain aerated water. In bottling saccharine waters, a syrup pump attached to the machine is brought into operation. The construction of this pump is extremely simple, and its action very effective; it constitutes one of the most recent improvements effected in this class of machines, as it dispenses with the separate operations of syruping. The pump, which is made of glass, is shown in the figure attached to the upper part of the machine. It is connected with a receptacle behind containing the syrup, and is worked by a treadle in the following manner: when the bottle is laid on the table, as described above, and held up to the nipple by the handle at the bottom of the guard, the syrup is injected into the bottle by pressing on the iron treadle at the foot of the machine; this is to be done before letting in the aerated water. When the foot is taken off the treadle, the spring on the top of the pump causes the plunger again to rise, and so draws a fresh charge of syrup into the pump; it is then ready again for discharging into the bottle, the last action being entirely self-acting. The syrup pan or jar should be fixed, by preference, on a level with the syrup pump, but it may be above or below, if inconvenient otherwise. The connection between jar and pump may be made with ordinary flexible tubing. When not in use, the cock at the back of the pump should be turned off.

The machine for filling the ordinary bottles, or cork bottling rack, is shown in Fig. 288. The bottom of the bottle is placed in the cup, which is moved by the foot lever, the mouth being pressed against an indiarubber washer. A wet cork is placed in the nozzle piece, and the handle of the rack brought half over; this drives in the cork a certain distance, leaving sufficient space between its compressed end and the bottle mouth for filling. The syrup, if being used, is then injected by the pump, the aerated water being let in afterwards. When sufficiently full, the cork is driven in by pulling the handle right over. The filled bottle is next passed on to the wiring stand, shown in Fig. 289, the nose piece of which holds in the cork, and separates the two folds of the double wire while it is being fastened over the cork and around the neck.

288.



289.



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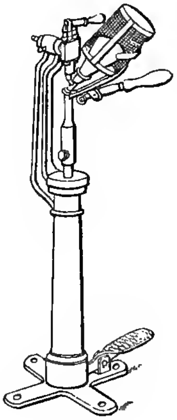
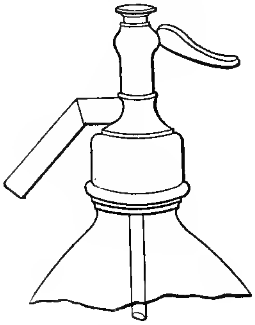
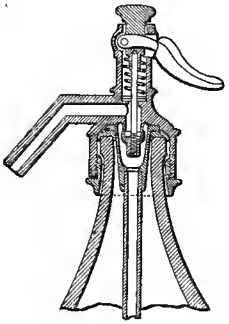


291.



292.



The distance from the mixing machine to the bottling machine is not of any importance, provided that the connecting pipes be of pure tin, or of some material not affected by aerated water.

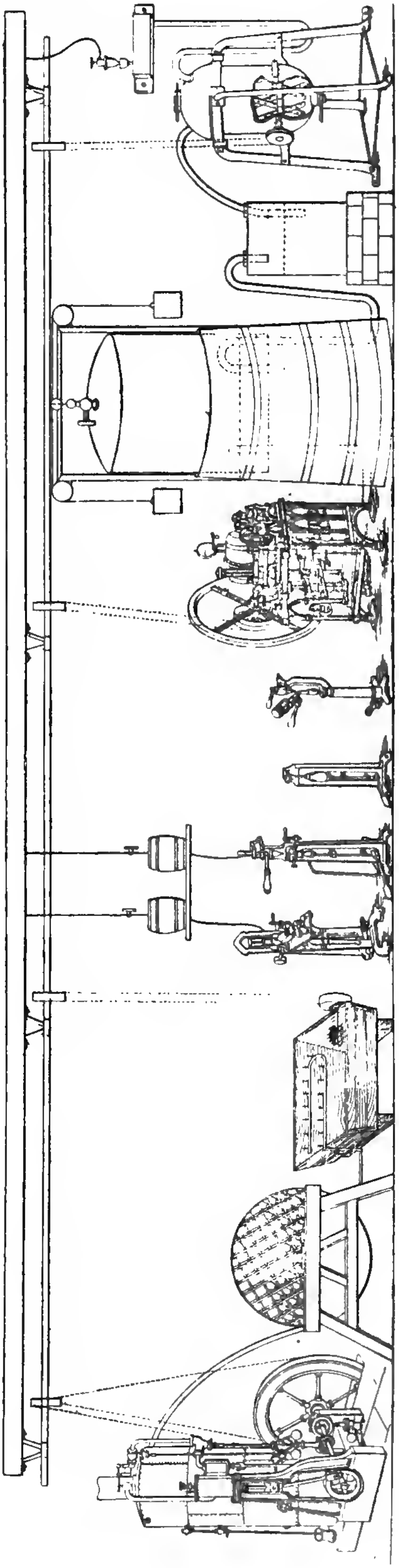
A slightly different apparatus, shown in Fig. 290, is used for filling siphons. In this, a valve is held up by a spring, which when compressed by the handle is forced away from its seating and allows the liquid to escape. The siphons are filled upside down, the pressure on the button head, when the spout is forced into the filling nozzle in the process of filling, opening them for the purpose. The construction of the siphon itself is shown in Figs. 291 and 292.

In Fig. 293 is shown, besides all the machines already described, a vertical boiler with engine on the same base. It should be large enough to allow for extra steam for heating water for syrup-making, washing, and other purposes. Next to the boiler is the bottle-soaking wheel, which revolves slowly in hot water for the purpose of thoroughly cleaning the bottles. At the side of the wooden tank are revolving brushes which cleanse both the interior and exterior. They are then placed on the rinsing tube jets, which are supplied with cold water. At the other end of the figure is shown the acid tap, made either self-closing or adjustable; this is supplied from the acid tank placed on the floor above, and delivers the acid into the box placed below it. In this figure, the most convenient arrangement of the several machines relatively to one another is shown. This arrangement is that recommended by the well-known firm of Messrs. Barnett, Son, and Foster, of London, who are the makers of the machines here illustrated.

An apparatus is shown in Fig. 294, in which the gas-holder is dispensed with, and the processes of generating, purifying, and bottling are combined. An arrangement identical in principle was patented in 1851.

The system described above is known as the "continuous" system; it is almost exclusively used in this country, and also, with various modifications, on the Continent. There is another system, which is sometimes called the "compression" system, and is in general use in America. The main difference between the two is, that in the latter the gas, as generated, is passed directly into the water without expansion; the water being aerated either in bulk or in the bottles. The first-mentioned, viz. the continuous system, aerates small quantities of water at a time, but rapidly; and if a small quantity only is required, makes it with nearly the same economy as if working up to its full producing power, only the requisite quantity of gas and water being used, and the pressure being kept up as the bottling proceeds. With the compression system, in order to keep an even pressure in the bottles, the surplus gas at starting must be blown off in filling, the elastic gas filling the place occupied by the water as the latter is withdrawn; thus the cylinder, when emptied of liquid, is full of compressed gas, and to refill it, the water must be pumped in against the pressure of the gas, or the latter be blown off, generally to waste.

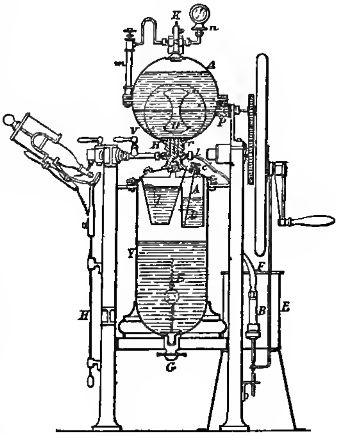
Although the two systems require different methods of generating and mixing, the bottling-off and filling machines apply to both with very little variation. Each system has its particular advantages for special purposes, according to the requirements of the retailer.



293.

Fig. 295 represents an apparatus much used in the United States for the manufacture of aerated waters by the compression system. The cylinder to the left of the figure is the generator; the carbonate and the water are placed in this and mixed by turning the handle which works an agitator in the interior. The acid is then run in from the vessel above, the connecting pipe being closed and locked by the cam action on the lever at top. The three other cylinders are the vessels in which the gas and water are mixed together; the smaller vessels above are merely purifiers: both cylinders and purifiers are filled about two-thirds full of water. The gas enters into the first purifier, from which it passes into the second, and thence into the third, and is thus rendered sufficiently pure for mixing. By shutting the cocks on the last two cylinders, the gas then goes into the first, and the agitator is set in motion until the pressure, as shown by the gauge above, has reached the proper height. The pressure required for bottles is about 60 lb., and that for siphons, or portable cylinders, about 150 lb.; at these points, the aerated water is withdrawn into the necessary receptacles, the cylinder remaining full of gas at that pressure. During the withdrawal of the contents of this cylinder, the gas is turned into the second one, and the process conducted as in the case of the first.

294.



The *third* cylinder, before having the gas let into it from the generator, is connected with the first cylinder by a pipe which passes underneath and is not shown in the figure. By this means, as much of the compressed gas contained in the first cylinder as the water in the last cylinder will absorb is drawn over, and the pressure in the first considerably reduced, thus making it easier to refill with water, since the resistance is considerably diminished. In recharging the first cylinder, when the middle one is empty, it is connected with the latter, and the extra pressure reduced as in the previous case. When the third is empty, its surplus gas is withdrawn in refilling the middle one, the process being, therefore, continuous. The pipe shown at the bottom of the figure and connected with the three cylinders is attached to a pump at the right-hand side, and is used for filling them with water.

295.

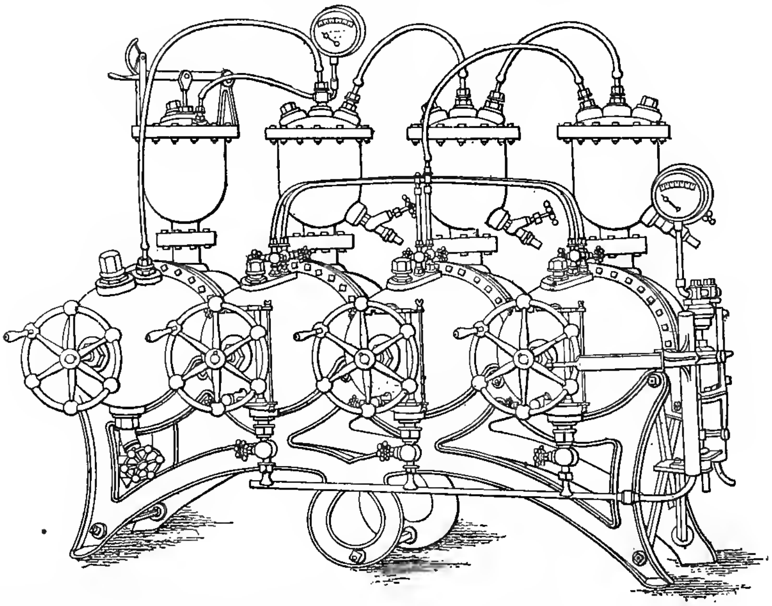
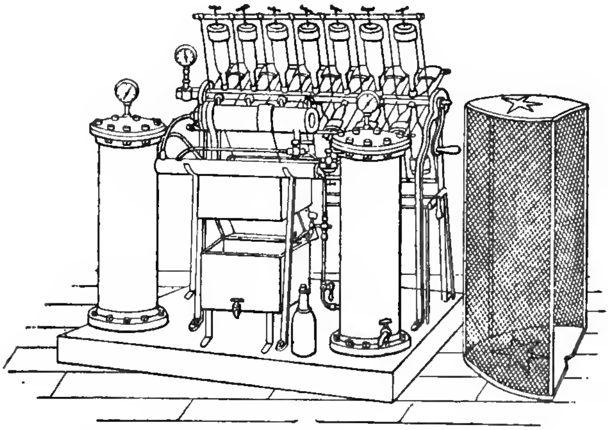
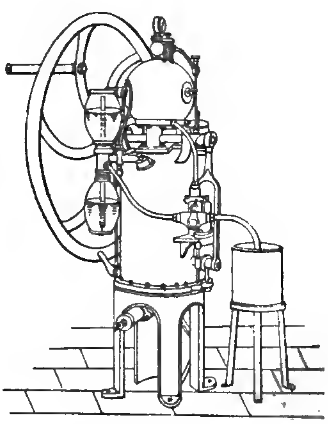


Fig. 296 shows another apparatus belonging to the compression system, recently introduced. The gas is generated by the action of heat upon bicarbonate of soda, which is placed over a fire in a closed vessel. One half of the gas contained in the salt is driven off by heat, leaving a residue which by dissolving and crystallizing becomes the ordinary washing soda. The gas when generated is deprived of moisture and filtered before passing into a long, narrow cylinder, furnished with a pressure gauge at one end. This cylinder has a row of nipples upon its upper surface against which the bottles previously filled with the liquid to be aerated are placed. The gas is then passed into them, and they are agitated by means of the handle shown at the side. At the right-hand side of the machine is placed a screen inside which the workman stands while conducting the process, in order to protect himself from danger in case of a bottle bursting.

296.



297.



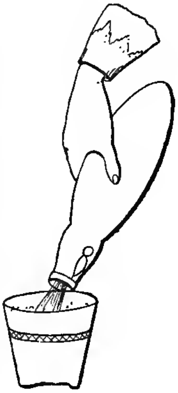
Another apparatus, devised and constructed by Mondollot, of Paris, is shown in Fig. 297. Its chief peculiarity is that it generates just sufficient gas at each revolution of the handle to aerate a definite quantity of water.

Arrangement of a Factory.—For the benefit of those who are about to engage in this manufacture a description is here given of the best and most convenient arrangement of the plant. The details must, of course, be varied in many cases to meet special requirements and circumstances.

Any well-lighted, ventilated and drained building of two floors, basement, and cellars may be utilized as a soda water factory. The cistern, which should be of slate, cast iron, or galvanized iron, and be supplied from the well or main, but *not* by lead pipes, should be placed at the top of the building. This cistern should be furnished with outlet pipes to convey water through a filter to the several machines and apparatus requiring it; and also with other outlets for sluicing the factory and other washing purposes. On the same floor there should be a crane for lifting in the various materials. A lift should run from the top floor to the cellars, and there should be, upon all floors, light and noiseless trollies, running on three or more wheels; these are useful for shifting crates about, as necessity arises. The first floor should be used for storing the acid and the carbonate; and the other portions of it may be partitioned off for a laboratory, solution and syrup-making rooms, and other purposes. The machinery, viz. the gas generator, purifier, and gas-holder, mixing and bottling machine, washing apparatus, and the motive power should be all situate on the ground-floor. By this arrangement, the generating apparatus is supplied with vitriol and carbonate, and the filling machines with dosing material, directly from above. This floor should be asphalted and well drained, so that it may be easily flushed whenever necessary. The cellars, which should be kept perfectly cool, may be utilized as stores for the finished product. Any place likely to give off effluvia, such as stables or closets, must be kept as far away as possible. When the production is over 2000 bottles a day, it is well to employ horse or steam power: in small factories, the horse which takes out the goods may be utilized by means of a simple horse-wheel. If steam be used, and steam is generally most convenient, the boiler should be of sufficient size to provide for jacket pans, for boiling water or syrups, or for steam coils in the water tubs and washing troughs. Syrups should be kept in stone jars, and all solutions in slate tanks, for sweetness and cleanliness. It should be borne in mind that whiting is very liable to absorb foul gases. Aerated water exerts a corrosive action upon lead; *all* pipes therefore which contain it must be of tin, or thickly tinned, the joints being covered with pure tin. Indiarubber pipes are apt to become foul and to decay. Mixing cylinders should be examined once a year and retinned whenever necessary, in order to avoid contamination. All water pipes and taps should be tested occasionally. When desired, meters for measuring carbonic acid gas and water may be used. Pipes and globes should be emptied, and cocks shut, when not in use, to prevent metallic contamination, or danger from frost in winter.

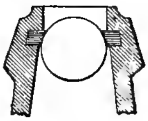
The cooler the water is kept, the more gas it absorbs; and it is also advisable to have thorough ventilation. The boiler should be covered with some non-conducting material, and the pumps kept perfectly cool. A steam engine attached to each of the mixing machines is hardly a gain. When the make is sufficiently large for the adoption of steam, several machines are generally used; to provide for cases of stoppage for repairs, the pumps may be required to work by manual labour. To avoid accidents, care should be taken to allow only those whose duty it is to see to the various parts of the machinery to have access to it.

298.



Bottles.—Many varieties of bottles to hold aerated waters have been introduced during the last few years. The ordinary corked bottle is too well known to need description, and is, moreover, rapidly falling into disuse. The use of corks in stoppering, to which there are many objections, has been almost superseded by the introduction of bottles of various kinds which are self-stoppering. Of these, one of the best known is that devised by Codd, and shown in Figs. 298 and 299. In this bottle, a glass ball, or marble, forms a joint against an indiarubber seating fixed in the mouth. The ball, being larger than the orifice of the bottle, is introduced in the process of making, and the narrow groove to hold the rubber ring is formed in finishing the mouth. A contraction in the neck prevents the ball from falling into the bottle, and it is securely held in pouring out by an indentation in the neck. In opening, a firm but gentle pressure forces the ball from its seating, when it immediately falls into the shoulder of the bottle. The advantages possessed by this bottle over the ordinary kind are numerous. The glass stopper is practically everlasting. No string or wire is needed. Skilled labour is not required, tyers, wirers, and fitters being at the same time dispensed with and the chances of breakage consequently diminished.

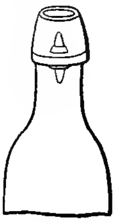
299.



Besides being conducive to cleanliness, it is claimed for this stopper that since it is not allowed to fall into the liquid, the full amount of gas is retained in the bottle. If the stopper were allowed to fall back into the bottle, a considerable percentage of the gas would be immediately discharged and wasted. This action may be seen by dropping a stone into an ordinary soda water bottle, when first opened; the gas at once collects in bubbles, which rush to the surface and are wasted. Codd's bottle, the merits of which are now widely recognized, is largely used by manufacturers of aerated waters.

Another bottle, on a similar principle, is that known as Lamont's, and shown in Fig. 300. The stopper is made either of ebonite or of glass, and is provided with an indiarubber ring fastened round it; this ring, when the bottle is full, is pressed tightly against a small rim in the neck. This bottle is opened in the same manner as Codd's, by pressing down the stopper.

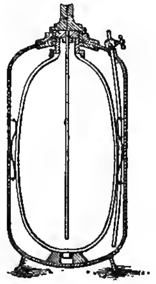
300.



If the aerated water is used for supplying iced fruit drinks from counter-fountains, portable cylinders, such as that shown in Fig. 301, are used; these are made of steel and copper, and ought to be glass-lined whenever the water is to remain in them for any length of time. In England, aerated waters are usually sent out in bottles; in France, siphons are more commonly used; in America, cylinders form the principal receptacles, and are largely supplied to chemists, confectioners, and fruiterers, many of these having large amounts invested in marble counter-fountains from which the drinks are dispensed.

Corks.—The corks should be carefully chosen, those only being selected which are capable of resisting a high pressure. Old wine corks may be used, but they must be well cleansed in a solution that will thoroughly purify them. They may be slightly moistened before using, in order that they may be readily compressed in the machine; large hard corks can be brought to almost any degree of softness by steaming. The use of corks has been to a large extent superseded by the self-stoppering bottles already described.

301.



It will be well to make here a few general remarks upon the most important points in the manufacture. Above everything else, it is indispensable that the maker of aerated beverages should have a constant supply of the purest and freshest water. On the purity of the water depends in a great measure the quality of the produce; and on its abundance and freshness depend the cleanliness and temperature of the work-room and the regular working of the entire process.

The most scrupulous cleanliness is also indispensable, and this fact cannot be too strongly insisted upon. No conceivable precaution which would help to ensure this condition should be omitted, since not only does the success of the business depend upon it, but the health of the hands employed also, and the cleanliness, or otherwise, of a factory is the first point to which a sanitary inspector visiting it would direct his attention. When, as is often the case, the factory is situate in the heart of a large town, the manufacture is sometimes carried on in cellars, by the help of artificial light. In such a case, it is essential that the rooms be thoroughly ventilated in order that the carbonic acid gas, of which a large quantity is inevitably wasted, may be carried away as soon as it is evolved, and the air thereby be kept pure and fresh. Refrigerators disposed around the apparatus are used with advantage, in order to preserve the required low temperature; in hot weather, indeed, it is impossible to acquire it in any other way. Although the expansion of the gas occasioned by a rise in temperature may not appear considerable, it becomes readily perceptible in practice, when liquids are sometimes saturated at a pressure of 10 or 14 atmospheres.

The factory should always be well provided with gas-producing materials, stored in the most convenient place. Acid cisterns should be kept carefully covered in order to prevent accidents, and the contents should be handled only by those whose duty it is to manipulate the supplies. The carbonate, of whatever description, and the vitriol must be of the purest; this is another point upon which much depends. Samples of the former ought to contain no foreign salts, and especially no salts of iron or earthy oxides. The acid ought to have been carefully rectified; the use of common vitriol imparts to the water a nitrous taste which can frequently be detected in the produce of inferior makers.

Beer. (Fr., *Bière;* Ger., *Bier.*)—Beer is a fermented liquor produced from malted barley, and flavoured by the addition of hops. Different varieties of this liquor are known as "bitter ale," "mild ale," "porter," and "stout," according to their flavour, strength, or colour, and to the nature and quantity of ingredients used in their production. Beer and porter are manufactured in enormous quantities in England, comparatively little being made anywhere else. The produce of some of the largest breweries, and particularly those of Burton-on-Trent, is famed throughout the whole of the civilized world. The article itself and its peculiarities are too well known to need description.

The materials employed in brewing are, in the main, water, barley, and hops, and since much care is requisite in making selection of the ingredients, it will be necessary to describe minutely those kinds of each which are best adapted to the requirements of the brewer. The process by which beer is brewed from these may be divided into two operations: malting and brewing. Full particulars of the operation of malting, or of converting barley into malt, and of the apparatus employed, will be found in the article on Malt, and hence it will be only necessary to point out here the nature of the changes undergone by the barley in its conversion. The subsequent processes of brewing will be treated in minute detail.

Water.—A constant, unfailing supply of good water is indispensable in brewing; though what really constitutes good water is a point upon which many brewers and chemists have long been at issue. Some rest their faith upon a soft water; others will use only the hardest water they can get; while others, again, are quite indifferent, and will use either. It is now, however, a generally accepted fact that water for brewing should not contain organic matter, but a considerable quantity of inorganic or saline constituents, these varying in nature and quantity, according as the beer to be made is required for keeping or for immediate consumption. English brewers are now agreed that the water should contain much carbonate and sulphate of lime. The former of these two ingredients is the most necessary, but they should both be present in the water from which ale is to be made; water used in brewing porter may contain the carbonate alone. For the best ales, the proportions seem to be from 10 to 20 grains a gallon of each. The excellence of the ales made by the Burton brewers is doubtless due to the quality of the water used by them; it is very hard, and contains, as will be seen from the analyses given below, a large proportion of alkaline sulphates and carbonates; this is the best argument that can be brought forward in favour of the use of hard water. The supply is derived entirely from springs, and not, as some suppose, from the river Trent. It has also been urged, as an advantage, that hard water increases the quantity of saccharine matter held in the wort, thus heightening the flavour and preventing it from becoming acid. The following tables represent analyses of the waters used by several of the largest brewing firms in the United Kingdom:—

Two Analyses of Burton Water.

	(1).	(2).	
Chloride of sodium	10·12	..	grains a gallon.
Sulphate of potash	7·65	..	,,
,, lime..	18·96	54·40	,,
,, magnesia	9·95	0·83	,,
Carbonate of lime	15·51	9·93	,,
,, magnesia	1·70	..	,,
,, iron	0·60	..	,,
Silicic acid	0·79	..	,,
Chloride of calcium	..	13·28	,,
	65·28	78·44	

Two Analyses of Edinburgh Water.

	(1).		(2).	
Chloride of sodium	11·71	..	7·78	grains a gallon.
Sulphate of lime	11·69	..	9·76	"
Chloride of magnesia	..	..	2·13	"
" potassium	2·86	..	0·56	"
Carbonate of lime	19·86	..	28·26	"
" magnesia	..	..	5·48	"
Phosphates	..	..	0·31	"
Oxide of iron	..	..	0·26	"
Silica	0·68	..	0·32	"
Sulphate of soda	4·46	..	..	"
" magnesia	10·90	..	..	"
Organic matter	..	..	1·56	"
	62·16		56·42	

Two Analyses of Dublin Water.

	(1).		(2).	
Carbonate of lime	12·42	..	14·21	grains a gallon.
Sulphate of lime	4·44	..	4·45	"
Carbonate of magnesia	1·23	..	1·22	"
Alkaline chlorides	1·84	..	1·83	"
Oxide of iron	1·24	..	0·24	"
Silica	1·24	..	0·26	"
Organic matter	1·38	..	1·30	"
	23·79		23·51	

When nothing but soft water can be had, it is possible to imitate the Burton water very closely by the addition of sulphate of lime, and the chlorides of sodium, magnesium, and calcium. These salts are added in the water cisterns or coppers. Gypsum, or sulphate of lime, which is sufficiently soluble, is used in lumps, one or two inches square; when added to the hot-water coppers, it is employed in a fine powder.

Barley.—The selection of the barley used by the brewer calls for the exercise of much skill and judgment; unless the quality be of the very best, it is impossible to obtain good malt, and without good malt, it is useless to attempt to make good beer. A practised brewer can judge of the quality of his barley by its appearance. The heaviest, if in good condition, is always the best; the grains should be plump, and of a pale-yellow colour; they should have a thin skin, and a free, chalky fracture. That which has been grown in a light soil and harvested early, is also preferable. It is of much importance to the maltster that barley be lodged in the stack for a few weeks before being thrashed, in order to allow the moisture from the soil to dry off before it comes into his hands. If this is done, the operation of drying in the kiln is avoided. In moist districts, however, where the grain never gets thoroughly dried, this process must invariably be had recourse to; the temperature of the kilns must never be allowed to rise above 50° (120° F.). Care must be taken to avoid breaking or crushing the grains of malting barley, so as to minimize the chances of its becoming mouldy in the subsequent processes of malting, a contingency which should be avoided in every possible way. It should also be screened before steeping, in order that the grains may all be of equal size on the spireing floor. These remarks, of course, apply only to the brewer who is, as he ought always to be, his own maltster.

Hops.—The wort made from barley alone has little or no flavour, but it is afforded an agreeable and permanent bitterness by the addition of hops, before fermenting. Hops are grown extensively in Kent and Sussex, the best varieties coming from the neighbourhood of Canterbury and Maidstone; the next in quality to these are the hops of Farnham and Worcester. Hops are of a light, straw-yellow colour, and have a peculiar, pleasant aroma, due to the presence of the bitter principle termed *lupulin.* The only important process in the preparation of hops is the drying, or curing. This is effected in rough kilns, termed in Sussex "oast-houses"; these should be heated to about 48° (120° F.), but in no case higher than this. The dried or cured malt must be packed into sacks and stored in close, dry rooms.

Foreign hops are largely used by brewers in this country, but as they are not so rich in flavour as the English, they are never used alone, but mixed in different proportions with the English kinds.

The general effect of hops upon the beer is to render it stimulant, and to impart to it a bitter flavour, thus neutralizing the unpleasant, sickly flavour of the malt. The tonic properties of bitter ales are due entirely to this bitter principle. The hops also tend to prevent the beer from turning sour.

Malting.—This process, which will be fully described in the article Malt, is the conversion of raw barley into malt, by a series of four processes, named respectively, steeping, couching, flooring, and drying. The grain is first steeped in water until it has taken up the quantity required for germination; it is then spread out in even layers on the floor of the malthouse, and repeatedly turned over until germination begins; when little rootlets appear at the extremities of the grains, the germination is checked by drying the malt rapidly in kilns.

During the first part of the process, namely, steeping in water, the grain swells up, increasing about one-fifth in bulk and one-third in weight; the absorbed water is assimilated by the starch of the grain during the after process of flooring, sugar being thereby produced. Only about half the starch contained in the grain is converted in this way into sugar, the germination being checked in the middle, since the continuance of the process would exhaust the grain, and the remainder of the valuable constituents would be taken up by the growth of the roots and stems. The chief object, therefore, of the process, is to check the germination as soon as the largest possible amount of starch has been converted into sugar; this is generally known to be the case when the plumule, or *acrospire*, has grown, under the husk, to two-thirds of the length of the grain. The following analyses by Proust will point out the nature of the changes undergone by barley in the process of malting:—

	Barley.	*Malt.*
Hordeine	55	12
Starch	32	56
Gluten	3	1
Sugar	5	15
Mucilage	4	15
Resin	1	1
	100	100

It will thus be seen that the amount of starch and convertible sugar has been nearly doubled, while the hordeine has been reduced to one-fourth, the remainder of it being converted into mucilage.

In the process of drying, not only is the water expelled from the grain, and further germination thereby prevented, but a considerable quantity of the unchanged starch is also converted into sugar. This is proved by the fact that if separate portions of malt be dried in the atmosphere and in the kiln, that dried in the kiln is found to have considerably more saccharine matter than the other. Malt dried in the kiln affords, also, an agreeable flavour to the beer made from it, besides tending to its preservation.

During germination, a peculiar nitrogenuous substance, called *diastase*, is formed in the grain, which is especially active in converting starch into sugar after the malt has been infused in water. The worts from malted barley contain about one part of diastase in 100.

Many brewers and distillers use a mixture of malted and unmalted barley for the formation of their worts, in order to save expense; the cost of malting, together with the duty on the article, rendering it much higher in price than the unmalted grain. With care, nearly as much saccharine matter can be extracted from such a mixture as from the unmixed malt, although the subsequent processes, in the former case, present many difficulties. In either case, the malt, or the mixture of malt and grain, must be ground or crushed before it is ready for use. This is performed in order to expose as large a surface as possible to the action of the water used in making the worts. The effect of the previous steeping, however, is to prepare it in some measure for the reception of the water, and hence it is not necessary to grind malt alone very finely. When a mixture is employed, a portion of the grains have not been thus prepared, and the whole must be ground more finely. A brighter and clearer wort is invariably obtained from unmixed malt, on account of the comparative absence of suspended starch.

Brewing.—The process of brewing comprises four distinct operations, namely (1) mashing, or the preparation of the sweet wort; (2) boiling, or the preparation of the bitter wort; (3) cooling, or the refrigeration of the worts; and (4) fermentation. These operations will now be described in their order.

Before describing the process of mashing, it is necessary to deal shortly with the hoppers, by which the crushed malt, or grist, is received after it leaves the malt mills. These hoppers are termed grist cases, and were formerly constructed of wood, but are now generally of iron. The iron can best be employed in the corrugated form, as the corrugation gives stiffness, with but little bracing. The form varies considerably and is determined by circumstances; in cases where special mashing machines are not employed, the mashing being wholly performed within the mash tun, the grist cases are generally made to deliver the grist into the tun at four places. The lower part of each case is divided to effect separate delivery into four hoppers, each of which has its separate spout for the delivery of the malt. At Bass's brewery, at Burton, the grist is delivered from the case into the mash tuns, the grist case being placed directly over the mash tun. For porter brewing, as carried on at the City of London Brewery, the grist cases are not in the same room as the mash tuns, but the grist is supplied to the tuns by shoots, passing through one of the walls, and constructed so as to be lifted up out of the way when not in use. Where mashing machines are employed, the circumstances determine the construction of the grist case.

There are many methods of conveying the grist from the malt mills to the grist case; but these again are determined by the arrangement of the brewery, and will be dealt with under another heading.

Mashing.—The malt having been crushed in the malt mill, is treated to prepare for the operation of mashing a saccharine wort. This is effected by mixing the crushed malt with water of a certain temperature; the malt contains the peculiar principle of fermentation referred to above, diastase, which is, however, not a true ferment. This substance possesses the property of converting starch into dextrine, and by prolonged action, into sugar, and is the cause of the formation of the saccharine wort by the mashing process. Payen and Persoz have determined that it depends, whether the starch shall be converted into dextrine or into sugar, upon the time during which the malt is digested and upon the temperature. They quote the following experiment as illustrative of the action. From 6 to 10 parts of finely ground malt are put into 400 parts of water heated to a temperature of 27° (80° F.), and 100 parts of starch are added, the mixture being stirred, and the temperature raised to 60° (140° F.). The temperature is again raised to 70° (158° F.), and maintained between that temperature and 75° (167° F.). In twenty to thirty minutes the solution, originally milky, becomes of a pasty consistency, and loses thickness. This loss of consistency takes place when the starch is converted into dextrine. In this condition, if the solution is rapidly raised to the boiling point, and sufficient water got rid of as steam, a thick gum is obtained. But if the solution, instead of being raised to the boiling point, is kept at a temperature of 70° to 75° (158° to 167° F.) for two or three hours, the starch, or the greater portion of it, will be converted into sugar. By removal of the water from this sugar solution, by evaporation at the same temperature, a syrup results resembling that produced by the action of sulphuric acid on a solution of starch. Substituting in this experiment, for the mixture of malt and starch, a mashing of malt alone, the diastase, having a smaller proportion of starch to act upon, more quickly yields a saccharine liquid. Pure diastase will convert 2000 times its own weight of starch into sugar, the time of the action being inversely as the proportion of starch. This experiment illustrates in an important manner the operation of mashing, as it shows that by the duration of the mash, the wort may be made to contain greater or less proportion of dextrine not converted into sugar.

Dextrine, like sugar, is fermentable, and can be converted into alcohol. Sugar is, however, easily fermentable; dextrine is only fermentable with difficulty, and it requires a greater proportion of ferment, and a higher temperature in the fermentation tun. Dextrine may be considered to exert such an influence on the fermentation of the wort as to enable the brewer, by its means, to control the action in the tun, and is specially valuable for his use in proper proportions. These proportions depend chiefly on the class of beer to be made, as well as upon the season of the year at which the brewing takes place. An entirely saccharine wort yields too energetic a fermentation for the brewer to keep the process, even at ordinary temperature, under control. In such a case the sugar is wholly decomposed, and the wort converted into alcohol and water, or if too much oxygen is absorbed, into vinegar. In worts containing dextrine in a certain proportion, there first occurs a fermentation, agreeing with fermentation commonly so termed, during which the sugar and dextrine together undergo transformation into alcohol. There also occurs a second period during which the fermentation of the dextrine is continued, after the sugar has been decomposed; this period is productive in brewing of some of the most valuable properties of beer; it may be termed the period of dextrinous or after-fermentation. This after-fermentation is much slower than that of the first period, and to it is due the briskness to the palate of good beer, even after the beer has been a considerable time in cask. The carbonic acid evolved during this fermentation prevents the absorption of oxygen, and consequently the formation of acid. Beer to be kept a long time requires great care to be paid to the after-fermentation, and should be prepared from wort containing a larger proportion of dextrine. Beers brewed for rapid consumption may contain a very large proportion of sugar, but on this account will not keep, especially in hot weather. The proportion of dextrine in the wort depends upon the brewer's particular trade, and to a great extent upon the class of beer he brews, regulated by the mashing process.

Consideration of the preceding principles will show that the season of the year materially affects the brewing process. In summer, the risk of using a highly saccharine wort is greater than in winter, but the proportion of this risk will depend upon the plant and arrangement of the brewery. The proportion of dextrine and sugar contained in the wort may be regulated practically during the process of mashing, in two ways. The proportion of sugar may be increased by prolonging the mash with due regard to the maintenance of temperature; or the same result may be obtained by keeping the drained or filtered wort at a temperature of 74° (165° F.) Ure in experimenting on the wort drained from the mash tun, and kept at that temperature, found the proportion of dextrine to sugar, which was originally 16 to 3, to be changed to 17·8 to 1·2, the conversion of dextrine into sugar being almost complete. The influence of variation in the proportion of dextrine and sugar in the fermentation of the wort, must be entered into in greater detail when treating of the fermenting process.

It is necessary to be able to ascertain the proportion of dextrine or sugar contained in a wort. Ure describes two methods by which this can be done. The first consists in ascertaining the amount of sugar in a given wort of determined strength; and the second the amount of dextrine. It is more easy to determine the quantity of dextrine contained in a wort than the amount of sugar, but the proportion of sugar can be ascertained with greater accuracy. This will be described later under Sacchometry.

To ascertain the quantity of dextrine, add to a given volume of strong wort, having the density of about 30 lb. a barrel, an equal quantity of alcohol, or ordinary spirits of wine. This addition will cause the whole of the dextrine to be precipitated; and it is convenient to cause the precipitation to occur in a graduated tube, by which the bulk of the precipitate thrown down may be learned, and thereby its weight estimated. If the weight is less than 30 lb. a barrel, the proportion of alcohol must be increased; but if the wort is stronger, a smaller quantity of alcohol will effect the precipitation. It will be found useful, in practice, to have fixed to the tube a table, showing the relative proportion of alcohol required for worts of different strength.

The amount of sugar in a given wort may be ascertained by boiling 100 grains of the wort, with about 10 fluid oz. of the following solution:—

Sulphate of copper, crystals	100 grains.
Bitartrate of potash	200 "
Carbonate of soda, crystals	800 "
Boiling water, 1 pint, or	8750 "

To make this solution, the sulphate of copper should be first dissolved, and the bitartrate of potash added. The carbonate of soda should then be added, and the solution filtered. By boiling the wort with this solution, a red precipitate is obtained, which is to be collected and weighed. Three grains of precipitate indicate the presence of 1 grain of grape sugar in the wort.

It is customary to indicate the strength of the wort by the excess in pounds of the weight of the barrel of it, above the weight of a similar barrel of water. For instance, the weight of a barrel of water being 360 lb., and that of the barrel of wort 390 lb., the wort is said to be of 30 lb. gravity. Brewers' saccharometers are graduated to show the gravity of the worts in this way; a quarter of good malt generally yields sufficient extract with one barrel of water for a wort of 90 lb. gravity, or sometimes even as much as 95 lb. gravity a barrel. Upon this fact is based the method of calculating the quantity of water or liquor, as it is termed, to be used in the mashing. Porter and stout, in which a considerable proportion of black or brown malt is used, allow of a lesser amount of extract, or about that sufficient to make with one barrel of water, a wort of 84 to 86 lb. gravity. Those facts borne in mind, the quantity of liquor to be used in a given mashing may be thus calculated:—

If a mash of 50 quarters of malt be to be made and beer of 25 lb. gravity to be produced, the malt being of such quality as to yield 90 lb. a quarter, as estimated by the saccharometer, the quantity of beer produced will amount to $\frac{50 \times 90}{25} = 180$ barrels. If there were no losses during the mashes and in the subsequent processes, 180 barrels would be the quantity of liquor to be used; but the several following allowances have to be made. The goods, as the prepared malt is termed, retain by capillary action about ¾ barrel a quarter of malt mashed. The loss by evaporation during boiling in the copper has to be made up, as well as the evaporation during the cooling down from boiling point to the temperature when the beer is run into the fermentation tun. The last process generally incurs the loss of one-eighth of the total bulk, whilst the loss in the copper varies according to its evaporative effect. For 180 barrels, the total quantity of liquor may be calculated thus;—In addition to

	180 barrels.
One-eighth for evaporation during cooling	22½ "
For absorption..	37½ "
For boiling	8 "
	68 "

or a total of 248 barrels.

There are several ways of distributing this quantity of liquor. It is preferred in some cases to make only one mash, and to sparge the remainder; and in others as many as five successive mashes would be employed.

In some instances the malt and liquor are mixed in the mash tun by stirring oars; in others, by special machinery, afterwards to be described; the object being to thoroughly mix the malt and water to prevent balling or lumps occurring. The mash at first is recommended to be made as stiff as possible, 1½ to 2 barrels of water a quarter of malt being generally used.

In determining the temperature of the water to be employed in the mashing, it is necessary to prevent the liquor being admitted at so high a temperature as to set, or lock up, the goods, that is, to cause the starch to run into a cohesive or pasty state. The proper initial temperature will depend upon the quality of the malt employed. When the malt is high dried, the liquor may be used at a higher temperature. Mashing is sometimes commenced at 71° (160° F.), and liquor subsequently added at a temperature that will give a wort ready to be drawn off at about 63° (145° F.). This method has its advantages. The malt is first softened, and the more soluble portions are extracted without loss of starch. Once the process is operating well, the addition of liquor at a somewhat high temperature does not offer great risk. There must also be taken into account the loss of temperature due to conduction and radiation of heat, and to prevent excessive loss it is advisable to heat the mash tun with hot water, before commencing mashing operations. Another alteration of temperature is caused by the mixture of the liquor with the malt. For instance, if a quarter of unmalted barley, at a temperature of 10° (50° F.), is mixed with twice this volume of water at 65° (150° F.), the mixture will have about a mean temperature of 38° (100° F.). But when malt is mixed with water, the resulting temperature is above the mean, and the difference is greater when the malt is more highly dried. With highly dried brown malt, the temperature would rise to as much as 5° above the mean. If the malt has become mellowed by the absorption of moisture from the atmosphere, the temperature is less; this absorption is very likely to occur if the malt has stood long before grinding. The rise of temperature appears due to the chemical conversion of starch into sugar, and takes place during the first mash, when the conversion is most energetic. During the formation of starch, a froth rises to the surface of the liquor in the mash tun, affording an indication of the conversion proceeding properly.

The theory broached above as to the action of diastase, that it converted the starch into dextrine, in the first place, and some of that dextrine into sugar, is due to Mulder. Schwarzer states that at temperatures above 60° (140° F.), the ratio of glucose to dextrine is as 1 to 3; whereas below that point, the ratio is as one to one, or equal. Sullivan states that neither dextrine nor glucose is formed, but that the sugar termed maltase, intermediate between grape sugar and starch, is the resulting product. Diastase is dissolved in greater quantities from the malt by a long digestion at low than at high temperatures; and the action is most complete between 38° and 60° (100° and 140° F.). But the soluble matters of the mash suffer saccharine conversion more actively when the temperature is much higher.

From analyses that have been made of malt as well as barley, it appears that the available constituents of malt, as dried by ordinary means, amount to 78·3 per cent.; so that a quarter of good malt weighing 352 lb., will contain 275·5 lb. of available constituents. The remainder consists of water and husk. These available constituents are not all saccharine matter, but consist also of albumen and gluten, got rid of in after processes. The best practical results obtained, as measured by the saccharometers of Dring and Fage, give 243 to 256·5 lb. available constituents.

Of course the most important point with the brewer is to completely abstract the soluble substances from his malt, and to effect this with the least possible quantity of liquor, taking care to prevent the occurrence of acidity. In the opinion of Muspratt, too much water is used, and the diastase and gluten of the malt are considered to be capable of transforming a much larger quantity of starch into sugar than is present; and the water used is sufficient to hold in solution a greater quantity of saccharine matter than occurs in the brewing operation. According to this view, the usual methods of brewing are defective, for the reason that an unnecessarily large quantity of liquor is used.

As the diastase is most active when the solution of malt is dilute, and when the temperature is between 71° and 77° (160° and 170° F.), by sustaining an equalized temperature and employing only a moderate quantity of water, the conversion of starch into glucose will be complete almost in the first mashing, leaving nothing for subsequent sparging, except to remove the infusion absorbed by the goods. If this is accomplished with four to five barrels instead of with six to seven, there are the advantages that time and fuel employed in evaporation will be saved, as well as sounder beer produced, tendency to acetify being less with a strong wort than with a weak one. According to this view repeated mashes are to be avoided.

The English method of mashing employs a high initial temperature, and the following table by Graham gives the proportion per cent. of the constituents after three hours' mashing:—

	60° (140° F.)	65° (150° F.)	70° (160° F.)	76° (170° F.)	80° (175° F.)
Extract	70·00	69·75	69·00	67·25	..
Draff	22·28	23·65	23·96	24·39	..
Glucose	33·35	30·50	29·41	20·79	15·62
Dextrine	32·50	34·11	34·33	..	..
Soluble starch	..	traces	traces	41·13	..

These figures show that the higher the initial temperature, the less is the proportion of sugar and unconverted starch contained in the extract.

Considering that one of the first necessities of the brewer is to prevent other fermentations being set up than that desired, cleanliness is one of the essentials. Any albuminous substance tending to putrescence would communicate similar change to the wort. In no place is cleanliness more required than in the mash tun, which should be carefully washed with lime water after every mashing, unless mashings are made daily. This work should be completed on the day previous to that of the brewing, so that on the day of brewing operations may be commenced early in the morning, especially in hot weather.

The temperature of the atmosphere, the quantity of the malt, and the heats of the mashings should be carefully noted; Levesque has given the following practical example as a convenient illustration. For greater facility the example is reduced to one-quarter brewing, which can be multiplied by any number that may be required. The total quantity of beer or liquor is technically termed the length.

All waste of liquor is to be duly accounted for, and this calculation is to be made for a fair quantity of boiling-room in the copper, which ought to be one-fifth part of the whole content. A quarter of tender, well-made malt, thin skinned, of 44 lb. a bushel, or 352 lb. malt, as it is termed, will yield 2 bls. 0 fir. 3 gals. strong ale, of 40 lb. gravity a barrel, with 4 bls. 0 fir. 5 gals. liquor for the mashes, and 2 bls. 2 fir. more liquor for the return wort; making in the whole 6 bls. 2 firs. 5 gals. liquor a quarter. This, previous to brewing, is stated as follows:—

Weight of Malt, 44 lb. a bushel, 352 lb. a quarter. Gravity 95 lb. a quarter. Malt 1 quarter, Hops 12 lb.

	bls.	fir.	gals.
Length required, net quantity	2	0	3
Waste by fermentation	0	0	5
Waste by boiling one hour, one in ten	0	0	7½
Waste by evaporation, one in ten	0	1	5
Hops will imbibe, per 12 lb.	0	0	7½
For the copper wort	3	0	1
Malt will imbibe, a quarter	1	0	4
Quantity of liquor for the mashings of the strong	4	0	5
First mash, under the Malt	2	2	0
	1	2	5
Second mash, over the goods, and cover up immediately	0	3	5
	0	3	0
Third mash, over the goods, and cover up immediately	0	3	0
Fourth mash, under the goods, and mash for returns	2	2	0
Brought down	4	0	5
Total quantity of liquor a quarter	6	2	5

	bls.	fir.	gals.
Liquor	4	0	5
Length	2	0	3
Waste	2	0	2

If the second and third are mashed, the second heat must be 80° (175° F.), and the third 82°, (179° F.).

The work done is shown by the following table; the reference to the number of lb. of yeast a barrel will be explained subsequently:—

Temperature of air at time of mashing.	Malt.	Hops.	Liquor for each mash.	Heat of liquor.	Time of standing of the mash.	Gravity of extract.	Number of barrels in the gyle-tun.	Gravity a barrel.	Number of lb. in each wort.	Gravity a quarter.	Pitching heats, and lb. of yeast a barrel.	Advance of heat, and decrease of gravity, every six or twelve hours, to the cleansing point.		
	qr. bus.	lb.	bls. fir. gls.		h. min.	gravity	bls. fir. gls.		lb.			hr.	F.	gravity
40°	1 0	12	2 2 0	76°	2 0	40	2 0 8	37·47	83·20		50°		50°	36·48
			0 3 5	82		38						12	51	35
			0 3 0	87		36	is equal to	40·00			2·8749	24	52	33
			2 2 0	68	0 30	30	2 0 3				lb. a barrel.	36	54	30
						28						48	55	27
			6 2 5			24					lb. oz.	60	57	24
						19	2 2 0	4·72	11·80	95·00	6 14	72	59	21
						16						84	61	17·50
						12						96	63	15
						9)243						108	65	13
												120	70	12
						27 lb.						Cleansed.		

The malt should if possible be ground not longer than a day previous to mashing, and should never be kept for more than three or four days, because it absorbs moisture from the atmosphere, and becomes heated through internal decomposition of the saccharine constituents, which will make the beer bad in quality.

Mashing is performed in a vessel termed a mash tun, the contents being stirred either by hand with oars or by machinery. Different forms of mash tuns will be subsequently described.

After mashing the tub is carefully covered, to maintain the temperature of the mash and to exclude air from the wort. Allowed to rest for about two hours, it is drawn off to the copper. The following table, given by Lévesque, which, like the preceding, has been calculated on the basis of Fahrenheit's thermometer, relates to the temperature and time of standing of the mash; and shows reduction of the temperature of the air, the heat for mashing, at any required temperature, in which the degrees and hundredths of a degree show how far calculation may be relied upon; the hours and minutes for the standing of the mash, observing that when the air is higher than the given temperature, the time of the standing of the mash is to be diminished in ratio through the four classes of mashing heats. The heat of the tap is to be taken in the middle of the spending. For every shade of malt higher than the palest, a reduction of 5° must be made. If the liquor be cooled down in the mash tun to receive the malt, the liquor must be taken 8° lower than in the other method. In well-constructed breweries, the heats of the tap will correspond very nearly with the statement when the tun is mashed full or nearly so.

Temperature of the air at mashing.	Class I. Heat of the Mash, 146° to 148° F.	Time of standing of the mash.	Temperature of the air at mashing.	Class II. Heat of the Mash, 145° to 147° F.		Time of standing of the mash.	Temperature of the air at mashing.	Class III. Heat of the Mash, 144° to 146° F.		Time of standing of the mash.	Temperature of the air at mashing.	Class IV. Heat of the Mash, 143° to 145° F.		Time of standing of the mash.
	Firkins a Quarter, 6.			Firkins a Quarter, 7.	Firkins a Quarter, 8.			Firkins a Quarter, 9.	Firkins a Quarter, 10.			Firkins a Quarter, 11.	Firkins a Quarter, 12.	
F.°	deg. F.	H. M.	F.°	deg. F.	deg. F.	H. M.	F.°	deg. F.	deg. F.	H M.	F.°	deg. F.	deg. F.	H. M.
10	197·00	4 00	10	189·00	184·00	3 00	10	178·00	175·00	2 00	10	172·00	170·00	1 00
15	195·17	4 00	15	187·42	182·59	3 00	15	176·84	173·92	2 00	15	171·00	169·19	1 00
20	193·34	4 00	20	185·84	181·18	3 00	20	175·68	172·84	2 00	20	170·00	168·28	1 00
25	191·51	4 00	25	184·26	179·77	3 00	25	174·52	171·76	2 00	25	169·00	167·37	1 00
30	189·68	4 00	30	182·68	178·36	3 00	30	173·36	170·68	2 00	30	168·00	166·46	1 00
35	187·85	4 00	35	180·10	176·95	3 00	35	172·20	169·60	2 00	35	167·00	165·55	1 00
40	186·02	4 00	40	179·52	175·54	3 00	40	171·04	168·52	2 00	40	166·00	164·64	1 00
45	184·19	4 00	45	177·94	174·13	3 00	45	169·88	167·44	2 00	45	165·00	163·73	1 00
50	182·36	4 00	50	176·36	172·72	3 00	50	168·72	166·36	2 00	50	164·00	162·82	1 00
55	180·53	4 00	55	174·78	171·31	3 00	55	167·56	165·28	2 00	55	163·00	161·91	1 00
60	178·70	3 40	60	173·20	169·90	2 45	60	166·40	164·20	1 50	60	162·00	161·00	0 55
65	176·87	3 20	65	171·62	168·49	2 30	65	165·24	163·12	1 40	65	161·00	160·19	0 50
70	175·04	3 00	70	170·04	167·07	2 15	70	164·08	162·04	1 30	70	160·00	159·28	0 45
Heat of the tap from 144° to 146° F.			Heat of the tap from 143° to 145° F.				Heat of the tap from 142° to 144° F.				Heat of the tap from 141° to 143° F.			

71