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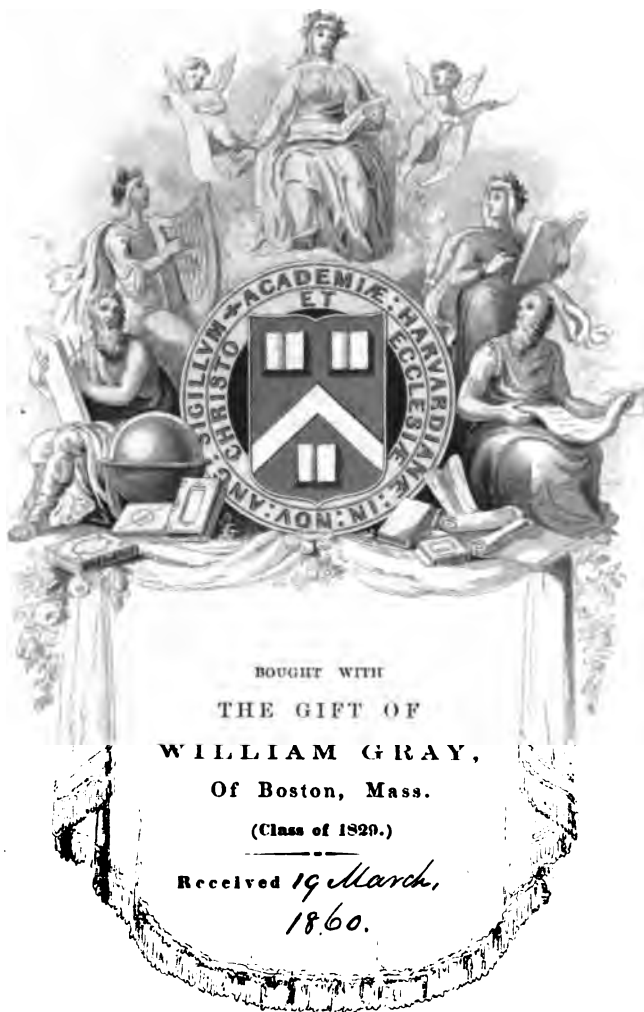
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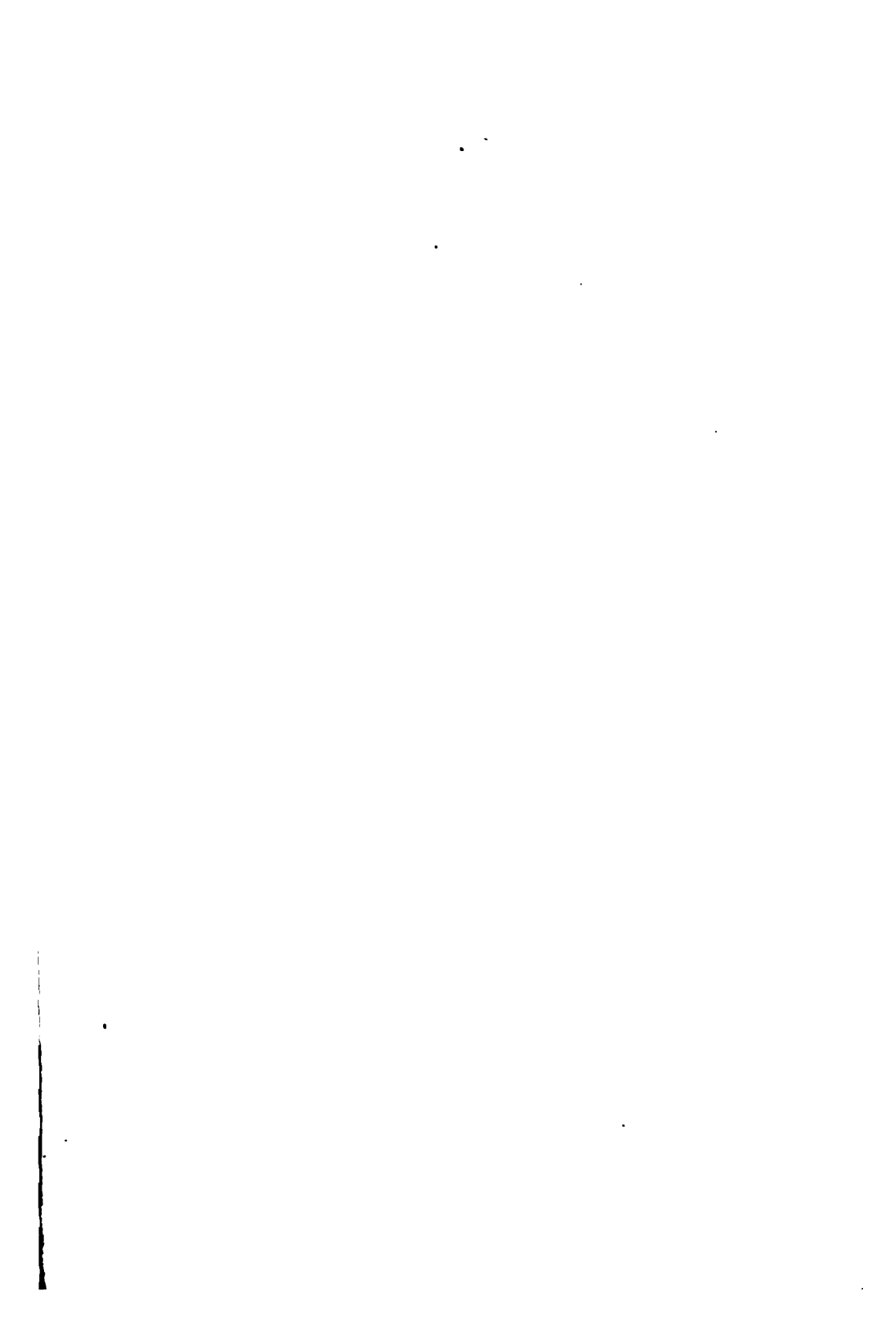
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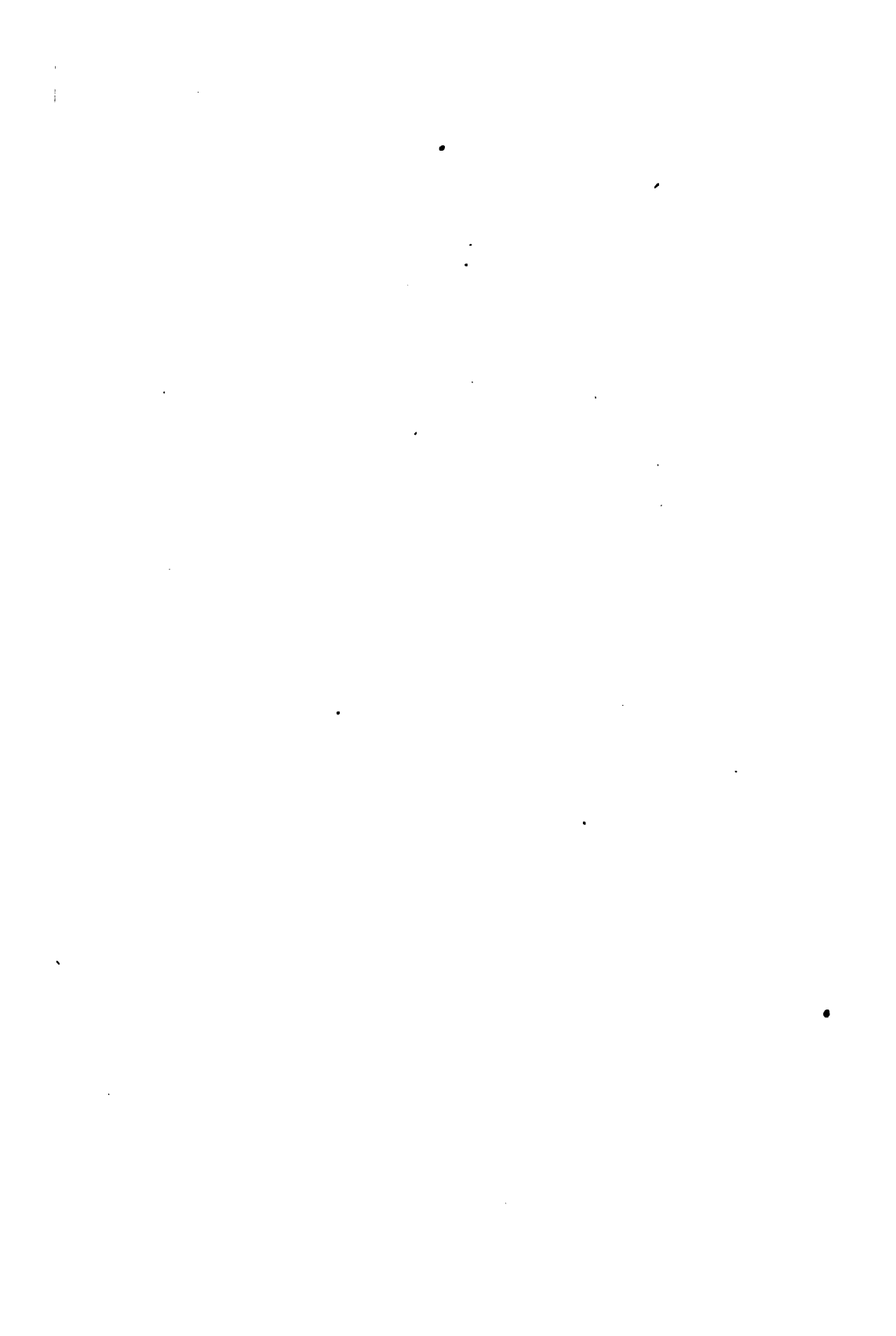
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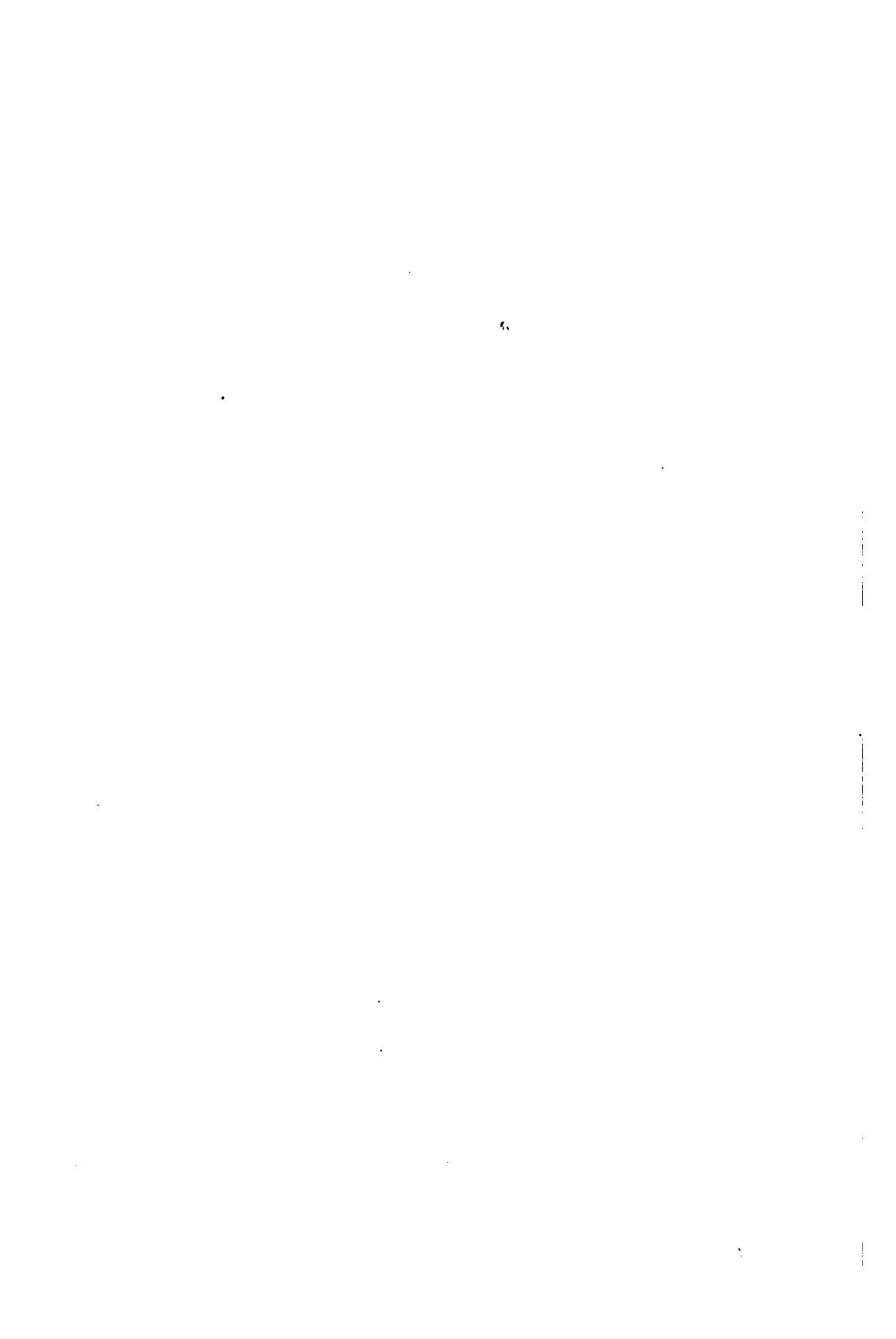




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H A N D - B O O K
OF
C H E M I S T R Y .

BY
LEOPOLD GMELIN

VOL. X.

ORGANIC CHEMISTRY,

VOL. IV.

ORGANIC COMPOUNDS CONTAINING EIGHT AND TEN ATOMS OF CARBON.

TRANSLATED BY
HENRY WATTS, B.A., F.C.S.

c L O N D O N :
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(VOL. IV. OF ORGANIC CHEMISTRY.)

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COMPOUNDS CONTAINING 8 At. CARBON.

I. MELLITENE SERIES.

A. UNKNOWN PRIMARY NUCLEUS. MELLITENE, C^8H^4 .

B. SECONDARY NUCLEI.

a. Unknown Oxygen-nucleus. $C^8H^2O^2$.

Mellitic Acid. $C^8H^2O^6 = C^8H^2O^3O^3$.

- KLAPROTH. *Scher. J.* 3, 461. — *Beiträge*, 3, 114.
VAUQUELIN. *Ann. Chim.* 36, 203; also *Scher. J.* 5, 566; also *Crell. Ann.* 180, 1, 405.
WÖHLER. *Pogg.* 7, 325. — *Pogg.* 52, 600; also *Ann. Pharm.* 37, 263.
LIEBIG & WÖHLER. *Pogg.* 18, 161.
LIEBIG & PELOUZE. *Ann. Pharm.* 19, 252.
ERDMANN & MARCHAND. *J. pr. Chem.* 43, 129.
R. SCHWARZ. *Ann. Pharm.* 66, 46.
KARMRODT. *Ann. Pharm.* 81, 164; abstr. *Pharm. Centr.* 1852, 225; *Jahresber.* 1852, 458.

Mellithsäure, Honigsteinsäure, Acide mellitique.—Discovered in Honeystone by Klaproth in 1799.

Source. Only in mellitate of alumina (mellite or honeystone),^a mineral occurring in beds of lignite. — The statement of Hünefeld (*Schw.* 49, 215) that mellitic acid may be obtained by treating amber with hot hydrochloric acid, requires confirmation.

Preparation. Finely pounded honeystone is treated with solution of carbonate of ammonia, whereby effervescence is produced; the liquid boiled till the excess of carbonate of ammonia is expelled; caustic ammonia added to precipitate alumina, inasmuch as the acid ammoniacal salt formed during the ebullition may dissolve a portion of that base; the liquid filtered and evaporated till neutral mellitate of ammonia crystallizes out; and this salt purified by recrystallization from water, a

small quantity of ammonia being each time added, to reconvert the acid salt produced by evaporation of the ammonia, into the crystallizable neutral salt. The purified ammoniacal salt is finally dissolved in water; the solution precipitated with acetate of lead or nitrate of silver; the washed precipitate decomposed by sulphuretted hydrogen if it contains lead, or by hydrochloric acid if it contains silver; and the liquid filtered and evaporated, whereby the excess of hydrochloric acid is expelled. (Wöhler.)

The lead-precipitate contains ammonia, which is transferred to the separated acid. Either, therefore, the acid must be reprecipitated with acetate of lead; the precipitate, which still contains a small quantity of ammonia, washed and again decomposed with sulphuretted hydrogen; and the acid thus liberated precipitated a third time with hydrochloric acid, in order to obtain a precipitate free from ammonia, and thence to separate the pure acid by sulphuretted hydrogen. — Or the ammonia-salt must be boiled with excess of baryta-water; the resulting baryta-salt decomposed by digestion with dilute sulphuric acid; the liquid filtered and evaporated till it crystallizes; and the crystals freed from adhering sulphuric acid by recrystallization. (Erdmann & Marchand.) — To prepare colourless mellitic acid from the brown acid mother-liquor obtained in the preparation of mellitate of ammonia, the colouring matter may be precipitated by chloride of barium; the mellitate of baryta thrown down from the filtrate by ammonia or by boiling with acetate of ammonia; and the mellitate of baryta converted into mellitate of ammonia by digestion with carbonate of ammonia; or the brown mother-liquor may be precipitated by a strong solution of sulphate of copper, and the crystallized mellitate of copper decomposed by hydrosulphate of ammonia. — In precipitating the purified ammonia-salt by nitrate of silver, it is necessary to drop the former into an excess of the latter; otherwise the precipitate retains ammonia. (Schwarz.)

2. Pulverized honeystone is boiled with water, the aqueous mellitic acid separated from the alumina by filtration, and evaporated. (Klaproth.) — The acid thus prepared contains alumina. (Wöhler.) — 3. Honeystone is digested with aqueous carbonate of potash, whereupon carbonic acid escapes with effervescence; the solution of mellitate of potash filtered, and mixed with nitric acid; and the liquid evaporated, whereupon the acid crystallizes out. (Vauquelin.) — The product thus obtained consists of acid mellitate of potash mixed with nitre. (Wöhler.)

Properties. As obtained by evaporation: White powder exhibiting scarcely any appearance of crystalline structure; as crystallized from the solution in cold alcohol by spontaneous evaporation: Delicate, silky needles united in stellate groups. Fusible by heat, tastes strongly acid. Permanent in the air. (Wöhler.)

	<i>Crystallized.</i>		<i>Wöhler.</i>		<i>Schwarz.</i>	
8 C	48	42·11	42·38	42·15		
2 H	2	1·75	1·82	1·77		
8 O	64	56·14	55·80	56·08		
$C^8H^2O^8$	114	100·00	100·00	100·00		

According to the radical theory, the hypothetical anhydrous acid $\bar{M} = C^4O^3 = 48$.

Decompositions. 1. The crystallized acid does not give off water at 200° , but at a higher temperature sublimes partly unaltered, while the

greater portion is decomposed, with separation of a large quantity of carbon, but without empyreumatic odour. (Wöhler.)—¶ According to Erdmann (*J. pr. Chem.* 52, 432), the sublimate obtained by heating mellitic acid consists of a new acid, viz. *Pyromellitic acid*, C^6O^3 or $C^{10}HO^6$, which melts in the neck of the retort, runs down and solidifies in a radiated crystalline mass. Water likewise passes over; gas is evolved, chiefly carbonic acid, and charcoal remains behind. ¶ — 2. Mellitic acid heated in the air, burns with a bright sooty flame, and aromatic odour, leaving a large quantity of charcoal which afterwards burns completely away. (Wöhler.)—Boiling nitric acid neither dissolves nor decomposes the acid (Klaproth, Wöhler); neither is it decomposed by boiling oil of vitriol. (Wöhler.)

Combinations. The acid dissolves readily in *Water*; the concentrated solution is of a syrupy consistence. (Wöhler.)

Boiling Oil of Vitriol dissolves the acid, and when evaporated by a stronger heat, leaves it undecomposed. (Wöhler.)

All *Mellitates*, when subjected to dry distillation, yield a large quantity of carbon and a small quantity of products containing hydrogen. (Wöhler.)—¶ Mellitates slowly distilled with strong sulphuric acid, yield pyromellitic acid, which passes over with the sulphuric acid, a large quantity of carbonic acid gas being at the same time evolved, together with carbonic oxide, and towards the end of the decomposition, sulphurous acid. (Erdmann.) ¶

Mellitate of Ammonia. — *a. Neutral.* — *Preparation* (p. 1). — Large, shining, transparent crystals, having a slight acid reaction. They exhibit, with the same amount of acid, but probably a different amount of water, two forms, both indeed belonging to the right prismatic system, but exhibiting very different angles. (Wöhler.)

a. Derived from a rhombic octohedron (*Fig.* 41), whose three axes are to one another as $\sqrt{3} \cdot 290 : \sqrt{7} \cdot 881 : 1$; crystallizes in the form represented in *fig.* 68; $p : y = 151^\circ 8'$; $p : i = 160^\circ 24'$; $u' : u = 114^\circ 16'$; $u : t = 122^\circ 5'$; the *t*-face longitudinally striated; no cleavage-plane parallel to *p*; fracture conchoidal. (G. Rose.)

β. Rhombic octohedron, in which the three axes are to one another as $\sqrt{2} \cdot 675 : \sqrt{7} \cdot 923 : 1$; crystalline form (*Fig.* 67); $p : a = 144^\circ 44'$; $a : a = 146^\circ 17'$; $a : u = 125^\circ 16'$; $u' : u = 119^\circ 41'$; $u : t = 120^\circ 9\frac{1}{2}'$; cleavage parallel to *p*; longitudinal fracture uneven; all the faces smooth. (G. Rose, *Pogg.* 7, 335.)

The salt *a* becomes milk-white and opaque by exposure to the air. The salt *β*, when taken out of the mother-liquor, becomes almost instantly opaque and friable, rather perhaps from shifting of the particles than from loss of water; in many cases, however, half of the crystal remains transparent. (Wöhler.)

	<i>Crystallized.</i>		<i>Erdm. & Mar.</i>		<i>Schwarz.</i>
8 C	48	23.76	24.12	23.91	
2 N	28	13.86	14.14	13.61	
14 H	14	6.93	7.09	7.16	
14 O	112	55.45	54.65	55.32	
<hr/>					
$C^6(NH^4)O^6 + 6Aq.$	202	100.00	100.00	100.00	

Or:

				Erdmann & Marchand.
2NH ³	34	16.83 17.00
C ⁸ O ⁸	96	47.53 47.79
8HO	72	35.64
C ⁸ (NH ⁴) ² O ⁸ 6Aq.	202	100.00	

The large transparent crystals analyzed by Schwarz were dried over chloride of calcium. Those examined by Erdmann & Marchand had the form α .

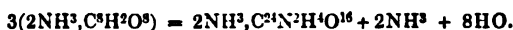
Those crystals which effloresce in the air, becoming opaque and like porcelain, losing at the same time exactly 2 At. water. At 100°, the crystals give off 24.1 p. c. water, together with a little ammonia, which, as the temperature rises, accompanies the escaping water in continually increasing quantity.

At 150° the salt is converted, in the course of a few hours, with evolution of large quantities of ammonia and water, into a pale yellow pulverulent mixture of paramide and acid euchroate of ammonia. (Wöhler.)

Formation of paramide:



Formation of euchroate of ammonia:



When the salt is heated to 160°, a further decomposition takes place, a bitter substance then mixing with the paramide. — When mellitate of ammonia is heated in a retort to 300°—350°, water passes over together with caustic ammonia and carbonate of ammonia; a pale green semifused sublimate, and a small quantity of white crystalline sublimate are formed; and a carbonaceous mass remains behind. This residu is a mixture of charcoal, greenish yellow shining needles, and a small quantity of acid matter, which may be dissolved out by water. Digested with ammonia, it yields a dark blue-green solution, which on cooling deposits a small quantity of delicate white laminae, which volatilize undecomposed in the form of a woolly sublimate. The green ammoniacal solution filtered from these laminae yields with hydrochloric acid, a dark blue-green precipitate, which is difficult to wash; black after washing and drying; shining; very friable; yields a dark green powder; and is resolved by heat into hydrocyanate of ammonia and charcoal. The hydrochloric acid solution filtered from this precipitate, soon deposits small yellow crystals, probably the same as those which are visible in the carbonaceous residue, and identical in composition with the yellow bitter substance. (Wöhler.) —†. According to N. W. Fischer (*J. pr. Chem.* 51, 113), the bluish green body which sublimes between 300° and 400° is accompanied by an amorphous, yellow, strongly bitter substance; the latter is soluble in boiling water, the former not; both yield easily soluble compounds with alkalis, and insoluble compounds with the oxides of the heavy metals. The residue which is left before the heat has been raised to 300°—400°, yields, on ignition, a sublimate of colourless crystalline needles, which are insoluble in water, dissolve in ammonia only at boiling heat, and separate on cooling in the form of a crystalline powder. Fischer regards it as probable that the blue, yellow, and colourless sublimates are isomeric compounds; inasmuch as the two former yield the latter when suddenly heated to redness, and the latter when slowly heated to 300°—400°, is

converted into the two former. ¶. — The concentrated solution of mellitate of ammonia, sealed up in a glass tube, is not altered by heating it for several hours to 200° (Wöhler). — The solution boiled in contact with the air, gives off ammonia and forms a much more soluble acid salt; consequently ammonia added to the liquid, after evaporation and cooling, throws down the neutral salt in the form of a crystalline magma. (Wöhler.)

b. Acid. — Ammonio-cupric mellitate obtained by precipitating cupric sulphate with neutral mellitate of ammonia, is decomposed by aqueous hydrosulphuric acid, and the filtrate evaporated till it crystallizes. Right rhombic prisms, truncated on the four lateral edges. $u : u : = 122^\circ$. (Erdman & Marchand.)

<i>Air-dried Crystals.</i>		Erdmann & Marchand.	
24 C	144	32.15	32.03
2 N	28	6.25	6.30
20 H	20	4.46	4.78
32 O	256	57.14	56.89
<hr/>		<hr/>	
$C^8(NH^4)^2O^8, 2C^8H^2O^8 + 8Aq.$	448	100.00	100.00

Mellitate of Potash. — a. Neutral. — Isomorphous with the neutral ammonia-salt *a.* (Fig. 68). $u' : u = 114^\circ$; $p : y = 151^\circ$; $p : i = 160^\circ$; $u : i = 123^\circ$ nearly. (Neumann.) The crystals are much inclined to effloresce. Crystals already partially effloresced give off 20.1 p. c. water at 170°, and the dry residue contains 49.51 p. c. potash: the composition of the crystals is therefore $C^8K^2O^8, 6 Aq.$ (Erdmann & Marchand.)

b. Acid. — The solution of 1 At. salt *a.*, and 1 At. mellitic acid in hot water, yields, on cooling, large opaque, right rhombic prisms, with the terminal edges truncated, and the acute lateral edges sometimes truncated, sometimes bevelled.

At a gentle heat, they give off water and become milk-white, and at 180° give off 17.93 p. c. (4 At.) water. They dissolve in water more readily than *a.*, and nitric acid added to the solution throws down a compound of the salt *b* with nitre. (Wöhler.)

<i>Crystallized.</i>		Wöhler.	
8 C	48.0	25.51	25.64
5 H	5.0	2.65	
KO	47.2	25.08	23.99
11 O	88.0	46.76	
<hr/>		<hr/>	
$C^8HKO^8, 4Aq.$	188.2	100.00	

By mixing concentrated solutions of the neutral salt and the free acid, Erdmann & Marchand precipitated a crystalline powder, which, after being dissolved in hot water, separated out in small broad nacreous crystals, containing 20.63 p. c. C, 2.74 H, and 30.49 KO; therefore = $2KO, 3C^4O^8 + 9Aq.$ [or perhaps = $C^8K^2O^8, C^8HKO^8 + 12Aq.$]

Acid Mellitate of Potash with Nitrate of Potash. — Formerly mistaken for the pure acid potash-salt. — Nitric acid is added to a saturated aqueous solution of the neutral or acid potash-salt, till a granular precipitate begins to appear, the mixture then heated till the precipitate dissolves, and left to cool slowly. Irregular six-sided prisms, bevelled with two faces resting on two lateral edges (nearly the same as Fig. 65). Of sour taste. The crystals give off 7 p. c. (6 At.) water at 150°, and when more strongly heated, are suddenly converted, with very strong intumescence, into a carbonaceous mass, exhibiting at the same time a glimmering light, visible even when excess of air is prevented. With sulphuric acid, they give off nitric acid. They are but very sparingly soluble in water. (Wöhler.)

MELLITENE: OXYGEN-NUCLEUS $C^6H^{10}O^8$.

	Crystallised		Wöhler.	
82 C	192	25.13	25.20
10 H	10	1.31	1.33
5 KO	236	30.89	30.40
NO ²	54	7.07		
34 O	278	35.60		
<hr/>				
4(C ⁶ H ¹⁰ KO ⁴) + KO,NO ² + 6Aq. 764	100.00		

Mellitate of Soda. — *a. With 8 At. Water.* — Separates from the warm concentrated aqueous solution in needles, which, at 100°, give off 22.6 p. c. (nearly 6 At.) water, and at 180°, 32.81 p. c. (8 At.) altogether.

β. With 12 At. Water. — Crystallizes from the cold saturated solution by spontaneous evaporation, in large, deeply striated crystals belonging to the doubly oblique prismatic system, which, at 160°, give off 38.88 p. c. (12 At.) water, and leave a residue containing 38.68 p. c. soda. (Erdmann & Marchand.)

Mellitate of Baryta. — Mellitic acid mixed with baryta-water or acetate of baryta, immediately forms a white precipitate; with chloride of barium, after a while, it forms transparent delicate needles; the precipitate and the crystals are soluble in hydrochloric and in nitric acid. (Klaproth.) — In rather strong solutions, mellitate of ammonia forms with baryta-salts a gelatinous precipitate, which aggregates in crystalline scales; in very dilute solutions it forms slender needles. The salt, after drying in the air, presents the appearance of a laminated mass, having an almost silvery lustre; at 100° it gives off merely hygroscopic water, but at 330° it yields 6.56 p. c. (2 At.) — Sometimes it contains a small portion of acid salt. (Schwarz.) — The salt obtained by precipitation with mellitate of ammonia, contains a small quantity of ammonia, is difficult to dry, and contains after drying, 59.1 p. c. baryta. (Erdmann & Marchand.)

	Dried at 330°.		Schwarz.	
8 C	48.0	19.26	19.26
2 BaO	153.2	61.48	60.80
6 O	48.0	19.26	19.94
<hr/>				
C ⁶ Ba ² O ⁶	249.2	100.00	100.00

Mellitate of Strontia. — The white precipitate which mellitic acid produces in strontia-water, is soluble in hydrochloric acid. (Klaproth.)

Mellitate of Lime. — The free acid forms with lime-water, white flakes soluble in hydrochloric acid (Klaproth); with an aqueous solution of gypsum it forms crystalline grains. (Vauquelin.) Mellitate of ammonia forms with chloride of calcium, large white flakes, which dry up to a loose, white mass, consisting of silky needles still containing more than 21 p. c. water. (Wöhler.) This precipitate, after drying in the air, contains, besides 0.38 p. c. ammonia, 33 p. c. water, which escapes very slowly at 130°; the residue contains 38.83 p. c. lime.

† *Mellitate of Magnesia.* — *a. With 12 At. Water.* — When a warm aqueous solution of mellitic acid is neutralized with carbonate of magnesia, the salt separates in the amorphous state in the form of clear oily drops, which become turbid on cooling, and solidify in the crystalline state on exposure to the air.

The salt gives off 8 At. water at 150°, and the whole at 180°. It dissolves but sparingly in water. (Karmrodt.)

Crystallized.		Karmrodt.	
2 MgO	40	16·10	17·53
C ⁸ O ⁸	96	39·34	40·17
12 HO	108	44·26	41·75
<hr/>			
C ⁸ Mg ² O ⁸ + 12Aq.	244	100·00	99·45

β With 14 At. Water. — Alcohol added to the aqueous solution of the salt α , renders it turbid, and after a few hours deposits small four-sided prisms. If too much alcohol be added, the solution remains milky for a week. (Karmrodt.)

Crystallized.		Karmrodt.	
2 MgO	40	15·26	15·43
C ⁸ O ⁸	96	36·64
14 HO	126	48·10	48·00
<hr/>			
C ⁸ Mg ² O ⁸ + 14Aq.	262	100·00	η

Mellitate of Alumina. — *a. Honeystone* occurs in honey-yellow transparent crystals, of sp. gr. 1·6, and belonging to the square prismatic system. (Fig. 23, 29, 32); $e : e' = 118^\circ 4'$; $e : e'' = 93^\circ 22'$; $e : q = 120^\circ 58'$; they exhibit strong double refraction. (Haüy.) When heated, it first becomes white and gives off 44·1 p. c. water, which escapes slowly at about the boiling point of oil of vitriol (Wöhler), then black by carbonization, and finally white by complete decomposition of the acid. (Klaproth.) When subjected to dry distillation, it yields, in addition to a mixture of 1 vol. hydrogen [carbonic oxide, inasmuch as it burns with a blue flame], and 4 vol. carbonic acid gas, 38 p. c. of slightly acid aromatic water, 1 p. c. aromatic oil (proceeding from admixed resin; Wöhler), 3 p. c. charcoal, 14·5 p. c. alumina, 1·2 p. c. silica, and 1 p. c. ferric oxide. (Klaproth.) — Honeystone thrown on melted nitre, exhibits a faint glow. It dissolves, with decomposition, in dilute nitric, sulphuric, or hydrochloric acid, but not in acetic acid; gives up its mellitic acid to boiling water, also to ammonia and carbonate of soda. (Klaproth.) Water boiled for some time with the mineral, extracts only part of the acid, together with a small quantity of alumina, so that an acid salt is formed, and a basic salt remains behind; aqueous mellitic acid likewise dissolves a large quantity of pounded honeystone. Carbonate of ammonia extracts the greater portion of the acid, even from entire crystals; but a small quantity of acid and ammonia remains with the alumina, so that its solution in nitric acid yields, on evaporation, crystals (Fig. 29 & 32), of regenerated honeystone. (Wöhler.) A honeystone from Walchow, containing a much larger proportion of alumina, is described by Duflos. (*J. pr. Chem.* 38, 323.)

Honeystone.		Wöhler.		Klaproth.	
2 AlPO ³	102·8	14·38	14·5	14·5
3 C ⁸ O ⁸	288·0	40·29	41·4	46·0
36 HO	324·0	45·33	44·1	38·0
Fe ² O ³ & SiO ²	1·3
Fe ² O ³ & resin	trace
<hr/>					
C ²⁴ Al ⁴ O ²⁴ + 36Aq.	714·8	100·0	99·8

δ. Mellitate of potash added to an aqueous solution of alum, throws down a large quantity of white flakes (Vauquelin); a white crystalline powder, containing only 9.5 p. c. alumina and 48.0 p. c. water; probably therefore an acid salt. (Wöhler.)

¶ *Mellitate of Manganese.* Obtained by saturating mellitic acid with carbonate of manganese. On heating the liquid, a white powder is precipitated, which, when examined by the microscope, is seen to consist of needles united in tufts. This salt is more soluble in cold than in hot water; the latter dissolves only $\frac{1}{100}$ of it. (Karmrodt.)

Crystallized.		Karmrodt.	
2 MnO	72	26.09	25.75
C ⁶ O ⁸	96	34.78
12 HO	108	39.13	40.01
<hr/>			
C ⁶ Mn ² O ⁸ + 12Aq.	276	100.00

Mellitate of Zinc. — a. With 10 At. Water. — Obtained by neutralizing aqueous mellitic acid with carbonate of zinc; it then separates as a crystalline powder, consisting of regular four-sided prisms. Begins to give off water at 205°. Cold water dissolves it pretty readily, but the salt separates out again when the solution is heated to 55°—60°. Dissolves readily in dilute acids, even in mellitic acid. (Karmrodt.)

Crystallized.		Karmrodt.	
2 ZnO	80	30.08	30.00
C ⁶ O ⁸	96	36.09	36.02
10 HO	90	33.83	33.67
<hr/>			
C ⁶ Zn ² O ⁸ + 10Aq.	266	100.00	99.69
			100.45

β. *With 6 At. Water.* — Separates on adding alcohol to the aqueous solution of a, in curdy flakes, which under the microscope, appear like a confused mass of fine needles. Gives off all its water at 160°. Much more soluble in water than a. (Karmrodt.)

Crystallized.		Karmrodt.	
2 ZnO	80	34.78	36.12
C ⁶ O ⁸	96	41.74	41.70
6 HO	54	23.48	22.35
<hr/>			
C ⁶ Zn ² O ⁸ + 6Aq.	230	100.00	100.17
			99.17

Mellitate of Lead. — Mellitic acid and mellitate of ammonia form with acetate and nitrate of lead, a bulky white precipitate, which, when washed on a filter, shrinks up to a heavy granular powder, insoluble in water, but soluble in nitric acid. (Klaproth, Vauquelin, Wöhler.)

If the mellitate of ammonia be not dropped into excess of the lead-salt, but the ammonia-salt be allowed to predominate, the precipitate contains ammonia. (Schwarz.)

Dried at 180°.		Erdmann & Marchand.	
2 PbO	224	70	69.74
8 C	48	15	14.57
H	0.26
6 O	48	15	15.43
<hr/>			
C ⁶ Pb ² O ⁸	320	100	100.00

	<i>Dried at 100°.</i>		<i>Erd. & Marchand.</i>	<i>Wöhler.</i>
2 PbO	224	66·28	67·5	67·05
8 C	48	14·20		
2 H	2	0·59	0·5	
8 O	64	18·93		
<hr/>				
C ⁶ Pb ² O ⁸ + 2Aq.....	338	100·00		

¶ *Ferrous Mellitate.* — 2FeO, C⁶Fe²O⁸ + 6HO. — Mellitate of ammonia forms with ferrous sulphate a greenish white precipitate, which disappears on heating the liquid; but on boiling, there is produced a lemon-yellow precipitate of basic ferrous mellitate, which assumes a light olive-green colour when dry; and consists of microscopic crystals, having the form of cubo-octohedrons. The salt gives off all its water at 190°. It is sparingly soluble in water, but dissolves readily in dilute hydrochloric acid.

	<i>Crystallized.</i>		<i>Karmrodt.</i>	
4 FeO	144	49·00	48·80	
C ⁶ O ⁸	96	32·65	32·51	
6 HO	54	18·35	18·49	
<hr/>				
2FeO, C ⁶ Fe ² O ⁸ + 6Aq.	294	100·00	99·80	¶

Ferric Mellitate. — The free acid added to a solution of ferric nitrate throws down a cream-coloured powder soluble in hydrochloric acid. (Klaproth.)

¶ *Mellitate of Cobalt.* — Separates on neutralizing a warm solution of the acid with carbonate of cobalt, as a brown glutinous mass, which, on cooling, solidifies in a single lump, or if it be stirred with a glass rod during the cooling, settles down in the form of a granular crystalline powder (a). Cold water dissolves only $\frac{1}{37350}$ of this salt; hot water a much larger quantity; and the hot solution, as it cools, deposits the salt in the form of a pale reddish powder (b), which, under the microscope, appears to consist of short rhombic prisms. (Karmrodt.)

	<i>Crystallized.</i>		<i>a.</i>	<i>Karmrodt.</i>	
				<i>b.</i>	
2 CoO	75	26·88	27·00	25·75	26·33
C ⁶ O ⁸	96	34·41			
12 HO.....	108	38·71	38·41	39·22	38·46
<hr/>					
C ⁶ Co ² O ⁸ + 12Aq.....	279	100·00			

Mellitate of Nickel. — a. *With 16 At. Water.* — A warm solution of mellitic acid saturated with carbonate of nickel, deposits a grass-green, semifluid mass, which, on cooling, becomes turbid and more compact, and may be washed by kneading between the fingers under water. The salt becomes hard and glossy by exposure to the air, assuming exactly the appearance of chrysoprase. Gives off 8 At. water at 100°, and 6 At. more at 180°, the last 2 At. going off at 300°. Dissolves slowly in water, readily in hydrochloric and nitric acid. (Karmrodt.)

	<i>Air-dried.</i>		<i>Karmrodt.</i>		
2 NiO	75	23·81	23·95	23·64	
C ⁶ O ⁸	96	30·47			
16 HO	144	45·72	45·58	46·16	46·24
<hr/>					
C ⁶ Ni ² O ⁸ + 16Aq.	315	100·00			

β . *With 6 At. Water.* — The liquid from which the preceding salt has been deposited, yields by evaporation delicate rhombic prisms, with two dihedral summits; dissolves in water much more readily than *a*. (Karmrodt.)

	Crystallised.		Karmrodt.		
2 NiO	75	33.33	32.65	32.27	33.01
C^8O^4	96	42.67			
6 HO	84	24.00	24.43	24.69	24.11
$C^8Ni^2O^8 + 6Aq.$	225	100.00			

Cupric Mellitate. — *a. Neutral.* — 1. Obtained by mixing the boiling solutions of mellitic acid and cupric acetate, in the form of flakes, which during washing lose a portion of their acid, and become crystalline and neutral. (Erdmann & Marchand.)

2. Neutral mellitate of ammonia forms with cupric sulphate, a bulky pale blue precipitate, which shrinks in washing to a light blue crystalline powder; it contains 20 p. c. water. (Wöhler.) The precipitate obtained with mellitate of ammonia or potash retains small quantities of the alkali. (Erdmann & Marchand.)

	Prepared <i>b</i> , (1); air-dried.		Erdm. & March.	
8 C	48	19.35	19.42	
8 H	8	3.23	3.23	
2 CuO	80	32.26	32.43	
14 O	112	45.16	44.87	
$C^8Cu^2O^8 + 8Aq.$	248	100.00	100.00	

¶ When this salt is subjected to dry distillation, water passes over, and an oily and a crystalline body volatilize; these may be separated by distillation with water, the oil then passing over first, and the solid body separating from the residual liquid in yellowish white crystalline flakes, which, from an analysis made with a very small quantity of substance, appeared to contain 75.1 p. c. carbon, and 3.3 hydrogen, corresponding to the formula $C^{28}H^{10}O^8$. (Erdmann.) ¶

b. Acid. — Free mellitic acid forms with cupric acetate (but not with the hydrochlorate,) a precipitate of the colour of verdigris. (Klaproth.) It forms with cupric acetate a thick light-blue precipitate, which changes to crystals when left for several days in the liquid. The crystals, after drying at 100° , do not give off any more water till they are heated enough to blacken and decompose them. (Liebig & Pelouze.) They are blue crystals which give off three-fourths of their water at 100° , but do not part with the last fourth completely, even at 230° . (Schwarz.) — The thick blue jelly obtained by cold precipitation of cupric acetate with mellitic acid in concentrated solution, becomes filled, after remaining for some time in the liquid, with crystalline points, which grow into small, transparent, dark blue crystals; if the jelly be pressed immediately after precipitation, a white mass is obtained, which, on drying, becomes blue and crystalline. (Erdmann & Marchand.)

Calculation, according to Gm.

16 C	96	20.64
17 H	17	3.65
3 CuO	120	25.81
29 O	232	49.90
$C^8Cu^2O^8, C^8HCuO^8 + 16Aq.$	465	100.00

Calculation, according to Erdm. & March.		Erdm. & March. <i>air-dried crystals.</i>	
12 C	72	21·69	21·06
12 H	12	3·61	3·59
2 CuO	80	24·10	25·51
21 O	168	50·60	49·84
<hr/>		<hr/>	
2 CuO, 3C ⁴ O ³ , + 12Aq.	332	100·00	100·00

Cupro-mellitate of Ammonia. — The dark blue solution of neutral cupric mellitate in ammonia, yields on evaporation, dark blue rhomboidal crystals, which turn green and give off ammonia when exposed to the air. (Wöhler.)

Ammonio-cupric Mellitate. — *a. With a comparatively large proportion of mellitate of ammonia.* — Dark blue crystals permanent in the air. (Wöhler.) [Perhaps = C⁸NH⁴CuO⁸ + xAq.]

b. With a smaller proportion. — The precipitate which mellitate of ammonia forms with cupric sulphate. Sky-blue microscopic crystals which at 120° slowly give off 27·3 p. c. water, with a trace of ammonia, and assume a greenish blue colour.

<i>Air-dried Crystals.</i>		Erdm. & March.	
16 C	96	19·92	19·53
N	14	2·90	3·04
20 H	20	4·15	4·35
3 CuO	120	24·90	23·20
29 O	232	48·13	49·88
<hr/>		<hr/>	
C ⁸ Cu ² O ⁸ , C ⁸ NH ⁴ CuO ⁸ + 16Aq.	482	100·00	100·00

According to Erdmann & Marchand, the formula of the salt is NII⁴O, C⁴O⁸ + 3(CuO, C⁴O³, HO) + 15Aq.

The filtrate obtained in precipitating cupric sulphate with mellitate of ammonia, deposits, on addition of ammonia, a light green *basic salt*, which, in the air-dried state, contains 8·45 p. c. C, 0·74N, 2·34H, 54·09CuO, 9·05SO³ and 25·33O. (Erdmann & Marchand.)

Mellitates of Mercury. — Mellitic acid forms with mercurous and also with mercuric nitrate, a white precipitate soluble in nitric acid. (Klaproth.)

¶ *Mercurous Mellitate.* — Mercurous nitrate forms with free mellitic acid and alkaline mellitates, a very fine-grained, white precipitate, nearly insoluble in water, but readily soluble in nitric acid. Gives off its water, amounting to 6·59 p. c. (4 At.) at 190°. (Karmrodt)

<i>Dried at 100°.</i>		Karmrodt.	
2 Hg ² O	416	75·92	76·56
C ⁸ O ⁸	96	17·52	
4 HO	36	6·56	6·59
<hr/>		<hr/>	
C ⁸ Hg ⁴ O ⁸ + 4Aq.	548	100·00	

Mercuric Mellitate. — Mellitic acid and mercuric oxide, triturated together with a small quantity of water, and gently warmed, unite into a white granular mass. Alkaline mellitates and even free mellitic acid added to a solution of mercuric nitrate, throw down bulky white pre-

cipitate, which, after drying, forms hard, heavy lumps, soluble in hot strong nitric acid, and not reprecipitated therefrom by ammonia. The salt gives off its water, amounting to 10·87 p. c. (4 At.) at 200°. (Karmrodt.)

		Dried at 100°.		Karmrodt.	
2 HgO	216 62·08	61·50
C ⁶ O ⁶	96 27·59	
4 HO	36 10·33	10·37
<hr/>					
C ⁶ Hg ² O ⁶ + 4Aq.	348 100·00		¶

Mellitate of Silver. — 1. Obtained by precipitating nitrate or acetate of silver with mellitic acid. (Vauquelin, Wöhler, Erdmann & Marchand.) — 2. By precipitating an excess of nitrate of silver with mellitate of ammonia, dropping the latter solution into the former (Schwarz.) Without this precaution, the precipitate, as Erdmann & Marchand found, retains a small quantity of ammonia and water, and assumes a violet-brown colour when heated. (Schwarz.) — The precipitate is silky, and imparts to the liquid the appearance of soapy water. (Vauquelin.) After drying, it forms a white powder (Wöhler); a shining scaly powder, which, under the microscope, appears to consist of transparent, colourless, square tables, often with truncated summits (Erdmann & Marchand); does not blacken when exposed to light (Liebig & Pelouze); remains white even at 200°. (Schwarz.) The mellitic acid may be reproduced by the action of hydrosulphuric or hydrochloric acid, even from the salt dried at 180°. (Liebig & Pelouze.) At a higher temperature, the salt deflagrates, and leaves metallic silver (Wöhler); the decomposition is not attended with electric excitement. (Erdmann & Marchand.) The residue consists of tumented carboniferous silver. (Liebig & Pelouze.) In a stream of hydrogen at 100°, the salt quickly blackens, with formation of water, and a loss of weight corresponding to half the oxygen of the oxide of silver; the residue dissolves in water, forming a dark brown-yellow, very acid liquid, which quickly changes, with deposition of silver specula, into a solution of mellitate of silver in free mellitic acid. Hence the hydrogen produces mellitate of suboxide of silver. (Wöhler, *Ann. Pharm.* 30; also *Pogg.* 46, 629.) The salt dried at 180°, and heated with iodine, yields iodide of silver, and a white crystalline sublimate, which has a rough, sour taste, reddens litmus strongly, dissolves readily in water, and is perhaps a compound of C⁴O⁴ with iodine. (Liebig & Pelouze.)

	Liebig & Pelouze.		Erdmann & Marchand.				
		<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>		
8 C.....	48 14·63 14·73 14·53 14·55 14·37	
2 Ag.....	216 65·86 65·71 65·90	
8 O.....	64 19·51 19·56	
H.....	 0·08 0·10 0·13	
<hr/>							
C ⁶ Ag ² O ⁶	328 100·00 100·00				

a was dried in vacuo at 180° [as it blackened during drying, it appears to have contained ammonia].—*b* is the salt prepared by (1), dried in vacuo at 130°.—*c* is a salt containing ammonia, dried in vacuo at 100°.—*d*, the same, dried in the air at 100°.

Mellitate of Silver and Potassium. — A mixture of nitrate of silver with mellitate of potash containing nitric acid, yields no precipitate, but after a while deposits small transparent prisms having a strong lustre (*Fig.* 70) *u' : u* = 121° 30'; *u' : t* = 119° 11' [15' ?]. The crystals, when

heated, first become opaque from loss of water, and then suddenly swell up with a kind of explosion; forming a long, involved mass, consisting of silver and carbonate of potash. (Wöhler.)

¶ *Mellitate of Palladium.* — Protoxide of palladium, obtained by precipitating the protochloride with carbonate of soda at a boiling heat, neutralizes mellitic acid completely. The brown liquid deposits no crystals, even when evaporated to a syrup, but on evaporation to dryness, leaves a brown amorphous residue of mellitate of palladium. (Karmrodt.)

Mellitate of Palladium with Ammonia. — Mellitate of palladium dissolves in ammonia, forming a colourless liquid, which, on evaporation, deposits colourless rhombic prisms often maced in twos and threes. The salt gives off all its water ($\frac{1}{4}$ At.) at 150° , together with a small quantity of ammonia. (Karmrodt.)

	Crystallized.		Karmrodt.	
4 NH ³	68.0	21.08
2 PdO	122.6	38.00	37.90	37.82
C ² O ⁶	96.0	29.76
4 HO	36.0	11.16	12.72	12.32
<hr/>				
4NH ³ ,C ² Pd ² O ⁶ + 4Aq	322.6	100.00		

Dry protochloride of palladium dissolves readily in concentrated mellitic acid, forming a brown solution. Ammonia added to this solution throws down a precipitate of protochloride of palladium with ammonia, which dissolves readily, with the aid of heat, in a slight excess of ammonia; and the solution when evaporated deposits pointed crystals, which, when dried at 100° , give off 7.595 p. c. water, and yield by ignition 32.91 p. c. metallic palladium. (Karmrodt.)

Mellitate of Palladium and Potassium. — Crystallizes from the mixture of the two salts, evaporated to a syrup, in indistinct prisms united in nodules. Deliquesces in the air. (Karmrodt.)

Mellitate of Palladium and Sodium. — Prepared like the potassium-salt. Crystallizes in maced triangular pyramids; containing 34 p. c. palladium. (Karmrodt.)

A solution of mellitic acid and urea in equal numbers of atoms yielded no crystals when evaporated to a syrup. Alcohol produced no change in the solution. (Karmrodt.) ¶

Mellitic acid dissolves readily in alcohol. (Wöhler.)

Conjugated Compound of Mellitic Acid.

Vinomellitic Acid ?

The probable existence of this acid is established by the following experiments:

When a solution of mellitic acid in absolute alcohol has been boiled for several hours, it no longer yields crystals on cooling; but when evaporated to a syrupy consistence, assumes a dark brown colour, and afterwards solidifies, on cooling, in a solid, transparent, gummy mass, which, like resin, does not absorb water. Nevertheless, when kept under water for some hours, it becomes white and opaque on the surface, and after 24 hours, through and through, the water at the same time becoming sour and milky. The undissolved portion, after washing with cold and

hot water, in which it dissolves to a small extent, forms a white, tasteless, easily fusible powder, which solidifies in a radiated mass on cooling, burns with a smoky flame like resin, and, when heated in a glass tube, yields a residue of charcoal, but no sublimate. It dissolves sparingly in hot water, readily in alcohol; the alcoholic solution reddens litmus, and yields a milky precipitate with water. It dissolves readily in ammonia, forming a solution which yields white flakes with hydrochloric acid; and, after the excess of ammonia has evaporated, has a bitter taste and acid reaction, and ultimately leaves a crystalline substance, which gives off ammonia when treated with potash. (Wöhler.)

When mellitic acid, containing a small quantity of sulphuric acid, is boiled for some time with absolute alcohol, in a flask provided with a long glass tube, which is kept cold, so that the alcohol as it evaporates may flow back again; then mixed with baryta-water, and exposed to the air till the excess of baryta is precipitated as carbonate; afterwards filtered from the precipitate of carbonate, sulphate, and mellitate of baryta, and evaporated in vacuo over oil of vitriol: it leaves a gummy mass, probably consisting of vinomellitate of baryta. This mass contains 36.57 p. c. BaO, 2.58 H, and about 34.02 C. It is free from sulphur. When burnt in the air, it leaves a mixture of carbonate of baryta and incombustible charcoal. It moves about on water like butyrate of baryta, and dissolves completely, but after being heated to 100°, leaves, when dissolved in water, a residue of carbonate of baryta. (Erdmann & Marchand.)

Schwarz did not succeed in his attempts to prepare a *mellitate of ethyl* or of *methyl*.

¶ Pyromellitic Acid.

O. L. ERDMANN. *J. pr. Chem.* 52, 432; abstr. *Ann. Pharm.* 80, 281; *Pharm. Centr.* 1851, 313; *Laur. & Gerh. compt. rend.* 1851, 93; *Jahresber.* 1851, 386.

Formation and Preparation. — By the dry distillation of mellitic acid and its salts (p. 3); also by distilling mellitates with oil of vitriol. The best mode of obtaining it pure is to decompose the soda-salt purified by recrystallization from dilute alcohol, with nitric or hydrochloric acid.

Properties. Crystallizes from a hot saturated aqueous solution in tables belonging to the doubly oblique prismatic (triclinometric) system. The solution has a strong acid taste and reaction. The crystallized acid gives off from 12.3 to 12.5 p. c. water between 100° and 120°.

Dried at 120°.			Or:			Erdmann.		
5 C.....	30	47.6	10 C.....	60	47.2	47.3	47.8	47.8
H.....	1	1.6	3 H.....	3	2.4	2.3	2.4	2.4
4 O.....	32	50.8	8 O.....	64	50.4	50.4	49.8	49.8
C ⁵ HO ⁴ ...	63	100.0	C ¹⁰ H ³ O ⁸ ...	127	100.0	100.0	100.0	100.0
Crystallized.			Or:			Erdmann.		
C ⁵ HO ⁴ ...	63	87.5	C ¹⁰ H ³ O ⁸	127	87.6	12.3	12.5	12.5
HO.....	9	12.5	2HO.....	18	12.4	12.3	12.5	12.5
C ⁵ HO ⁴ + Aq	72	100.0	C ¹⁰ H ³ O ⁸ + 2Aq	145	100.0			

[The percentages deduced from the two formulæ $C^5H^4O^4$ and $C^{10}H^3O^8$ agree too closely to enable us to decide between the two. According to the formula $C^5H^4O^4$, the formation of pyromellitic from mellitic acid may be represented by the equation :



According to the formula $C^{10}H^3O^8$ it may be :



Decompositions. The acid, when somewhat strongly heated, melts and sublimes with partial decomposition. The fused acid heated in the air, takes fire and burns with a luminous smoky flame.

Combinations. One part of pyromellitic acid, dried at 120° , dissolves in 70.42 parts of water at 16° . The acid likewise dissolves without decomposition in oil of vitriol, hydrochloric acid, and nitric acid, at a boiling heat.

The *Pyromellitates* of ammonia, potash and soda, are crystallizable, and dissolve readily in water, but are insoluble in strong alcohol. The solutions of the ammonia and soda salts form with chloride of barium, a white precipitate; with chloride of calcium, a white crystalline precipitate, slowly at ordinary temperatures, immediately on heating; with cupric sulphate, a greenish pulverulent precipitate if the solutions are strong; but when dilute solutions are used, small green crystals, in the cold, and a crystalline precipitate if heat be applied; with neutral acetate of lead and nitrate of silver, white crystalline precipitates. The aqueous solution of pyromellitic acid forms a white precipitate with acetate of lead, but no precipitate with any other salt.

Pyromellitate of Lime. $2C^5CaO^4 + 5Aq$, or $C^{10}HCa^2O^8 + 5Aq$. Crystalline. The air-dried salt gives off 24.6 p. c. water at 120° to 130° ; the dried salt yields 33.92 p. c. lime.

Pyromellitate of Lead. — Obtained by precipitating neutral acetate of lead with pyromellitic acid or pyromellitate of ammonia or soda. White crystalline precipitate.

<i>Dried at 120°.</i>			
10 C	60	17.6
H	1	0.3
7 O	56	16.4
2 PbO	224	65.7
2C ⁵ PbO ⁴ + Aq. 341 100.0			
Or:			
Erdmann.			
<i>a.</i>			
10 C	60	17.6
2 H	2	0.6
7 O	56	16.4
2 PbO	224	65.2
C ¹⁰ HPb ² O ⁸ + Aq. 342 100.0			
<i>b.</i>			
10 C	60	17.5
2 H	2	0.6
7 O	56	16.4
2 PbO	224	65.5
C ¹⁰ HPb ² O ⁸ + Aq. 342 100.0			

a was prepared by precipitation with the free acid; *b* with the soda or ammonia-salt.

Pyromellitate of Silver. — Obtained by precipitating nitrate of silver with pyromellitate of ammonia or soda. — Crystalline.

						Erdmann (mean.)			
5 C	...	30	...	17.7	10 C	60	17.6	17.8
					H	1	0.3	0.3
3 O	...	24	...	14.1	6 O	48	14.1	
AgO	...	116	...	68.2	2 AgO	232	68.0	67.9
<hr/>									
C^6AgO^4	170	...	100.0		$C^{10}HA_2O^8$	341	100.0		

Pyromellitic acid dissolves readily in *Alcohol*. (Erdmann.) ¶.

b. Nitrogen-nucleus. C^6NH^4 .

Paramide. $C^6NH^4 = C^6NH^3O^1$.

WÖHLER. (1841). *Pogg.* 52, 605; also *Ann. Pharm.* 37, 268.
R. SCHWARZ. *Ann. Pharm.* 66, 52.

Paramid, Dimellimide.

Formation. By the action of heat on mellitate of ammonia (p. 3).

Preparation. Neutral mellitate of ammonia in the state of fine powder is heated to $150^\circ - 160^\circ$ for some hours, with brisk agitation, in a porcelain basin placed in an oil-bath, till it no longer gives off the odour of ammonia; the pale yellow powder stirred up with cold water, washed therewith on the filter till the water no longer acquires any acid reaction, and consequently no longer extracts euchroate of ammonia; and the undissolved matter dried. (Wöhler.) — The quantity of paramide obtained is greater, the more strongly the mellitate of ammonia has been heated, and it is diminished by washing with water at 50° , instead of cold water. (Schwarz.) — If, however, the heat be too strong, the paramide becomes contaminated with the yellow bitter substance, which likewise sublimes in the decomposition of paramide by heat, and is difficult to separate. (Wöhler.)

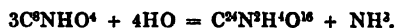
Properties. White, rather closely aggregated, inodorous, tasteless mass, which turns yellowish in the air by absorption of ammonia, and when triturated with water, acquires the odour and consistence of damp clay. (Wöhler.)

				Wöhler.	Schwarz.				
8 C	48	50.53	51.17	50.01	
N	14	14.74	1.65	13.47	
H	1	1.06	1.52	
4 O	32	33.67	35.00	
<hr/>									
C^6NH^4	95	100.00				100.00	

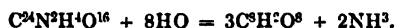
[Paramide is not an amidogen-compound, but contains nitrogen as such; for its formation is attended with the evolution not of two, but of four atoms of water to 1 At. ammonia.]

Decompositions. 1. Paramide remains unaltered at 200° , but at a higher temperature becomes carbonized, and gives off ammonia, with sublimation of a bluish-green semifused substance, and sulphur-yellow, very bitter needles. (Wöhler.) — Dissolved in dilute potash it decomposes, gradually at ordinary temperatures, instantly when heated, with evolution

of ammonia, and then no longer yields a precipitate with hydrochloric acid, the paramide being in fact converted into euchroic acid, which may be recognized by the blue deposit which it forms on zinc, and afterwards into mellitic acid. The solution of paramide in aqueous ammonia behaves in a similar manner, excepting that part of the euchroate of ammonia formed from it remains unaltered. (Wöhler.)—Conversion of paramide into euchroic acid :



Transformation of euchroic into mellitic acid :



3. Paramide boiled for several days with a large quantity of water, dissolves completely, forming acid mellitate of ammonia and a small quantity of euchroate; heated with water in a sealed glass tube, it is completely converted into acid euchroate of ammonia (Wöhler):



4. Paramide boiled with aqueous acetate of lead is also completely converted into mellitate of lead and acetate of ammonia. (Wöhler, *Ann. Pharm.* 66, 53.) Nitric acid and aqua-regia neither decompose nor dissolve paramide. (Wöhler.)

Combinations. Paramide is not soluble in water or in alcohol. (Wöhler.)

It dissolves in hot oil of vitriol, whence it is precipitated in its original state by water.

In aqueous potash or ammonia, it swells up into a yellow flocculent mass; dissolves on addition of water; and, by gradual addition of hydrochloric acid before decomposition (*supra*) has commenced, may be precipitated unaltered in the form of a white powder, with milky turbidity. (Wöhler.)

Silver-compound. When paramide in excess is shaken up with very dilute ammonia, and the liquid quickly filtered and mixed with nitrate of silver, a voluminous, gummy precipitate is obtained, drying after washing, into yellow lumps, which assume a pure yellow colour at 150°, become brown and give off ammonia at 200°, blacken and evolve hydrocyanic acid at a higher temperature, and finally leave a residue of metallic silver.—The compound heated to 200° appears to be C^8NAgO^4 ; after heating to 150°, NH^3, C^8NAgO^4 . (Laurent, *N. Ann. Chim. Phys.* 23, 121.)

<i>Calculation, according to Laurent.</i>			Wöhler.
			At 200°.
8 C	48	23.76	
N	14	6.93	
Ag	108	53.47	52.74
4 O	32	15.84	
<hr/>			
C^8NAgO^4	202	100.00	
<i>Calculation, according to Laurent.</i>			Wöhler.
			At 150°.
8 C	48	21.92	22.74
2 N	28	12.79	
3 H	3	1.37	0.82
Ag	108	49.31	51.22
4 O	32	14.61	
<hr/>			
NH^3, C^8NAgO^4	219	100.00	

[A closer agreement between calculation and analysis might be obtained by supposing that the yellow compound has already lost some of its ammonia at 150° , and that the brown compound still retains a portion of ammonia at 200° , whence also it gives off hydrocyanic acid at a higher temperature.]

Euchoic Acid. $C^{24}N^2H^4O^{16} = C^{24}Ad^2O^{10}, O^6$.

WÖHLER (1841). *Pogg.* 52, 610; also *Ann. Pharm.* 37, 273.

R. SCHWARZ. *Ann. Pharm.* 66, 49.

From *λυσιος*, having a beautiful colour. — *Euchronsäure. Acide euchoïque, Acide mellamique* (Laurent).—*Formation* (p. 16, 17).

Preparation. The same process as for obtaining paramide (p. 16.) On evaporating the aqueous filtrate obtained in washing out the paramide, euchoate of ammonia separates in white crusts. The solution of this salt in the smallest possible quantity of boiling water, supersaturated while hot with hydrochloric or nitric acid, deposits nearly all the euchoic acid, as it cools, in the form of a white crystalline powder, which may be purified by recrystallization from hot water. (Wöhler.) — If the mellitate of ammonia has not been heated strongly enough, acid mellitate of ammonia remains mixed with the euchoate. (Wöhler.)

To obtain the greatest possible quantity of euchoate of ammonia (and therefore proportionally less paramide) from the pale yellow residue produced by roasting mellitate of ammonia, the residue should be digested with a small quantity of water at $40^\circ - 50^\circ$; the liquid filtered; the undissolved portion, after removal from the filter, again treated with a small quantity of water at 40° to 50° ; the solution again filtered, &c. &c. as long as the filtrate contains euchoate of ammonia. The filtrates must then be added by drops to tolerably strong hydrochloric acid, which will separate the euchoic acid in crystalline scales; these scales washed several times on the filter with cold water, then pressed, and recrystallized several times from hot dilute nitric or hydrochloric acid, whereby the ammonia, which adheres with considerable obstinacy, will be completely removed. The mother-liquor of the crystals still contains, besides sal-ammoniac, a small quantity of euchoic acid, which may be reconverted into mellitic acid by evaporation to dryness and boiling with aqueous ammonia, and recovered by precipitation with a baryta-salt, or, after driving off the excess of ammonia, with a copper-salt. (Schwarz.)

Properties. The dry acid is colourless and opaque; its aqueous solution reddens litmus strongly and tastes like cream of tartar. (Wöhler.)

	Dried at 200° .		Wöhler.		Schwarz.	
24 C	144	47.37	48.66	47.44		
2 N	28	9.21	10.98	9.18		
4 H	4	1.31	1.66	1.46		
16 O	128	42.11	38.70	41.92		
$C^{24}N^2H^4O^{16}$	304	100.00	100.00	100.00		

Wöhler himself states that the nitrogen-determination is not to be depended on. [The acid may be regarded either as a mellitic acid conjugated with paramide :



or as a bibasic acid, $C^{24}Ad^2O^{10}, O^6$, whose nucleus, like that of mellitic acid, contains twice

as many atoms of carbon as other atoms. — The formula $C^8NH^2O^6$, proposed for this acid by Laurent (*N. Ann. Chim. Phys.* 23, 121), does not agree either with the analysis of the acid or with that of its salts. Gerhardt however suggests (*Compt. rend.* 1849, 209) that the acid may have been partially decomposed by drying at 200° before it was analysed.]

Decompositions. The acid remains unaltered at 280° , but at a higher temperature melts, boils, and decomposes, yielding hydrocyanate of ammonia, and a dark green, bitter sublimate. (Wöhler.) — 2. Zinc, protoxide of iron, or the electric current, throws down from an aqueous solution of euchronic acid, a dark blue substance, called *Euchrone*, of unknown composition, insoluble in water, but dissolving with purple colour in alkalis, and quickly oxidizing again in the air to euchroic acid. (Wöhler.) — The deep blue, closely adhering deposit with which zinc becomes covered in the aqueous acid, detaches itself on immersion for a short time in very dilute hydrochloric acid, and may then be collected on a filter, washed, and dried. The black mass thus obtained, which is free from zinc, is instantly oxidized, by the slightest heating, and converted into euchroic acid; it dissolves in aqueous ammonia or potash, with a more splendid colour than that of permanganate of potash; but the solution becomes decolorized from above downwards, on exposure to the air, and very quickly if agitated. In the boiling acid, zinc acquires a similar coating, but a trace of gas is evolved at the same time, and the liquid deposits a white powder, probably mellitate of zinc. — A mixture of aqueous euchroic acid and protochloride of iron forms with alkalis a thick, deep violet-coloured precipitate, which immediately becomes rust-brown on exposure to the air, and dissolves without colour in hydrochloric acid, because the resulting sesquioxide of iron is reduced to the state of protoxide by the euchrone, which is thereby reconverted into euchronic acid. These phenomena are not produced by protochloride of tin or protochloride of manganese. — Platinum in galvanic combination with zinc does not act upon the aqueous acid, but decomposes its ammonia-salt. (Wöhler.) — The aqueous acid is likewise decomposed by the galvanic current, and covers the negative platinum with a deep blue deposit, which however soon ceases to increase. — Euchrone is not produced by the action of sulphuretted hydrogen, sulphurous acid, hyposulphites, or arsenites (Schwarz). — 3. Euchroic acid mixed with a quantity of water not sufficient to dissolve it in its unaltered state, and heated to 200° in a sealed glass tube, dissolves completely in the form of acid mellitate of ammonia. (Wöhler.)



Euchroic acid dissolved in water does not decompose when boiled in contact with the air. Hydrochloric acid and nitric acid exert no decomposing action upon it. (Wöhler.)

Combinations. With *Water.* — *a. Hydrated Euchroic acid.* — The crystals obtained by cooling the hot aqueous solution, are colourless, transparent, very short prisms, macted in a peculiar manner (Wöhler); crystalline scales. (Schwarz) When heated, they become opaque from loss of water, which, after they have been heated to 200° , amounts to 10.54 p.c. (4 At.) (Wöhler.) — *b.* The acid dissolves very sparingly in cold water, better in hot. (Wöhler.)

Euchroate of Ammonia.—*a. Neutral.*—Obtained by evaporating the wash-water of paramide (vid. *Preparation of euchroic acid*), in white, scarcely crystalline crusts, which are decomposed by hydrochloric or nitric, but not by acetic acid. (Wöhler.)

Dried at 200°.				Wöhler.
24 C	144	42·60	42·98	
4 N	56	16·57		
10 H	10	2·96		2·92
16 O	128	37·87		
<hr/>				
$2 NH^3, C^8N^2H^4O^{16}$	338	100·00		

b. Acid.—Sometimes precipitated from the aqueous solution of the salt *a*, instead of the pure acid, and separates from solution in hot water, in yellowish crystals larger than those of the pure acid. (Wöhler.)

Schwarz's *Paramidic Acid*, respecting whose relation to salifiable bases nothing is yet known, stands in close relation to this salt. For if paramide be dissolved in ammonia, and the solution immediately filtered into hydrochloric acid, paramidic acid is precipitated as a white powder, which under the microscope, appears to consist of fine needles. This acid gives with zinc the blue reaction of euchroic acid; its solution in ammonia, from which it may at first be precipitated unchanged by hydrochloric acid, is converted, in 24 hours at ordinary temperatures, but immediately on boiling, into aqueous mellitate of ammonia. It dissolves to a certain extent in hot water, and separates from the solution in the form of powder. The acid dried without heat in vacuo loses 3·01 p. c. water at 170°. (Schwarz.)

Paramidic Acid dried at 170°.			
24 C	144	47·53	47·25
3 N	42	13·86	13·78
5 H	5	1·65	2·10
14 O	112	36·96	36·87
<hr/>			
$C^8N^2H^4O^{14}$	303	100·00	100·00

[Therefore, acid euchroate of ammonia minus 2 At. water. $NH^3, C^8N^2H^4O^{16} - 2HO = C^8N^2H^4O^{14}$].

Euchroate of Baryta.—Precipitated in the form of a pale yellow powder, when baryta-water is dropt into an excess of warm aqueous euchroic acid. (Schwarz.) [Schwarz assigns to this salt the formula $BaO, HO + C^8N^2O^6 (= C^8N^2Ba^2O^{16})$ with which however his (probably misprinted) analysis, assigning to the salt 25·8 p. c. C, 51·4BaO and 0·5H, does not at all agree.]

Euchroate of Lead.—The boiling aqueous solution of euchroic acid, mixed with a dilute solution of neutral acetate of lead, yields on cooling a yellow powder, which appears crystalline under the microscope. (The filtrate separated from this precipitate, deposits mellitate of lead as a white powder when boiled.) The air-dried salt gives off 11·36 p. c. (6 At.) water at 160°, but nothing more at a stronger heat, till it begins to decompose. (Wöhler.)

Dried at 100°.				Wöhler.
2 PbO	224	42·43	42·41	
24 C	144	27·27		
2 N	28	5·30		
4 H	4	0·76		
16 O	128	24·24		
<hr/>				
$C^8N^2H^2Pb^2O^{16} + 2HO$	528	100·00		

The salt dried at 100° is $C^8N^2H^2Pb^2O^{16}$ (Schwarz).

Euchroate of Silver. — Obtained as a pale sulphur-yellow heavy powder, by precipitating a dilute solution of nitrate of silver with a hot aqueous solution of euchroic acid. This precipitate redissolves on agitation, so long as only a comparatively small quantity of euchroic acid has been added, but falls down again as the liquid cools. When boiling aqueous euchroic acid is precipitated by an insufficient quantity of nitrate of silver, the filtrate still contains some of the salt in solution, which may be precipitated without alteration by the addition of a small quantity of ammonia (*vid. inf.*). Euchroate of silver dried at 150° gives off 2.11 p. c. (2 At.) water at 200°, and when more strongly heated, decomposes quietly, giving off a gas, which burns with a bluish flame, and has at first an aromatic odour, like that of burning mellitic acid, but afterwards smells like cyanic acid; the residue consists of metallic silver mixed with charcoal. The salt is insoluble in aqueous ammonia, but is divided thereby into a white gummy mass, the greater part of which passes through the paper when filtered. (Wöhler.)

<i>Dried at 200°.</i>			Wöhler.
24 C	144	19.67	
2 N	28	3.83	
4 Ag	432	59.01	58.53
16 O	128	17.49	
<hr/>			
$C^{24}N^2Ag^4O^{16}$	732	100.00	
<hr/>			
<i>Dried at 150°.</i>			Wöhler.
24 C	144	19.20	20.23
2 N	28	3.73	
2 H	2	0.27	0.19
4 Ag	432	57.60	56.77
18 O	144	19.20	
<hr/>			
$C^{24}N^2H^2O^{16} + 2HO$	750	100.00	

CAUTCHENE SERIES.

A. PRIMARY NUCLEUS. C^8H^6 .

Cautchene. C^8H^6 ?

BOUCHARDAT (1837). *J. Pharm.* 23, 457; also *Ann. Pharm.* 27, 30; also *J. pr. Chem.* 13, 114.

Formation and Preparation. — When cautchouc is subjected to dry distillation, and the receiver connected with two Woulfe's bottles cooled with freezing mixtures, cautchene condenses in these bottles together with butylene (C^4H^6). Either the butylene is allowed to evaporate rapidly from this mixture, so that the cold thereby produced may cause the remaining cautchene to solidify in a crystalline mass, which must then be quickly pressed between bibulous paper; or the mixture is distilled, first at +10°, till the greater part of the butylene has passed over, then at +18°; the second distillate cooled to -18°; and the crystals freed from adhering butylene by pressure between paper.

Properties. At -18° , white, opaque, crystalline mass, composed of needles; melts at -10° to a transparent oil of sp. gr. 0.65 at -2° ; boils at 14.5° .

			Bonchardat.
8 C	48 88.89 85.75
6 H	6 11.11 14.18
C^6H^4	54 100.00 99.93

[The calculation certainly differs considerably from Bonchardat's analysis; but he himself states that the analysis was very difficult in consequence of the volatility of the body; moreover there are palpable errors in his numerical data. The boiling point for C^6H^4 , calculated according to Gerhardt's law (vii. 57) is $+25^\circ$.]

Cautchene, mixed with oil of vitriol, evolves heat, and forms a black mixture, from which water throws down a brown resinous matter.

It is insoluble in water and alkalis, but dissolves very readily in *Alcohol* and *Ether*. (Bonchardat.)

B. SECONDARY NUCLEI.

a. Oxygen-nuclei.

a. Oxygen-nucleus. $C^6H^4O^2$.

Fumaric Acid. $C^6H^4O^2 = C^6H^4O^2, O^2$.

LASSAIGNE. *Ann. Chim. Phys.* 11, 93; also *N. Tr.* 4, 2, 231.

PFÄFF. *Schw.* 47, 476.

WINCKLER. *Repert.* 39, 48 and 368; 48, 39 and 363.

PELOUZE. *Ann. Chim. Phys.* 56, 72; also *Pogg.* 36, 53; also *Ann. Pharm.* 11, 263.

LIEBIG. *Ann. Pharm.* 11, 276.

DEMARÇAY. *Ann. Chim. Phys.* 56, 429; also *Ann. Pharm.* 12, 16; also *Pogg.* 36, 55.

SCHÖDLER. *Ann. Pharm.* 17, 148.

RIECKHER. *Ann. Pharm.* 49, 31.

DELFFS. *Pogg.* 80, 435; abstr. *Jahresber.* 1850, 371.

Lichenic Acid, Fumarsäure, Flechtensäure, Paramaleinsäure, Glauciumsäure, Acide fumarique, Ac. paramaleique.

Lassaigne, in 1819, showed that in the dry distillation of malic acid there is produced, besides maleic acid (VIII. 150), another acid, which was further investigated by Pelouze in 1834, under the name of paramaleic acid. Pfaff, in 1826, found lichenic acid in Iceland moss; and fumaric acid was obtained by Winckler in 1833, from fumitory. Demarçay, in 1834, showed that fumaric acid, and Schödlér, in 1836, that lichenic acid is identical with paramaleic acid.

Sources. In *Fumaria off.*, *Lichen islandicus*, *Glaucium luteum*, and *Corydalis bulbosa*.

Formation. By the dry distillation of malic acid, and by heating certain malates.

Preparation. 1. *From Fumitory.* The aqueous decoction of the fresh flowering herb, together with the roots, after straining, subsidence, and decantation, is evaporated, first over the open fire and then in the water-bath, to a thin syrup; and this syrup, while still hot, mixed with a small quantity of hydrochloric acid, and left for about a fortnight in a cool place, till the fumaric acid has separated in hard brown crystals. The mother-liquor is then diluted with water and poured off; the crystals washed with cold water, suspended in water, and slightly supersaturated with carbonate of potash; the filtrate slightly supersaturated with sulphuric acid, heated in the water-bath, and filtered from the resulting dark brown resinous precipitate; the still brownish crystals of fumaric acid which form on cooling dissolved in hot water; and the solution digested with animal charcoal and filtered: it then, on cooling, yields snow-white crystals, amounting to 0.156 p. c. of the fresh herb. (Winckler.)—Two modes of preparation, in which the fumarate of lime contained in the expressed juice, is decomposed with oxalic acid, are also given by Winckler. (*Repert.* 39, 368.)—This salt separates spontaneously from the *Extractum Fumarice*, after two years' standing, in crystalline grains, which may be obtained by diluting the extract with an equal quantity of cold water, then decanting and washing with cold water; when decomposed with aqueous oxalic acid, they yield a brownish acid, which may be freed from an admixed red-brown substance, by mixing it with quartz-sand and subliming, or by solution in ether and filtration. (Winckler, *Repert.* 39, 48.)—Trommsdorff (*N. Tr.* 25, 2, 152.) precipitates the recently expressed juice of fumitory—after separation of the scum which forms on boiling—with acetate of lead; decomposes the washed precipitate with sulphuretted hydrogen, and obtains, by evaporating and cooling the filtrate, brownish crystals which may be purified with animal charcoal.—A similar process is followed by Demarçay. ¶ Delffs washes the yellowish green precipitate thrown down by acetate of lead (after it has somewhat diminished in volume by standing); dries it in the air on bibulous paper; rubs it to powder; stirs it up with nitric acid gradually added (whereupon the mass swells up, but gives off only a small quantity of nitrous vapours); agitates the resulting mixture of nitrate of lead and free fumaric acid, after 24 hours, with a little water; filters; washes the residue with water; and extracts the fumaric acid with boiling alcohol of ordinary strength. The alcoholic solution is then evaporated; the residue dissolved in ammonia; the excess of ammonia expelled from the solution by heating; and a certain quantity of lead which remains in it, removed by sulphuretted hydrogen (the greater part of the colouring matter also separates with the sulphide of lead); the bifumarate of ammonia brought to the crystallizing point; the crystals, if much coloured, purified by pressure and recrystallization; the salt then dissolved in hot water; and the solution treated with nitric acid (which, if added in slight excess, generally effects the complete destruction of the colouring matter), to separate the fumaric acid, which then, after the liquid has cooled, crystallizes out completely, but only after a considerable time. By this process, Delffs obtained more than 5 drams of pure fumaric acid from 20 pounds of the herb. ¶.

From Iceland Moss.—64 pts. of the lichen are macerated for some time in water containing carbonate of potash; the filtrate precipitated with acetate of lead; the washed brownish precipitate decomposed with sulphuretted hydrogen; the filtrate evaporated; and the crystals of the acid, which still contain lime, purified. (Pfaff.)—The chopped lichen

is macerated for six days with water and milk of lime, the mixture being frequently stirred; the expressed turbid liquid evaporated to half its bulk; acidulated with acetic acid; then heated; mixed with basic acetate of lead, as long as reddish flocks containing brown colouring matter continue to separate; and filtered hot. The filtrate, on cooling, deposits white or brown-yellow needles of the lead-salt, which may be decomposed with sulphuretted hydrogen or sulphuric acid, and, on further evaporation, an additional quantity of the impure lead-salt. The impure acid is purified by boiling with dilute nitric acid, and cooling to the crystallizing point. (Schödler.)

3. *From Glaucium luteum.* — The expressed juice is boiled and precipitated by ammonia; the filtrate evaporated; mixed while still hot with a small quantity of nitric acid; then with nitrate of lead; and left to cool till the lead-salt separates, mostly in the crystalline form. (Probst, *Ann. Pharm.* 31, 248.)

4. *From Malic or from Maleic acid.* — Malic acid is heated for some time to a temperature a little above 130° , whereupon water passes over, together with maleic acid, and fumaric acid remains behind in the solid state; or, crystallized maleic acid is boiled in a long glass tube, so that the evolved water may continually flow back again, till the maleic is converted into fumaric acid. (Pélouze.)

Properties. The acid obtained from malic acid crystallizes from the aqueous solution, in broad, striated, colorless prisms, sometimes rhombic, sometimes hexagonal (Pelouze); — that obtained from fumitory, in scales united in stellate groups (Winckler); that from Iceland moss, in needles (Pfaff); in crystals aggregated in cauliflower-like tufts (Schödler). — The acid sublimes in long white needles. (Lassaigne, Winckler.) — Requires a high temperature to melt it; volatilizes somewhat above 200° , even before melting (giving off vapours which attack the eyes strongly — Winckler); and sublimes for the most part unaltered, but partly resolved into water and fumaric anhydride. — It is inodorous, tastes very acid, and reddens litmus strongly. (Winckler, Pelouze, and others.)

	Crystallized.			Pelouze.		Liebig.	Demargay.	Schödler.	
	a.	b.	c.	d.	e.				
8 C	48	41.38	41.92	42.64	41.63	41.03	41.85		
4 H	4	3.45	3.62	3.76	3.53	3.56	3.44		
8 O	64	55.17	54.46	53.60	54.84	55.41	54.71		
$C^8H^4O^2$	116	100.00	100.00	100.00	100.00	100.00	100.00		

a and *c* are paramaleic acid crystallized from water; *b*, obtained by sublimation; *d* is fumaric, and *e*, lichenic acid.

Pelouze, Reickher, and others, regard the acid as monobasic = $C^4H^2O^4$, like maleic acid; and therefore, in the hypothetical anhydrous state, as $C^4HO^2 = Fu$.

Decompositions. 1. When fumaric acid is heated, a small portion of it is resolved into fumaric anhydride ($C^8H^2O^4$), which volatilizes, and water. (Pelouze.) — 2. It may be set on fire by a flaming body, and then burns with a pale blue flame. (Winckler.) — 3. When triturated and heated with peroxide of lead, it first gives off water and then takes fire, without emitting any odour of formic acid. (Rieckher.) — 4. The colourless solution of the acid in oil of vitriol, turns brown when heated (Winckler), and gives off sulphurous acid. (Rieckher.) — The

aqueous solution of the acid is not altered by eight days boiling, or when heated in a sealed glass tube to 250°, not being in fact converted into malic acid. (R. Hagen, *Ann. Pharm.* 38, 276.)—The acid is not decomposed by boiling with nitric acid of sp. gr. 1.4, but remains unaltered when evaporated (Winckler), and separates out on cooling, with peculiar whiteness and brilliancy. (Demarçay, Schödler.)—It is not decomposed by boiling with water and peroxide of lead, or bichromate of potash, and does not precipitate platinum-black from bichloride of platinum. (Rieckher.)

Combinations. Fumaric acid dissolves in 390 pts. of water at 10°, and in a much smaller quantity of hot water (Winckler) in 210 pts. water at 12° (Lassaigue); in 216 pts. at 17° (Probst).

The *Fumarates* are either neutral = $C^6H^2M^2O^2, O^6$, or acid = $C^6H^3MO^2, O^6$. Some are crystalline, others pulverulent, and most of them have a mild taste. (Winckler.) None of them, excepting the ammonia, copper, and mercury salts, become carbonized till they are heated above 250°. (Winckler, Rieckher.) They are decomposed by phosphoric, sulphuric, hydrochloric, and nitric acid; but fumaric acid expels acetic acid from the acetates. Many fumarates dissolve in water, but none in strong alcohol. (Winckler.)

Acid Fumarate of Ammonia.—The acid neutralized with aqueous caustic ammonia, or carbonate of ammonia, gives off part of the ammonia by evaporation in the air, or in a non-exhausted receiver over lime and oil of vitriol, or in vacuo over hydrate of potash, and leaves the acid salt in oblique rhombic prisms, truncated on the acute lateral edges, readily soluble in water and alcohol. (Rieckher.)—Transparent, colourless, shining, right four-sided prisms, or needles united in stars; they have a mild taste, redden litmus, do not sublime without decomposition, dissolve readily in cold water, but are insoluble in alcohol. (Winckler.)—¶ Prisms belonging to the oblique prismatic (monoclinometric) system, with angles of about 70° and 110°, and terminal faces inclined to the acute lateral edges at angles of 60° and 120°; cleavage distinct parallel to these terminal faces; in many crystals the terminal faces are replaced by two faces resting on the obtuse lateral edges, and meeting in the longer diagonal. (Delfs.) Pasteur (*N. Ann. Chim. Phys.* 31, 91) also obtained this salt in prisms belonging to the monoclinometric system, and with angles of 110°, both with fumaric acid prepared from fumitory, and with acid obtained from malic acid. ¶

	<i>Air-dried Crystals.</i>		Rieckher.
NH ³	17	12.78
C ⁶ H ⁴ (O).....	116	87.22
<hr/>			
C ⁶ H ² (NH ⁴)O ⁸	133	100.00

Rieckher supposes the salt to contain 1HO less.

Fumarate of Potash.—Obtained by neutralizing the acid with aqueous carbonate of potash and evaporating. Large, transparent, colourless rhombic tables and four-sided prisms, often aggregated in stars, permanent in the air, and having a mild, scarcely saline taste. (Winckler.) Laminæ united in radiating groups. (Pelouze.) The salt effloresces during the evaporation of its solution, but deposits shining striated prisms

at the bottom of the vessel; sometimes the solution yields on evaporation, a liquid which in 12 to 24 hours, is converted into a crystalline powder. (Rieckher.) The crystals become opaque at a gentle heat (Winckler), and give off 17.06 p. c. (4 At.) water at 100° (Rieckher); at a higher temperature, they melt imperfectly, blacken, swell up to ten times their original bulk, and leave a residue of charcoal and carbonate of potash. (Winckler.) The salt dissolves readily in water (very readily, according to Pelouze), but not in alcohol (Winckler), slightly in weak alcohol. (Rieckher.) From a concentrated aqueous solution, acetic acid throws down the acid potash-salt; alcohol, the neutral salt containing 16.61 p. c. (therefore also 4 At.) water of crystallization. (Rieckher.)

	Crystallized.		Rieckher.	
2 KO	94.4	41.33 41.42
$C^8H^2O^8$	98.0	42.91
4 HO	36.0	15.76 17.06
<hr/>				
$C^8H^8K^2O^8 + 4Aq$	228.4	100.00	

b. Acid. — From the cold-saturated aqueous solution of the salt *a*, water saturated with fumaric acid precipitates the salt *b* in needles: 1 pt. of fumaric acid is saturated warm with aqueous carbonate of potash, 1 pt. of fumaric added, and the solution evaporated and cooled. (Rieckher.) Shining, tufted needles and oblique four-sided prisms, permanent in the air, and having a pleasant, strongly acid taste. (Winckler.) They give off 2 At. water at 200° (Rieckher), and decompose at a higher temperature like the salt *a*. (Winckler.) They dissolve much less abundantly in cold water than the salt *a*, plentifully in boiling water, are nearly insoluble in cold alcohol of 81 per cent, but dissolve sparingly therein at a boiling heat, and crystallize on cooling. (Winckler.)

	Dried at 230° .		Rieckher.	
KO	47.2	30.61 30.82
$C^8H^2O^7$	107.0	69.39
<hr/>				
$C^8H^2KO^7$	154.2	100.00	

The existence of a *fumarate of potash and ammonia* is doubtful. (Rieckher.)

Neutral Fumarate of Soda. — $C^8H^2Na^2O^8$. — The salt precipitated by alcohol from the aqueous solution is a crystalline powder containing 10.03 p. c. (2 At.) water; when the solution is evaporated, the salt crystallizes in needles and prisms containing 25.12 p. c. (6 At.) water. The water escapes for the most part at 100° , completely at 200° , and the residue contains 38.77 p. c. soda. (Rieckher.) Crystalline mass consisting of needles, permanent in the air, having a faint silky lustre, and a warm saline taste; it behaves in the fire like the potash-salt, dissolves readily in cold water but is insoluble in alcohol. (Winckler.)

It does not appear possible to prepare an *Acid fumarate of soda* or a *fumarate of soda and potash*. (Rieckher.)

Fumarate of Baryta. — The free acid does not precipitate baryta-water (Lassaigne), or chloride of barium. (Rieckher.) Very dilute solutions of fumarate of ammonia and chloride of barium mixed together, deposit, after a while, colourless, nearly transparent rhombic prisms variously modified, having a vitreous lustre, and a very slight taste with somewhat acid after-taste; they effloresce readily in the air, giving off 15 per cent. of water, and at 100° the loss amounts to 20.81 per cent.

The salt takes fire when held over a flame, and leaves carbonate of baryta mixed with charcoal. It dissolves very sparingly in water and is insoluble in alcohol. (Winkler.)—A moderately concentrated aqueous mixture of fumarate and acetate of baryta does not yield any deposit, though left to itself for several hours; but on scratching the sides of the vessel with a glass rod, a crystalline powder is immediately deposited on the rubbed parts, and gradually increases. On mixing the boiling saturated solutions, this powder is deposited even without friction. The salt loses only 0·6 p. c. water at 100°, and 1·2 p. c. in all at 200°; it is therefore anhydrous. It dissolves very slowly, not only in water and alcohol, but likewise in aqueous fumaric and other dilute acids; consequently no acid salt appears to be formed. (Rieckher.)—Schödlér obtained with lichenic acid, four-sided prisms containing 56·91 p. c. baryta.

	Dried		Winckler.	Rieckher.
			At 100°.	At 200°.
2 BaO	153·2	60·59	60·34	60·45
C ⁶ H ² O ⁸	98·0	39·01		
<hr/>				
C ⁶ H ² Ba ² O ⁸	251·2	100·00		

Acid fumarate of potash does not form a double salt with carbonate of baryta.

Fumarate of Strontia.—Aqueous fumaric acid does not precipitate strontia-water. (Pelouze.) From acetate of strontia it throws down, after some time only, if the solution be very dilute, a white crystalline powder which gives off 19·82 p. c. water at 100°, and 20·66 p. c. (6 At.) in all, at 200°, and is as sparingly soluble in water as the baryta-salt. (Rieckher.)

	Dried at 230°.		Rieckher.
2 SrO	104	51·49	51·22
C ⁶ H ² O ⁸	98	48·51	
<hr/>			
C ⁶ H ² Sr ² O ⁸	202	100·00	

Fumarate of Lime.—Occurs in fumitory.—Fumaric acid does not precipitate lime-water (Lassaigne), or chloride of calcium. (Rieckher.) From a hot-filtered solution of carbonate of lime in fumaric acid, or from a mixture of fumarate of potash with acetate of lime, colourless, shining scales separate after a while, which are tasteless, permanent in the air, and scarcely soluble in water or alcohol. (Winckler.)—An aqueous mixture of fumaric acid and acetate of lime deposits highly lustrous crystals, which are sparingly soluble in water, insoluble in alcohol, give off the greater part of their water at 100°, and the whole, amounting to 25·66 p. c. (6 At.) at 200°. (Rieckher.)

	Dried at 230°.		Rieckher.	Winckler.
2 CaO	56	36·36	36·22	38·82
C ⁶ H ² O ⁸	98	63·64		
<hr/>				
C ⁶ H ² Ca ² O ⁸	154	100·00		

Fumarate of Magnesia.—Fumaric acid mixed with aqueous acetate of magnesia and evaporated to a syrup, yields no crystals; but if the greater part of the acetic acid be expelled by thorough drying in the water bath, and the residue exhausted with alcohol, fumarate of magnesia remains undissolved in the form of a white powder, which gives off 34·48 p. c. (8 At.) water at 200°, but only half that quantity at 100°. (Rieckher.)

		Dried at 200°.		Rieckher.
2 MgO	40	29.98	29.82
$C^8H^2O^6$	98	71.02	
<hr/>				
$C^8H^2Mg^2O^8$	138	100.00	
		Dried at 100°.		Rieckher.
2MgO	40	22.99	23.19
CH O ¹⁰	134	77.01	
<hr/>				
$C^8H^2Mg^2O^8 + 4Aq.$	174	100.00	

Alumina and *Chromic Oxide* do not appear to combine with fumaric acid (Rieckher); the alkaline fumarates yield no precipitate with alum. (H. Rose.)

Fumarate of Manganese. — Fumarate of soda added to sulphate of manganese throws down, after a while, a small quantity of a white powder. (Winckler.) The acid heated with aqueous acetate of manganese, yields a yellowish white powder, which gives off 24.7 p. c. (6 At.) water at 200°, and dissolves sparingly in water, not at all in alcohol, and with decomposition in acids. (Rieckher.)

		Dried at 200°.		Rieckher.
2 MnO	72	42.35	41.09
$C^8H^2O^6$	98	57.65	
<hr/>				
$C^8H^2Mn^2O^8$	170	100.00	

Antimonic oxide does not dissolve in a warm aqueous solution of acid fumarate of potash. (Rieckher.)

Fumarate of Zinc. — Obtained by saturating the boiling aqueous solution of the acid with oxide or carbonate of zinc, and evaporating the filtrate to the crystallizing point. Short, thick, oblique four-sided prisms, colourless, with a vitreous lustre; having an astringent and afterwards sweetish metallic taste; permanent in the air, but efflorescing when heated; taking fire and blackening at higher temperatures, and burning away, with residue of zinc-oxide; readily soluble in water; insoluble in alcohol. (Winckler.) — A solution of acetate of zinc in warm aqueous fumaric acid, left to evaporate in a warm place, yields Winckler's air-permanent, four-sided prisms, which give off 13.24 p. c. (6 At.) water at 120°, dissolve in water and in weak alcohol, and are precipitated by ammonia; but if the solution be left to evaporate in a cooler place, larger efflorescent crystals are obtained, containing 29.06 (8 At.) water. (Rieckher.)

		Dried at 120°.		Reickher.
2 ZnO	80	44.94	44.47
$C^8H^2O^6$	98	55.06	55.53
<hr/>				
$C^8H^2Zn^2O^8$	178	100.00	100.00

No fumarate of zinc and potassium appears to exist. (Rieckher.)

Fumarate of Lead. — *a. Sexbasic.* — 1. Obtained by precipitating basic acetate of lead with fumaric acid [with neutral fumarate of potash?]. — 2. By treating the salt *c* with ammonia. The salt does not part completely with its hygroscopic water till it is heated to 200°, and bears a temperature of 230° without decomposition. (Rieckher.)

b. Tribasic. — Obtained by precipitating basic acetate of lead with acid fumarate of potash. The white, quickly sinking precipitate, gives

off all its water at 130°, and bears a temperature of 230° without decomposition. (Rieckher.)

<i>Salt a, dried at 230°.</i>			Rieckher.
6 PbO.....	672 87·27 86·7
C ⁸ H ² O ⁶	98 12·73	
4PbO, C ⁸ H ² Pb ² O ⁸			
	770 100·00	
<i>Salt b, dried at 230°.</i>			Rieckher.
3 PbO.....	336 77·42 77·2
C ⁸ H ² O ⁶	98 22·58	
PbO, C ⁸ H ² Pb ² O ⁸			
	434 100·00	

c. Neutral. — Malate of lead is converted at 220° into fumarate (Rieckher.) The dilute potash-salt mixed with acetate of lead acidulated with acetic acid, throws down a white crystalline powder, which dissolves on boiling, and crystallizes after a while on cooling, in white shining tufts of needles. (Winckler.) The free acid behaves in a similar manner with neutral acetate of lead. (Lassaigne, Pelouze). The dried salt does not decompose at 200°. (Rieckher.) When heated over a flame, it takes fire and burns away with a glimmering light, leaving a mixture of lead and a small quantity of protoxide. (Winckler.) The needles, after drying in the air, contain 16·28 p. c. (6 At.) water (Pelouze); 9·31 p. c. (4 At.) according to Rieckher. The salt dissolves readily in nitric acid, with separation of fumaric acid; it is nearly insoluble in cold water and in strong acetic acid, but dissolves with tolerable facility in boiling water, separating out again unchanged on cooling. (Winckler.) It is insoluble in alcohol. (Rieckher.)

<i>Dried between 140° and 200°.</i>			Pelouze.	Rieckher.	Winckler.
2 PbO	224 69·57 69 69·41 72·7
C ⁸ H ² O ⁶	98 30·43			
C ⁸ H ² Pb ² O ⁸					
	322 100·00			

The ammonia-salt does not precipitate *ferrous sulphate*. (Winckler.)

Ferric Fumarate. — Recently precipitated ferric hydrate does not dissolve in aqueous fumaric acid, even with the aid of heat. (Rieckher) The aqueous acid forms a brownish yellow precipitate with ferric sulphate. (Lassaigne.) Fumarate of ammonia or soda forms with sesquichloride of iron a pale brown-red precipitate insoluble in excess of the ammonia-salt (whereby it is distinguished from the precipitate formed by succinic acid.) (Winckler.) The precipitate is chamois-coloured like ferric succinate. (Pelouze.) Mere traces of ferric oxide remain unprecipitated; the precipitate is cinnamon-coloured, very bulky, and difficult to wash; soluble in acids but not in ammonia; and whether precipitated from cold or from hot solutions, contains after drying at 200°, 44·08 p. c. ferric oxide, whence its formula is Fe²O³, C⁸H²O⁶. (Rieckher.)

Fumarate of Cobalt. — The red mixture of fumarate and acetate of cobalt does not yield crystals by evaporation, but when mixed with alcohol after concentration, deposits a rose-coloured pulverulent precipitate, which, after washing with alcohol and drying in the air, gives off 15·79 p. c. (nearly 4 At.) water at 100°, and 23·84 p. c. (6 At.) in all at

200°; it dissolves easily in water or ammonia, sparingly in weak alcohol. (Rieckher.)

		<i>Dried at 200°.</i>			Rieckher.
2 CoO.....	75	43.35	43.17
$C^8H^2O^6$	98	56.65	
<hr/>					
$C^8H^2Co^2O^8$	173	100.00	

Fumarate of Nickel. — Obtained like the cobalt-salt. Pale green powder, which, after drying in the air, gives off 26.49 p. c. (rather more than 6 At.) water, 30.61 p. c. (8 At.) in all at 200°, and at 230°, suffers a total loss of 36.22 p. c. with colouring and partial decomposition. It dissolves in water, weak alcohol, and ammonia. (Rieckher.)

		<i>Dried at 200°.</i>			Rieckher.
2 NiO.....	75	43.35	42.92
$C^8H^2O^6$	98	56.65	
<hr/>					
$C^8H^2Ni^2O^8$	173	100.00	

Cupric Fumarate. — Fumarate of potash added to cupric sulphate throws down a pale blue crystalline powder soluble in hydrochloric or nitric acid, insoluble in water and alcohol. (Winckler.) Aqueous cupric acetate heated with fumaric acid till the latter dissolves, deposits a blue-green crystalline powder. This salt, after drying in the air, gives off 17.67 p. c. (rather more than 4 At.) water at 100°, and 23.61 (6 At.) in all at 200°; at 230°, it suffers a total loss of 48 or 49 per cent., assuming at the same time a brown colour and being partially decomposed. It dissolves readily in nitric acid with separation of the acid; slowly in water and alcohol; and is insoluble in boiling fumaric acid. (Rieckher.)

		<i>Dried at 200°.</i>			Rieckher.
2 CuO ²	80	44.94	44.49
$C^8H^2O^6$	98	55.06	
<hr/>					
$C^8H^2Cu^2O^8$	178	100.00	

		<i>Dried at 100°.</i>			Rieckher.
2 CuO.....	80	40.82	40.42
$C^8H^4O^8$	116	59.18	
<hr/>					
$C^8H^2Cu^2O^8 + 2 Aq$	196	100.00	

Cuprofumarate of Ammonia. — The dark blue solution of cupric fumarate in ammonia yields by evaporation, small, dark blue, shining octohedrons. (Winckler.) When a layer of alcohol is poured upon the above solution, the salt separates in delicate blue, silky needles. (Rieckher.)

Mercurous Fumarate. — An aqueous solution of mercurous nitrate forms with fumaric acid or alkaline fumarates, a white crystalline precipitate which suffers no perceptible loss and no change of colour at 100°. (Rieckher.)

		<i>Air-dried.</i>			Rieckher.
2 Hg ² O.....	416	80.93	81.13
$C^8H^2O^6$	98	19.07	
<hr/>					
$C^8H^2Hg^2O^8$	514	100.00	

Mercuric Fumarate. — The ammonia-salt added to a solution of corrosive sublimate, throws down a white powder (Winckler); it does not form any precipitate. (H. Rose, *Pogg.* 7, 87.) The potash-salt throws down, from the solution, a mixture of yellow needles and a white crystalline salt. Free fumaric acid gives no precipitate, either with corrosive sublimate or with mercuric nitrate; it does not dissolve mercuric oxide even with the aid of heat. (Rieckher.)

Fumarate of Silver. — Free fumaric acid added to nitrate of silver throws down a fine white powder. (Lassaigne.) The acid, even when dissolved in 200,000 pts. of water, still precipitates silver-solution; and alkaline fumarates precipitate it even at higher degrees of dilution; so completely indeed that the filtrate shows no turbidity on the addition of hydrochloric acid. (Pelouze.) The powder, after being washed and dried in the dark, is white, tolerably heavy, nearly tasteless, and adheres to the fingers. (Winckler.) It turns brown when heated, afterwards decomposes with slight detonation and sparkling, and leaves a bulky, velvet-black mass, which leaves metallic silver when burnt. (Winckler.) When heated, it deflagrates like gunpowder. (Demarcay, Rieckher.) It dissolves readily in nitric acid, with liberation of fumaric acid. (Winckler.) It is insoluble in water (Winckler, Pelouze), and is not decomposed by continued boiling therewith. (Rieckher.) It dissolves readily in ammonia, and when the ammonia evaporates, yields delicate shining prisms, which give off potash when treated with ammonia. (Winckler.)

	Dried at 100°.		Demarcay.	Liebig.	Schödler.	Winckler.
2 AgO	232	70.30	69.10	69.89	70	72.81
8 C.....	48	14.55	14.64			
2 H	2	0.60	0.69			
6 O	48	14.55	15.57			
<hr/>						
C ⁸ H ² Ag ² O ³	330	100.00	100.00			

Fumaric acid dissolves readily in 82 per cent. *Alcohol* (Winckler); it dissolves in 21 pts. of cold alcohol of 76 per cent. (Probst.) It dissolves readily in *Ether*. (Winckler & others.)

Conjugated Compound of Fumaric Acid.

Fumaric Ether. C¹⁶H¹²O⁸ = 2C⁸H⁶O, C⁸H²O⁴.

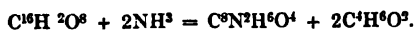
ROB. HAGEN (1841). *Ann Pharm.* 38, 274.

Formation and Preparation. A solution of fumaric or of malic acid in absolute alcohol is saturated with hydrochloric acid gas; the mixture distilled; and the fumaric ether, which passes over after the hydrochloric ether, and when the heat has risen considerably, collected in a separate receiver and dried over chloride of calcium.

Properties. Oily liquid, heavier than water and having a pleasant fruity odour.

				Hagen.
16 C.....	96	55·81 55·80
12 H	12	6·93 6·97
8 O	64	37·21 37·23
$C^{16}H^{12}O^8$				172
		100·00 100·00

Decompositions. 1. The ether heated with potash-ley, is resolved into fumarate of potash and alcohol. — 2. Treated with aqueous ammonia it deposits after some time, crystals of fumaramide:



It is slightly soluble in water. (Hagen.)

B. Oxygen-nucleus. $C^6H^4O^4$.

Fumaric Anhydride. $C^6H^2O^6 = C^6H^2O^4, O^2$.

PELOUZE. (1834.) *Ann. Chim. Phys.* 56, 72; also *Ann. Pharm.* 11, 263.

Anhydrous Fumaric Acid; Anhydrous Maleic Acid.

Produced, with formation of water, when maleic or fumaric acid is heated.

Crystallized maleic acid is rapidly distilled, with change of receiver, till nothing but crystallized fumaric acid remains behind; and the last distillate (the first being watery) is repeatedly rectified in the same manner, the first watery portion of the distillate being each time set aside, till the last distillate passes over completely, without first yielding water, and without leaving a residue of fumaric acid.

The anhydride melts at 57° and boils at 176°.

				Pélouze.
8 C	48	48·98 48·73
2 H	2	2·04 2·13
6 O	48	48·98 49·14
$C^8H^2O^6$				98
		100·00 100·00

The anhydride slightly heated above its boiling point, decomposes, turning brown and giving off gas. (Pelouze).

Pelouze regards this body as the so-called anhydrous maleic acid = C^4HO^3 . But as fumaric acid is formed in its preparation, it may just as well be anhydrous fumaric acid, i. e., fumaric anhydride, a view which is supported by the fact that no other monobasic acid yields an anhydrous acid or anhydride.* The question might be decided by ascertaining whether this body when treated with aqueous alkali yields a maleate or a fumarate. (Gm.)

* This was written before Gerhardt's discovery of the anhydrous monobasic acids. [W.]

b. *Amidogen-nuclei.*a. *Amidogen-nucleus.* $C^{\circ}AdH^{\circ}$.**Sulphosinapic Acid.** $C^{\circ}NH^{\circ}S^{\circ}=C^{\circ}AdH^{\circ},S^{\circ}$.

WILL. (1844.) *Ann. Pharm.* 52, 30. — Further: *Ann. Pharm.* 92, 59.

Formation. By decomposing oil of mustard with alcoholic potash.

Preparation. Oil of mustard is slowly dropt into a concentrated solution of hydrate of potash in absolute alcohol, care being taken that the liquid does not get too hot; the brown-red liquid decanted, after several hours, from the crystallized carbonate of potash; diluted with water; separated by a wet filter from the oil which has sunk to the bottom, and the pale yellow filtrate evaporated nearly to a syrup: this when set aside, deposits shining crystals of the potassium-salt. — If the evaporation be carried too far, a thick brown-red oil rises to the surface of the liquid; and when this oil is dissolved in water, a yellow powder separates, which coheres in lumps. The liquid decanted from the carbonate of potash may likewise be evaporated in vacuo without addition of water, till, in the course of a few days, it solidifies to a radiated mass, which may be freed from the oil by ether, then dissolved in absolute alcohol, and filtered from the carbonate of potash. The alcoholic filtrate contains the potassium-salt, together with free potash. — The potassium-salt cannot be obtained in a state of perfect purity.

When the solution of the potassium-salt diluted with a moderate quantity of water is neutralized with acetic acid, a yellowish turbidity is produced, arising from separated sulphur. The liquid filtered therefrom, which is inodorous, even when heated, forms with acetate of lead a lemon-yellow precipitate, which soon becomes yellowish-red and afterwards black, the odour of oil of mustard being then evolved with continually greater intensity. The green precipitate obtained with copper-salts likewise turns brown and afterwards black, and still more quickly, the precipitate obtained with nitrate of silver, the odour of oil of mustard being perceptible in each case. These three precipitates decompose even when they are immediately thrown on a filter and washed with cold water.

To obtain the *lead salt* undecomposed, the liquid filtered from the oil, after dilution with water (*vid. sup.*) is diluted with 200 times its bulk of water, neutralized with acetic acid, which at this degree of dilution produces no turbidity, and precipitated by acetate of lead.

The finely divided precipitate aggregates on agitation in lemon-yellow curdy flakes, which, after the greater portion of the liquid has been decanted, must be quickly thrown on the filter, washed with cold water (till the wash-water is no longer acid), pressed between a large quantity of paper, and dried as quickly as possible in vacuo over oil of vitriol. During these processes, however, a certain amount of decomposition always takes place, from formation of oil of mustard and sulphide of lead, the latter causing a yellowish grey or even black colouring. At 100° , this decomposition takes place completely, colourless drops of oil of mustard distilling over, while sulphide of lead, mixed with sulphur,

remains, without any evolution of water or carbonic acid. [But sulphuretted hydrogen might be evolved, according to the equation: $C^6NH^6PbS^4 = C^6NH^5S^2 + PbS + HS$; as no means were adopted to prevent access of air, this sulphuretted hydrogen may have been partially decomposed, inasmuch as Will found the sulphide of lead mixed with sulphur.]—With sulphuric acid, the lead-salt gives off abundance of sulphuretted hydrogen, without the slightest odour of oil of mustard. — The potassium-salt, when heated, likewise yields oil of mustard and a brown liver, and with sulphuric acid, a large quantity of sulphuretted hydrogen, but no sulphur.

				Will.		
8 C	48	20·34	19·72
N	14	5·93	5·01
6 H	6	2·54	2·66
Pb	104	44·07	45·20
4 S	64	27·12	26·73
<hr/>						
C ⁶ NH ⁶ PbS ⁴	236	100·00	99·32

¶. Will regards sulphosinapic acid as a compound of sulphocyanide of allyl (CH⁵), with sulphuretted hydrogen: $C^6NH^7S^4 = C^6H^5, C^2NS^2 + 2HS = \begin{matrix} C^2N \\ C^6H^5 \end{matrix} \left\{ \begin{matrix} S^2 + H \\ S^2 + H \end{matrix} \right\} S^2$. Gerhardt regards it as sulphocarbamic acid in which 1 At. H is replaced by allyl.

Sulphocarbamic acid.
NH²(CS)². S }
H . S }

Allylsulphocarbamic acid.
NH(C⁶H⁵) (CS)². S }
H . S }

The sulphosinapates may also be readily obtained by mixing oil of mustard with the alcoholic solutions of the corresponding hydrosulphates. In this manner the whole of the oil of mustard may be converted into sulphosinapic acid.

Sulphosinapate of Ammonium. — When oil of mustard is dropt into a colourless, saturated solution of hydrosulphate of ammonium, NH⁴S, H the odour of the latter immediately disappears, the liquid becoming strongly heated and solidifying in a few minutes to a magma of colourless laminæ of the sulphosinapate.

				Will.				
8 C	48	32·00	31·70	31·36
10 H	10	6·66	6·90	6·77
2 N	28	18·67	17·40	
4 S	64	42·67	43·03	43·30
<hr/>								
C ⁶ NH ⁶ (NH ⁴)S ⁴	150	100·00	99·03	

This salt has but little stability, decomposing by keeping.

Sulphosinapate of Potassium. — An alcoholic or even an aqueous solution of hydrosulphate of potassium, to which mustard-oil is added as long as the odour of the latter is destroyed, yields by slow evaporation in vacuo — provided the quantity of material be not too small — large rhombic tables often an inch in diameter; by quicker evaporation, needle-shaped crystals are formed. These crystals are transparent and colourless so long as they remain in the liquid; but when exposed to the air, they become opaque and yellow, losing their form and becoming partially insoluble in water, which then leaves a viscid sulphur-coloured residue. — The aqueous solution of the recently prepared salt may be heated without giving off the odour of mustard-oil; but on mixing the heated solution with nitrate of silver, sulphide of silver is precipitated,

SULPHOSINAPIC ACID.

and the odour of mustard-oil becomes immediately perceptible; the dried compound likewise gives off mustard-oil when heated.

<i>Crystallized.</i>				Will.
8 C	48.0	28.04		
6 H	6.0	3.50		
N	14.0	8.18		
4 S	64.0	37.38	38.09	
K	39.2	22.90	22.50	
$C^8NH^6KS^4$				171.2 100.00

Sulphosinapate of Sodium. — Obtained by mixing a warm alcoholic solution of hydrosulphate of sodium with mustard-oil as long as the odour of the latter is destroyed. Separates in nacreous laminæ, which are unctuous to the touch, and when heated, first melt, and then give off abundance of mustard-oil. The salt contains 6 At. water of crystallization. It cannot be kept without decomposing.

<i>Crystallized.</i>				Will.
8 C	48.0	22.96	23.70	
12 H	12.0	5.74	5.93	
N	14.0	6.69		
4 S	64.0	30.60		
6 O	48.0	22.96		
Na	23.1	11.05	11.20	
$C^8NH^6NaS^4 + 6Aq.$				209.1 100.00

Sulphosinapate of Barium. — 1. Obtained by heating oil of mustard with a solution of sulphide of barium supersaturated with sulphuretted hydrogen and mixed with a little alcohol — 2. By diffusing hydrate of baryta and oil of mustard in water, adding alcohol, and passing sulphuretted hydrogen through the liquid. — 3. It is likewise deposited from the mother-liquor of the alcoholic solution of the compound of mustard-oil with sulphide of barium (p. 49). — Forms crystalline laminæ like the soda-salt, and very easily soluble.

<i>Crystallized.</i>				Will.	
				a.	b.
8 C	48.0	20.20	19.90		
10 H	10.0	4.23	4.60		
N	14.0	5.95			
4 S	64.0	27.05	26.50		
4 O	32.0	13.57			
Ba	68.6	29.00	30.44	30.4	
$C^8NH^6BaS^4 + 4Aq.$				236.6	100.00

a, Prepared by method (3); b, by method (1).

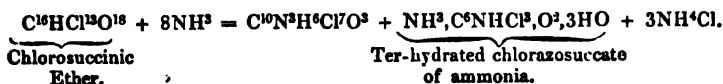
Sulphosinapate of Calcium. — When milk of lime is mixed with mustard-oil, a little alcohol added to dissolve the latter, and sulphuretted hydrogen in excess passed through the liquid, the odour of the mustard-oil disappears altogether, and a clear solution is obtained; which, after evaporation in the water-bath, leaves the calcium-compound in the form of a slightly yellow, transparent jelly. When completely dried, it is decomposed, with abundant evolution of mustard-oil. (Will.) ¶.

β . *Amidogen-nucleus.* C^6AdHCl^4 .**Chlorazosuccic Acid.** $C^6NH^2Cl^4O^4 = C^6AdHCl^4, O^4$.

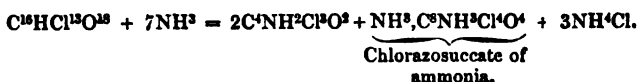
MALAGUTI (1846.) *N. Ann. Chim. Phys.* 16, 72; abstr. *J. pr. Chem.* 37, 435.

GERHARDT. *N. J. Pharm.* 14, 235 and 291.

Formation. By the action of dry ammoniacal gas on perchlorosuccinic ether. The products of the reaction are chlorocarbethamide, chlorazosuccate of ammonia, and sal-ammoniac. For this decomposition, Malaguti, who regards chlorocarbethamide (ix, 228) as $C^{10}N^3H^4Cl^7O^3$, gives the following equation:



If, on the other hand, we represent chlorazosuccic acid by Gerhardt's formula, $C^6NH^2Cl^4O^4$, and regard chlorocarbethamide, according to Gerhardt's most recent experiments, as chloracetamide = $C^4NH^2Cl^2O^2$, the equation will be:



Preparation. Ammoniacal gas is passed over pulverized perchlorosuccinic ether contained in a tubulated retort, as long as the gas is absorbed and heat evolved; the mass then pulverized; ammoniacal gas again passed over it; the operation repeated as long as any absorption takes place; the mass treated with pure ether; the solution of chlorazosuccate of ammonia and chlorocarbethamide (chloracetamide) filtered from sal-ammoniac and a trace of paracyanogen; the liquid evaporated; the residue treated with a small quantity of water; the liquid again filtered; the chlorocarbethamide (chloracetamide) remaining on the filter repeatedly washed with a small quantity of water, till the water which runs away is no longer bitter; and the brown filtrate mixed with hydrochloric acid, whereby the chlorazosuccic acid is precipitated in the form of a brown oil which soon solidifies in a crystalline mass. The brown acid is freed from the brown matter (paracyanogen?) by repeated solution in ammonia and precipitation by hydrochloric acid, after which it crystallizes in a state of purity by spontaneous evaporation from its alcoholic solution. (Malaguti.) Gerhardt precipitates the acid from the solution of its ammoniacal salt by nitric acid, and washes it with cold water.

Properties. Four-sided prisms acuminated with pyramids. Melts

under water at 83° to 85°, and *per se* at 200°, but begins to sublime at 125°, and to show colour at 150°. Tastes extremely bitter.

Calculation, according to Gerhardt.			
8 C	48·0	20·12
N	14·0	5·86
3 H	3·0	1·26
4 Cl	141·6	59·35
4 O	32·0	13·41
<hr/>			
C ⁸ NH ³ Cl ⁴ O ⁴	238·6	100·00

Calculation, according to Malaguti.		Malaguti.	
6 C	36·0	20·78
N	14·0	7·98
H	1·0	0·77
3 Cl	106·2	61·03
2 O	16·0	9·63
<hr/>			
C ⁶ NHCl ³ O ³	173·2	100·00

[Malaguti's formula is improbable on account of the uneven number of the atoms and the mode of formation of the acid; Gerhardt's requires much less N and much more H and O than are given by experiment,—a result which Gerhardt attributes to a partial decomposition by drying before the analysis. A repetition of the analysis is desirable.]

The acid is insoluble, or nearly so, in *water*.

It effervesces with carbonates.

Its solution in aqueous *Ammonia* evaporated in *vacuo* yields the ammonia-salt, half in crystals, half as a syrup. This salt, when heated to 100°, gives off carbonic acid (and as Malaguti supposes, but has not proved, also carbonic oxide), and is converted into a mixture of chlorosuccilamide (ix, 272) and sal-ammoniac, which may be separated by ether. (Malaguti.) Equation according to Malaguti:



But, according to Gerhardt's more probable assumption, chlorosuccilamide = C⁶NH⁴Cl³O³, *i. e.*, the acetamide of the propylene-series, and hence the equation is:



The concentrated solution of the ammonia-salt forms with *lime-salts*, a white precipitate, consisting of fine needles; with *copper-salts*, a lilac; and with *mercury* and *silver-salts*, a white amorphous precipitate. (Malaguti). It does not precipitate chloride of barium, sulphate of magnesia, sulphate of zinc, or sulphate of manganese. (Malaguti.)

The *silver* precipitate, which is at first amorphous, becomes crystalline in a few seconds. Washed with cold water and dried at 100°, it leaves, when ignited, 40·23 p. c. chloride of silver, consequently contains 30·3 p. c. silver. (Malaguti.) The formula C⁶NH²AgCl⁴O⁴ requires 31·25 p. c. silver, but Malaguti's formula C⁶NAgCl³O³, 37·9 p. c. (Gerhardt.)

The acid dissolves very readily in *alcohol* and *ether*. (Malaguti.)

γ. *Amidogen-nucleus.* $C^8Ad^2H^2O^2$.**Fumaramide.** $C^8N^2H^6O^4 = C^8Ad^2H^2O^2, O^2$.ROB. HAGEN. (1841.) *Ann. Pharm.* 38, 275.

Fumaric ether, mixed with aqueous ammonia, and set aside for some time in a cold place, deposits white scales of fumaramide.

				Hagen.	
8 C.....	48	42·11	42·37
2 N.....	28	24·56	24·53
6 H.....	6	5 26	5·33
4 O.....	32	28·07	27·77
<hr/>					
$C^8N^2H^6O^4$	114	100·00	100·00

Fumaramide yields by dry distillation, ammonia, a crystalline sublimate, and a carbonaceous residue. Heated with aqueous alkalis, it gives off ammonia, and when heated for some time with water, it is converted into fumarate of ammonia :



It is insoluble in cold water, but dissolves in boiling water and separates out unchanged on cooling. It is insoluble in alcohol. (Hagen.)

¶ *Fumaramide with Mercuric Oxide.* — Red oxide of mercury boiled in water with fumaramide is rapidly decolorized, and yields a white pulverulent compound, which must be carefully washed with boiling water and dried at 100°. It is decomposed by hydrochloric acid and sulphuretted hydrogen. (Dessaignes, *N. Ann. Chim. Phys.* 34, 143; *Ann. Pharm.* 82, 233.)

Dried at 100°.				Dessaignes.	
2HgO	216	65·45	64·58
$C^8N^2H^6O^4$	114	34·55	64·99
<hr/>					
$C^8N^2H^6O^4, 2HgO$	230	100·00		

¶ **Fumarimide.** $C^8NH^2O^4$;

DESSAIGNES. *Compt. rend.* 30, 324; *N. J. Pharm.* 17, 349; *Jahresber.* 1850, 414.

J. WOLFF. *Ann. Pharm.* 75, 293.

Formed by the action of heat on bimalate of ammonia. When this salt is heated in an oil-bath to 160°—200°, it melts, swells up, gives off water containing a very small quantity of ammonia, and leaves a reddish, transparent, somewhat resinous mass, very sparingly soluble in water even at a boiling heat. This residue, after being washed with hot water, forms an amorphous powder, having a pale brick-red colour and earthy taste. When dried at 100°, it exhibits the composition of fumarimide + 1 At. water. (Dessaignes.) — When the residue obtained as above is exhausted

with boiling water, the wash-water yields on cooling a fine white powder, which remains suspended in the liquid, but is immediately precipitated by acids. This substance, after being several times dissolved in water and reprecipitated, exhibits nearly the composition of anhydrous fumarimide. (Wolff.) — As a small quantity of ammonia is always evolved in the dry distillation of the bimalate, a corresponding quantity of malic acid must be set free; consequently a certain quantity of maleic and fumaric acids must be formed together with the fumarimide, and the soluble parts of the residue contains malic acid, both active and inactive. If the bimalate be moistened with ammonia, before heating it to 200°, the residue yields scarcely anything to water. (Pasteur, *Ann, Pharm.* 82, 231.

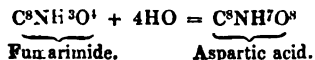
<i>Anhydrous.</i>		Wolff.	
8 C	48	49·5	50·1
N	14	14·4	12·2
3 H	3	3·1	4·1
4 O	32	33·0	33·6
<hr/>			
C ⁸ N ² H ³ O ⁴	97	100·0	100·0
<hr/>			
<i>Hydrated, dried at 100°.</i>		Dessaignes.	
8½ C	48	45·29	45·57
N	14	13·20	13·22
4 H	4	3·77	3·87
5 O	40	37·74	37·34
<hr/>			
C ⁸ N ² H ³ O ⁴ + Aq.	106	100·00	100·00

Wolff supposes that the substance which he analysed was contaminated with aspartic acid.

The composition of fumarimide is that of (unknown) fumaramic acid *minus* water:

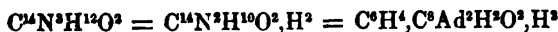


Fumarimide is a very stable substance. It dissolves in hot concentrated acids, whence it is precipitated by water, without alteration, even after boiling for some seconds. But if heated for 5 or 6 hours with hydrochloric or nitric acid, and then evaporated to dryness, it yields a crystalline residue containing a combination of hydrochloric or nitric acid with inactive aspartic acid (Dessaignes, Wolff):



Bimalate and bifumarate of ammonia yield by dry distillation, a substance closely resembling fumarimide in most of its reactions, but not identical with it. (Dessaignes.) ¶

Sinapoline.



ED. SIMON. (1840). *Ann. Pharm.* 33, 258; *Pogg.* 50, 377.

WILL. *Ann Pharm.* 52, 25.

Formation. In the decomposition of mustard-oil by hydrated oxide of lead or aqueous fixed alkalis (p. 45.)

Preparation. 1. One part of mustard-oil is mixed with 12 pts. of recently precipitated oxide of lead, and 3 pts. of water, and digested for several days in a closed vessel at a gentle heat and with frequent agitation, till the odour of mustard is no longer perceptible; the mass then dried in an open basin on the water-bath; and the sinapoline extracted from it by hot water or alcohol. (Simon.) The hydrated oxide of lead must be well washed; the digestion in the water-bath continued, as long as fresh portions of lead-oxide become blackened; the mixture immediately exhausted by boiling with water; and the liquid filtered to separate the sulphide, carbonate and excess of oxide of lead; pure sinapoline then crystallizes out on cooling. (Will.)— 2. Oil of mustard is boiled with a large quantity of baryta-water; the liquid evaporated to dryness after the odour of mustard has disappeared [during which however, some of the sinapoline may volatilize]; and the sinapoline extracted from the residue by alcohol or ether. (Will.)

Properties. Sinapoline crystallizes from the hot aqueous solution in colourless, shining laminæ, unctuous to the touch. (Will.) They melt at 90° (Simon), at 100° (Will), without loss of weight, and immediately solidify on cooling in a beautiful crystalline mass. (Will.) Sinapoline may be sublimed (Simon), but undergoes partial decomposition at the same time (Will); when distilled with water, it passes over undecomposed. (Simon.)

	<i>Crystallized.</i>		<i>Will.</i>	
14 C	84	60.00	59.72	
2 N	28	20.00	19.99	
12 H	12	8.57	8.78	
2 O	16	11.43	11.51	
$C^{14}N^2H^{12}O^2$	140	100.00	100.00	

Decompositions. 1. Sinapoline decomposes between 170° and 180° . (Simon.)— 2. Nitric acid converts it into an acid, and its solution in oil of vitriol turns brown when heated. (Simon.)— It may be boiled with potash without giving off ammonia, and melts in the potash to oily drops without decomposition. (Will.)

Combinations. Sinapoline dissolves in *Water*, abundantly at the boiling heat. (Simon, Will.)

It dissolves without decomposition in cold *oil of vitriol* and cold nitric acid (Simon), likewise in other acids, and may be separated by ammonia. (Will.)

It absorbs dry *hydrochloric acid gas*, with rise of temperature sufficient to melt it, and without separation of water. The saturated compound contains 25.555 pts. hydrochloric acid to 100 pts. sinapoline = 35.77 : 140, therefore equal numbers of atoms. It is viscid, does not give off hydrochloric acid when dry air is passed over it, but emits fumes of hydrochloric acid in moist air, and deposits a portion of the sinapoline on addition of water. (Will.)

Aqueous sinapoline precipitates aqueous *protochloride of mercury* and *bichloride of platinum*. (Will.)

It dissolves in *alcohol* and *ether*. (Simon, Will.)

c. *Nitrogen-nuclei.*a. *Nitrogen-nucleus.* $C^{\circ}NH^{\circ}S^{\circ}$.Oil of Mustard. $C^{\circ}NH^{\circ}S^{\circ} = C^{\circ}NH^{\circ}S^{\circ}$.

- THIBIERGE. *J. Pharm.* 5, 439; also *N. Tr.* 4, 2, 252.
 JUL. FONTENELLE. *J. Chim. méd.* 1, 131.
 HORNEMANN. *Berl. Jahrb.* 29, 1, 29.
 BOUTRON & ROBIQUET. *J. Pharm.* 17, 296.
 HENRY & PLISSON. *J. Pharm.* 17, 451.
 DUMAS & PELOUZE. *Ann. Chim. Phys.* 53, 181; also *J. Chim. méd.* 9, 641; also *Ann. Pharm.* 10, 324; also *Pogg.* 29, 119.
 ASCHOFF. *N. Br. Arch.* 3, 7; also *J. pr. Chem.* 4, 314.
 WITSTOCK. *Berl. Jahrb.* 35, 2, 257.
 ROBIQUET & BUSSY. *Ann. Chim. Phys.* 72, 328; also *J. Pharm.* 26, 116; also *J. pr. Chem.* 19, 232.
 BOUTRON & FREMY. *J. Pharm.* 26, 112.
 LÖWIG & WEIDMANN. *J. pr. Chem.* 19, 218.
 WILL. *Ann. Pharm.* 52, 1. — Further *Ann. Pharm.* 92, 59.
 WERTHEIM. *Ann. Pharm.* 55, 297.
 GERHARDT. *Compt. rend.* 20, 894; also *N. Ann. Chim. Phys.* 14, 125; also *J. pr. Chem.* 35, 487.

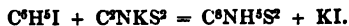
Volatile Oil of Mustard, Ethereal Oil of Mustard, Sulphocyanide of Allyl, Esence de moutarde.

Sources. The seed of black mustard—not that of white mustard,—contains a substance (myronic acid) not very well known in the free state, which, in presence of water, is decomposed by the emulsion-like myrosin likewise present, with formation of oil of mustard (pp. 50—54). The seeds of many other cruciferous plants behave in the same manner, but yield oil of garlic at the same time (ix, 372); the moist parts of cruciferous plants contain oil of mustard already partially formed.

Formation from Oil of Garlic. When the precipitate which an alcoholic solution of oil of garlic forms with corrosive sublimate is mixed with excess of sulphocyanide of potassium, and the mixture heated to 120—130°, a mixture of oil of mustard and oil of garlic distils over. (Wertheim.) The precipitate is in fact $C^{\circ}H^{\circ}S^{\circ}$, $2HgS + C^{\circ}H^{\circ}Cl$, $2HgCl$; this latter member, with $3C^{\circ}NKS^{\circ}$ forms $C^{\circ}NH^{\circ}S^{\circ} + 2C^{\circ}NHgS^{\circ} + 3KCl$; but at the same time, the first member $C^{\circ}H^{\circ}S^{\circ}, 2HgS$ is resolved into oil of garlic, $C^{\circ}H^{\circ}S^{\circ}$, and residual sulphide of mercury, $2HgS$. (Wertheim.)

¶ *Formation from Oil of Asa fetida.* — Concentrated alcoholic solutions of crude oil of *Asa fetida* and corrosive sublimate yield a white flocculent precipitate which, when boiled with strong alcohol, is resolved into a soluble compound ($C^{12}H^{10}S^{\circ} + 5HgS$) + $C^{12}H^{10}C^{\circ} + HgCl$, which separates on cooling in white microscopic crystals, and an insoluble compound ($C^{12}H^{10}S^{\circ} + 2HgS$) + $4Hg^2Cl + 4Hg^2S^{\circ}Cl$; and when either of these compounds is triturated with sulphocyanide of potassium, a strong odour of oil of mustard is evolved, and a few drops of the oily liquid which passes over on heating the mixture forms with ammonia crystals resembling thiosinamine (p. 57). (Hlasiwetz, *Ann. Pharm.* 71, 28.)

3. From *Iodopropylene*, by the action of sulphocyanide of potassium (or of silver):



It would appear from this reaction that oil of mustard is the sulphocyanide of sulphopropylene C^6H^6S (identical or isomeric with oil of garlic) the latter being formed from iodopropylene by the substitution of S for I. (Berthelot & De Luca, *Compt. rend.* 39, 746; *N. Ann. Chim. Phys.* 44, 495. — N. Zinin, *Petersb. Acad. Bull.* 13, 288; *Ann. Pharm.* 95, 128.)

Preparation of crude oil of mustard. — The bruised seed of black mustard is macerated over night with 3 to 6 pts. of cold water, and then distilled as long as any oil passes over with the water. — The mustard may be previously freed from the fixed oil by pressure. If the seeds are not macerated before they are heated, the myrosin is rendered inactive by the heat, before all the oil is formed, and consequently the product is smaller. At each distillation of a fresh quantity of mustard, the watery distillate obtained in former operations and already charged with oil of mustard, may be used with advantage. — In the ordinary mode of distillation, the sides of the still become too strongly heated, and consequently the quantity of oil is smaller than that which is obtained by vapour-distillation, viz. by passing steam from a small boiler through a bent leaden tube into the still in which the mustard is mixed with cold water. (Wittstock.) If the distillation be too long continued, the oil redissolves in the water which passes over. (Aschoff.) — The distillate may be made to run from the condensing tube into a wet filter covered with a glass plate; the water then passes through, and the oil collects at the apex of the filter, from which, at the end of the distillation, it may be run off by piercing the filter at the bottom. (Wittstock.)

100 pts. of mustard yield 0.2 pts. of oil (Boutron & Robiquet); 0.55 pts. (Aschoff); 0.8 pts. (Hesse, *Ann. Pharm.* 14, 41); 1.2 pts. (Hoffmann, *Berl. Jahrb.* 35, 2, 251); by ordinary distillation after maceration with water, 0.5 pt.; after maceration with the mustard-water of the previous distillation, 0.7 pt.; by vapour-distillation, when the mustard is macerated with common water, 0.7 pt.; and when it is macerated with the mustard-water of the preceding distillation, 1.1 pt. (Wittstock.)

The crude oil of mustard thus obtained is more or less yellow, but exhibits in other respects the properties of the purified oil.

Purification. By simple rectification (Dumas & Pelouze); by distillation with an equal quantity of water (Aschoff); by placing it in contact with chloride of calcium, then decanting and distilling, a small quantity of black-brown resin remaining behind. (Will.) — If the crude oil of mustard be heated for some time in a distillatory apparatus to 100° , a colourless oil passes over, having an ethereal odour and lighter than water; the residue begins to boil at 110° , and its boiling point becomes constant at 155° . Crude oil of mustard, therefore, contains one or more lighter and more volatile oils. (Robiquet & Bussy.) These might arise from adulteration. (Will.)

¶ *Preparation from Iodopropylene.* — 1. Iodopropylene and sulphocyanide of potassium in nearly equal numbers of atoms are heated to 100° in sealed flasks with addition of a small quantity of water. On opening the flasks after some hours, and pouring water into them, a solution of iodide of potassium is obtained, with an oily liquid floating

on the surface. This oil, when separated from the watery liquid and distilled, begins to boil at 100°, but the greater part distills over at about 150°. The more volatile portion appears to contain a small quantity of oil of garlic, due to some secondary reaction; but the principal part of the distillate consists of oil of mustard (Berthelot & De Luca.)—Or iodopropylene is distilled with an alcoholic solution of sulphocyanide of potassium, the alcoholic distillate mixed with water, and the oil thereby separated, distilled as above, the portion which passes over between 145° and 150° being collected apart. (Zinin.)—2. Oil of mustard may be distilled with still greater facility by the action of sulphocyanide of silver on iodopropylene. The action takes place at ordinary temperatures, iodide of silver being formed, while the iodopropylene disappears and is replaced by oil of mustard. At 100° sulphide of silver is formed. (Berthelot & De Luca.) ¶

Properties. Colourless transparent oil. (Dumas & Pelouze, Aschoff, Will); refracting power=1.516 (Will); sp. gr. 1.015 at 20° (Dumas & Pelouze); 1.009 to 1.010 at 15° (Will); boiling point 143° (Dumas & Pelouze); perfectly constant at 148°. (Will.) Vapour-density=340. (Dumas & Pelouze); 3.54. (Will.)—The oil has a sharp penetrating taste and odour; excites tears; inflames and blisters the skin. (Thibierge.)—Neutral to vegetable colours. (Thibierge)

			Löwig & Weidmann.	Will.	Dumas & Pelouze.	Henry & Plisson.	Berthelot & De Luca (<i>artificial</i>).
8 C.....	48	48.49	49.29	49.40	49.98	53.28	
N.....	14	14.14		14.12	14.45	14.92	
5 H.....	5	5.05	5.21	5.24	5.02	11.18	
2 S.....	32	32.32	52.07	31.96	20.25	11.18	32.3
O					10.30	9.44	
<hr/>							
C ⁸ H ¹⁴ S ²	99	100.00		100.72	100.00	100.00	

	Vol.	Density.
C-vapour.....	8	3.3280
N-gas.....	1	0.9706
H-gas.....	5	0.3465
S-vapour.....	$\frac{1}{2}$	2.2185
<hr/>		
Vapour of oil of mustard.....	2	6.8636
	1	3.4308

As Dumas & Pelouze found too small a quantity of sulphur, they concluded that the oil contained oxygen,—an error which was corrected by Löwig & Weidmann.—Wertheim and Will are disposed to regard oil of mustard as sulphocyanide of allyl, =C⁸H¹⁴C²NS². This view is supported by the convertibility of oil of garlic into oil of mustard, and *vice versa*; also by the formation of oil of mustard from iodopropylene.

Decompositions. 1. The oil kneaded with alumina yields by *dry distillation*, carbonic acid, carburetted hydrogen, and a small quantity of sulphuretted hydrogen gas, together with water. (Fontenelle.)—2. Exposed to daylight for three years in well closed vessels, it gradually becomes brownish-yellow, and deposits an orange yellow amorphous substance. (Will.) This body, after being washed with ether and dried in vacuo, contains 28.60 p. c. C. 5.87 H, 20.72 S, and (as loss) 44.81 N. It has the aspect of pseudosulphocyanogen. It swells up and assumes a

dark colour when heated, gives off a strong odour of oil of mustard, and leaves a dull, perfectly combustible charcoal. It dissolves in warm potash-solution, forming a yellow liquid, from which acetic acid precipitates light yellow flocks; and the liquid filtered therefrom still gives a light yellow precipitate with acetate of lead, but does not redden ferric salts, and therefore does not contain hydrosulphocyanic acid. (Will.)—3. The aqueous solution of the oil, after exposure to the air for some hours, loses its sharpness, but retains its taste and mustard odour, and deposits a grey powder, containing sulphur. (Thibierge.)—The oil undergoes no change by exposure to the air or to oxygen, even for a considerable time, becoming neither acid nor alkaline. (Boutron & Robiquet.)

4. When *chlorine gas* is very slowly passed into a retort filled with oil of mustard, very volatile crystals are formed, having a silky lustre (with evolution of hydrochloric acid, according to Dumas & Pelouze). These crystals become coloured and decompose when exposed to the air, and are dissolved by a large excess of chlorine, yielding a viscid, no longer crystallizable liquid. Potash-ley converts them into a resinous substance insoluble in potash. They are insoluble in water and ether, but dissolve in alcohol in all proportions. (Boutron & Fremy.)—5. *Bromine* acts upon oil of mustard with frothing and evolution of heat, and forms a brown resin nearly insoluble in water; the solution contains sulphuric and hydrobromic acid. (Aschoff.)—6. *Iodine* dissolves quickly in the oil, forming a dark red-brown liquid. (Aschoff.)

7. *Nitric acid* quickly decomposes the oil, with evolution of a large quantity of nitric oxide, and formation of a large quantity of nitric acid [sulphuric?] (Boutron & Robiquet.)—Even with moderately strong nitric acid, the oil becomes very strongly heated, with brisk evolution of nitric oxide; assumes first a light green, then a reddish-yellow colour, and lastly thickens and dissolves, forming a yellow liquid, on which a yellow, porous, resinous substance, nitrosinapylic resin, floats. If the action of the nitric acid be continued, this substance disappears, forming a yellow solution of nitric, sulphuric, oxalic, and nitrosinapylic acid. (Löwig & Weidmann.) Hlasiwetz (*Ann. Pharm.* 76, 294,) likewise obtained formic acid.

The *nitrosinapylic resin*, if taken out as soon as all the oil has disappeared, and washed with water, melts at the heat of the water-bath, to a dark yellow mass, which gradually solidifies and becomes quite solid on cooling. At a stronger heat, it decomposes after previous fusion. It dissolves partially in dilute ammonia, potash, or baryta; forming a dark yellow liquid, from which acids separate yellow flakes; the undissolved portion dissolves in strong boiling potash. The entire resin dissolves sparingly in ether, but not in water or alcohol. It contains 36.65 p. c. C, 23.56 N, 3.12 H, 16.04 S, 20.63 O, and is therefore C^oN³H⁴S¹⁰O³. (Löwig & Weidmann.) As it is but partially soluble in dilute alkalis, it cannot be a simple compound. (Berzelius, *Jahresber.* 21, 362.) [The perfectly formed resin is perhaps free from sulphur, and = C^oN³H⁴O⁴ = C^oNX³H⁴.]

The yellow solution of the four acids, yields by evaporation and cooling, crystals of oxalic acid, whereas the mother-liquor chiefly contains sulphuric and *nitrosinapylic acid*, in case this latter acid has not been decomposed during the evaporation by too great an excess of nitric acid. To obtain the nitrosinapylic acid from this liquid, it is saturated with carbonate of baryta, filtered from the sulphate and oxalate of baryta, the baryta carefully precipitated from the filtrate by

sulphuric acid, and the filtrate evaporated over the water-bath to the consistence of an oily liquid. This liquid solidifies on cooling, to a yellow, waxy, easily fusible mass, which, however, if too strong a heat has been applied, is no longer soluble in water. The acid gives off ammonia when boiled with excess of potash. It dissolves in water, forming a solution which reddens litmus. Its solution in aqueous potash is yellow. The solution of the baryta-salt (*vid. sup.*) evaporated over the water-bath, leaves the dry baryta-salt in the form of a reddish yellow, shining, amorphous, brittle mass, which yields a yellow powder; after being heated for some time over the water-bath, it leaves, when dissolved in water, traces of a red powder; at a higher temperature, it suddenly rolls together in masses, and decomposes, the decomposition beginning at a point and spreading through the whole mass. It dissolves with yellow colour in water, but is insoluble in alcohol and in ether. It contains 39.25 p. c. BaO, 18.23 C, 16.16 N, 1.66 H, 2.74 S, and 21.96 O, and is therefore $\text{BaO}, \text{C}^6\text{N}^2\text{H}^2\text{S}^1\text{O}^9$. [If the sulphur be regarded as unessential, the baryta-salt may be $\text{C}^6\text{NX}^3\text{Ba}, \text{O}^4$, and the acid $\text{C}^6\text{NX}^4, \text{O}^4$.] The aqueous solution of the baryta-salt forms with neutral acetate of lead, a yellow precipitate, which dissolves slowly in cold, more readily in hot water, and after drying at 100° , contains 15.93 p. c. C and 1.65 H, which leads to the same formula. With mercurous nitrate or nitrate of silver, the baryta-salt likewise forms a yellow precipitate, but it does not precipitate a solution of ferric or mercuric chloride. Nitrosinapylic acid is insoluble in alcohol and ether. (Löwig & Weidmann.)

Oil of mustard oxidized with *chromic acid* yields a large quantity of acetic and a very small quantity of propionic acid. (Hlasiwetz.)

8. With *hydrated oxide of lead*, oil of mustard yields sinapoline, carbonate of lead, and sulphide of lead (E. Simon, Will):



Perhaps, 2 At. oil of mustard give up 2CS^2 , which then, with the 6PbO , forms $2(\text{PbO}, \text{CO}^2)$ and 4PbS . (Will.)—1 pt. of oil of mustard mixed in a close vessel with 12 pts. of recently precipitated hydrated oxide of lead and 3 pts. of water, and digested at a gentle heat for several days, with frequent agitation, disappears and loses its sharp odour, the mixture acquiring an odour of garlic and turnips, which, however, is completely destroyed by evaporating the liquid, together with the blackened oxide of lead, in the water-bath, during which process, the last portions* of sulphur are precipitated as sulphide of lead. The remaining black pulverulent mixture, when evaporated in the chloride of calcium bath, gives off water and a large quantity of ammonia, while sinapoline and sulphide of lead remain behind. (Ed. Simon, *Pogg.* 50, 377.)

Heavy metallic oxides in the dry state, and metallic salts dissolved in absolute alcohol, abstract sulphur from oil of mustard, but very slowly and imperfectly. (Will.)—Thus nitrate of silver (or dehydrated acetate of lead), dissolved in absolute alcohol, yields a black precipitate when heated with oil of mustard; but the liquid still retains sulphur, even after the mixture has been boiled for several days. A few drops of water, however, immediately produce an evolution of carbonic acid, and precipitate all the sulphur as sulphide of silver, while sinapoline remains in the liquid. (Will.) Oil of mustard dissolved in water forms with basic acetate of lead, a white precipitate, which turns grey after a while, and ultimately black; with acetate of copper, it forms after 24 hours a red-brown precipitate; with nitrate of silver a precipitate which soon

turns black; and with terchloride of gold, a yellow precipitate. (Hornemann.) — It forms with nitrate of silver a black precipitate, and with terchloride of gold a yellow-brown precipitate. (Aschoff.) — It does not precipitate neutral acetate of lead, protochloride of tin, ferrous salts, or ferric salts. (Hornemann).

9. *Aqueous potash, soda, or baryta*, likewise forms, with oil of mustard, sinapoline, an alkaline carbonate and a sulphide; but if the mixture be too much heated, ammonia is evolved in consequence of further decomposition. (E. Simon, *Ann. Pharm.* 33, 258; Will.) — A few drops of oil of mustard, heated to the boiling point with baryta-water, precipitate a large quantity of carbonate of baryta without any evolution of ammonia, the filtrate containing sinapoline and sulphide (but no sulphocyanide) of barium. (Will.) — ¶. Hlasiwetz finds that, when oil of mustard is boiled for some time with solution of caustic soda, in such a manner that the vapour may be condensed and flow back again, the remainder of the sulphur then removed by means of a warm solution of oxide of lead in potash, and the oil washed with dilute sulphuric acid and water, and lastly rectified, a colourless oil of fishy odour is obtained; the same oil is formed when oil of mustard is treated with lime; Hlasiwetz assigns to it the formula, $6C^6H^6O^2 + HO$. The remaining alkaline liquor contains traces of propionic acid, sulphide of sodium, and carbonate of soda. During the action of the soda-solution on oil of mustard, ammonia appears to escape. With oil of mustard from another source, Hlasiwetz obtained, by boiling with solution of soda, an oil having the odour and composition of sage-oil; it contained 80.0 p. c. C, 11.1 H, and 8.9 O. T.

Earlier statements: An alcoholic solution of oil of mustard, mixed with potash-ley and distilled after several days, yields alcohol having an odour of mustard, and a residue consisting of a dark brown oil and aqueous sulphocyanide of potassium. (Hornemann.) — The solution of 1 pt. of crystallized baryta in 256 pts. of mustard-water gradually yields a yellowish grey precipitate containing carbonate of baryta, sulphur, and a less volatile oil; and on distilling the liquid filtered therefrom, ammonia is given off, carbonate and sulphate of baryta are precipitated, and sulphocyanide of barium remains in solution. (Hornemann.) — Fixed alkalis form with oil of mustard, a sulphocyanide and a sulphide of the alkali-metal. (Dumas & Pelouze.) — Oil of mustard, heated with potash-solution, gives off ammonia, and, after some days, deposits crystals [of sinapoline?]. (Aschoff.) — The oil mixed with potash-solution, gives off ammonia, and forms sulphide of potassium, together with a crystallized nitrogenous substance [sinapoline], from which the remainder of the sulphur may be extracted by boiling with oxide of lead. (Simon, *Pogg.* 44, 599; Marchand & Simon, *J. pr. Chem.* 19, 235.) — Oil of mustard agitated with concentrated potash in a stoppered bottle, dissolves completely, forming a brown, faintly smelling liquid, which, when neutralized after a few days, with caustic potash, deposits a few oily drops and small radiating crystals, not of bitartrate of potash, but of a peculiar substance [sinapoline]. The liquid separated from these crystals yields by distillation, a very yellow and strongly alkaline distillate, which blackens lead-salts, whereas the residual liquid precipitates them white. (Boutron and Fremy.)

10. When oil of mustard is dropt into a saturated solution of potash-hydrate in absolute alcohol, great heat is produced, which, if 1 or 2 grammes of the oil are quickly added, may rise in a few seconds to violent ebullition, attended with projection of the mixture; but no permanent gas is evolved, excepting perhaps a little ammonia. The brown-

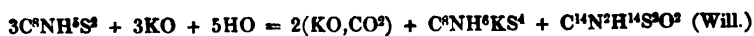
red mixture exhibits, instead of the pungent odour of oil of mustard, merely a mild garlic odour; deposits, after a while, crystals of mono-carbonate of potash with 2 At. water; and when decanted from these crystals and mixed with water, is resolved, with milky turbidity, into aqueous sulphosinapic acid (p. 33), holding in solution a certain quantity of oil which may be dissolved out by ether, and an oil which sinks to the bottom, and if the mixture has been heated to the boiling point, is dark-coloured, and contains insoluble flakes. (Will.)

The *peculiar oil* obtained by keeping the mixture cold, when separated from the aqueous sulphuric acid by collecting it on a wet filter, purified from potash by washing with water, rectified with solution of common salt, and freed from the water which makes it turbid, by standing for several days over chloride of calcium, and decantation, is transparent and colourless; has a density of 1.036 at 14°; has a mild alliaceous odour; a taste which is not burning but cooling; boils between 115° and 118°; but is partially decomposed by distillation, even in a stream of gas, ammonia being formed, as shown by the vapour browning turmeric paper slightly, and a brown resin remaining, which gives off a large quantity of ammonia when more strongly heated, and from which, by continued boiling with water, a volatile alkaloid, not yet further examined, may be extracted. The oil, when boiled with baryta-water, forms sulphide of barium, and a non-volatile substance which remains in solution and appears to be an alkaloid. From lead and silver salts it also precipitates the sulphides on boiling. It forms a precipitate with alcoholic corrosive sublimate, and if the solution be not too dilute, likewise with alcoholic bichloride of tin. It is sparingly soluble in water, but dissolves in all proportions, in alcohol and ether. (Will.)

			Will.	Will.	Will.
			<i>The oil once,</i>	<i>twice,</i>	<i>three times</i>
					<i>rectified.</i>
28 C.....	168 50.76 50.35 50.20
3 N.....	42 12.69 12.30 10.40 9.73
25 H.....	25 7.55 7.88 7.84
4 S.....	64 19.33 20.50		
4 O f.....	32 9.67 8.97		
<hr/>					
C ²⁸ N ³ H ²⁵ S ⁴ O ⁴ ..	331 100.00 100.00		

As the oil gives off ammonia at each rectification, whereby the amount of nitrogen is principally diminished, it is probable that the original oil, before the first rectification was C²⁸N³H²⁵S⁴O⁴ + NH³ = C²⁸N⁴H²⁵S⁴O⁴, or divided by 2: C¹⁴N²H¹²S²O², and therefore C¹⁴N²H¹²O² (sinapoline) + 2HS (Will).

According to this assumption, the equation for the decomposition of oil of mustard by alcoholic potash should be the following:

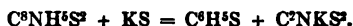


11. When oil of mustard is mixed with pulverized *soda-lime*, and heated for some time to 120° in a sealed tube, the sharp mustard odour is found, on opening the tube, to be replaced by an aromatic alliaceous odour; and on distilling the liquid, oxide of allyl (ix. 363.) is obtained, while sulphocyanide of sodium remains, often mixed with sulphide of sodium, produced by the secondary action of the excess of soda on the sulphocyanide of sodium. (Wertheim.)



Pulverized hydrate of potash acts in the cold upon oil of mustard, just like alcoholic potash; but the products do not come out so pure, because it is more difficult to prevent the temperature from rising too high. In this case also the potassium-salt $C^6NH^6KS^4$ is produced without any evolution of gas, but no sulphocyanide of potassium. The mass dissolved in water, and slightly supersaturated with acid, sometimes shows a slight reddening with ferric salts; but the colour is altogether different from that which is produced by sulphocyanide of potassium, and disappears on the addition of more acid. (Will.)— Even when oil of mustard is heated with hydrate of potash, whereby violent action and ebullition are produced, no hydrogen is evolved, but only ammonia, and the residue contains $C^6NH^6KS^4$. (Will.) Hydrate of potash, thrown in pieces into oil of mustard, produces a violent action, evolves hydrogen, and forms a potash-salt soluble in water and alcohol, the acid of which is oily and floats on water without dissolving. (Boutron & Fremy.)

12. Oil of mustard and *monosulphide of potassium*, heated together for some time to 100° in a sealed tube, yield a distillate of oil of garlic, and a residue of sulphocyanide of potassium. (Wertheim.)



If a polysulphide of potassium be used, crystalline needles sublime, consisting probably of an oil of garlic with a larger amount of sulphur. (Wertheim.)

13. *Potassium* acts upon oil of mustard, even at ordinary temperatures, with evolution of gas, and when heated produces a fiery explosion. When this does not take place, sulphocyanide of potassium appears to be formed, together with an oil different from oil of mustard. — Potassium immersed in the oil, becomes covered with gas-bubbles, and forms a brown mixture; when the mixture is gently heated in closed (but not in open vessels), a slight fiery explosion takes place, accompanied by black smoke and evolution of ammonia; and the residue, if more strongly heated, gives off a small quantity of gas which burns with a red flame, and leaves sulphocyanide and sulphide of potassium, mixed with charcoal. (Aschoff.)— Oil of mustard, even when dehydrated by chloride of calcium and then rectified, acts immediately on potassium at ordinary temperatures, the action being accelerated by gentle heating in a retort (if too strongly heated the liquid would take fire). The mass becomes slightly coloured; gives off a gas not yet examined; yields a distillate of oil of garlic [or something similar], and leaves a white residue of sulphocyanide of potassium. The oil thus obtained is colourless; exhibits the odour and reactions of oil of garlic, giving a black precipitate with nitrate silver, white with corrosive sublimate, and yellow with bichloride of platinum; and contains 58.8 p. c. C, and 8.4 H. But when rectified with potassium, it gives up more sulphur to that metal. The resulting sulphocyanide of potassium forms with a mixture of ferrous and cupric sulphates, a white precipitate uncontaminated either with cyanide or sulphide of copper. (Gerhardt.) [As the evolved gas was not examined, Gerhardt gives no equation for this decomposition. As oil of mustard contains only 2 S, oil of garlic 1 S, and sulphocyanide of potassium 2 S, the reaction is not very intelligible. Moreover, Gerhardt's oil differs from oil of garlic in many respects.] Compare Liebig. (*Ann. Pharm.* 57, 116.)

14. Oil of mustard coats certain of the *heavy metals* with sulphide. — The oil, shaken up with water and mercury, blackens the mercury immediately, but nevertheless retains its pungent odour for several days,

and yields by distillation a pungent oil, still containing a large quantity of sulphur. (Boutron & Robiquet.) In contact with mercury and oxygen gas, it forms sulphide of mercury, becomes thicker, and acquires the power of reddening litmus. (Aschoff.) In the preparation of oil of mustard, the still becomes coated with sulphide of copper, not, however, if the distillation be performed with steam. (Wittstock.)

15. In contact with *ammonia*, oil of mustard is immediately converted into thiosinamine (p. 57).

† It absorbs ethylamine with great rapidity, and is converted into *thiosinethylamine* (p. 61); it appears to act in a similar manner on methylamine, propylamine, and amylamine. (Hinterberger, *Ann. Pharm.* 83, 346.)

17. With *aniline* and *naphthalidine*, it forms compounds which do not appear to be of basic nature. (Zinin, *Ann. Pharm.* 85, 328.) †

Combinations. — The oil, when it has not been dried with chloride of calcium, contains in solution a small quantity of *water*, and therefore becomes turbid in the cold (Wittstock). — It dissolves sparingly in water; this *mustard-water* is obtained in the preparation of oil of mustard.

With the aid of heat it dissolves a very large quantity of *phosphorus*, which, on cooling, first separates in the liquid form, and then solidifies at a temperature below 43°. (Fontenelle, Dumas & Pelouze.)

With the aid of heat, it dissolves a very large quantity of *sulphur*, which crystallizes out on cooling. (Fout. Dum. & Pel.)

† *Mustard-oil with Sulphide of Potassium.* — *a.* $C^oNH^oS^o,2KS$: — Deposited in the form of a white granular salt, on mixing an alcoholic solution of monosulphide of potassium with oil of mustard, the former slightly in excess, and evaporating at a gentle heat. Gives off oil of mustard when heated, but does not change colour. (Will. *Ann. Pharm.* 92, 62.)

			Will.
8 C.....	48.0	22.92	
N	14.0	6.68	
5 H	5.0	2.39	
4 S.....	64.0	30.57	
2 K	78.4	37.44	39.2
<hr/>			
$C^oNH^oS^o,2KS$	209.4	100.00	

b. $C^oNH^oS^o,K.S$. — Separates from the mother-liquor of the salt *a*, when left to stand in vacuo over oil of vitriol, in needle-shaped crystals, having a scarcely perceptible yellowish tinge. (Will.)

			Will.
8 C.....	48.0	31.13	
N.....	14.0	9.08	
5 H.....	5.0	3.24	
3 S.....	48.0	31.13	
K.....	39.2	25.42	25.0
<hr/>			
$C^oNH^oS^o,K.S$	154.2	100.00	

Mustard-oil with Sulphide of Barium — $C^oNH^oS^o,2Ba.S$. — When oil of mustard is gradually added to a warm yellow solution of sulphide of barium (as obtained by treating the crude sulphide with water), till its odour remains permanent, the filtered liquid yields on cooling colour-

less or slightly yellowish laminæ, which crumble to a white powder when exposed to the air. The salt smells of mustard-oil, and burns with a glimmering light when somewhat strongly heated. Precipitated from the aqueous solution by alcohol. Crystallizes with 2 At. and with 6 At. water. (Will. *Ann. Pharm.* 92, 65.)

	With 2 At. Water.		Will.	
8 C	48·0	16·77		
N	14·0	4·89		
7 H	7·0	2·45		
4 S	64·0	22·36		
2 O	16·0	5·59		
2 Ba	137·2	47·94	49·1	47·3
<hr/>				
$C^8NH^5S^2, 2BaS + 2Aq$	286·2	100·00		
	With 6 At. Water.		Will.	
8 C	48·0	14·90		
N	14·0	4·05		
11 H	11·0	3·41		
4 S	64·0	19·86		
6 O	48·0	14·90		
2 Ba	137·2	42·88	41·6	
<hr/>				
$C^8NH^5S^2, 2BaS + 6Aq$	322·2	100·00		¶.

Mustard-water forms with *mercurous* nitrate a white precipitate (Hornemann), which turns grey (Aschoff). It likewise forms a white precipitate with *mercuric* nitrate, and, after a while, with *corrosive sublimate*. (Hornemann.) Oil of mustard dissolved in alcohol, forms with corrosive sublimate, a precipitate which contains mercury and chlorine in unequal numbers of atoms. (Will.)

Under certain circumstances, a crystallizable compound of oil of mustard with *bichloride of platinum* may be obtained, which, in presence of water, is gradually decomposed, with evolution of carbonic acid, and formation of a dark pulverulent body. (Will.)

Oil of mustard dissolves very readily in *alcohol* and *ether*. (Dumas & Pelouze, Fauré & others.)

APPENDIX TO OIL OF MUSTARD.

1. Formation of Oil of Mustard.

- BOUTRON & ROBIQUET. *J. Pharm.* 17, 294; abstr. *Schw.* 63, 94.
 FAURÉ. *J. Pharm.* 17, 299; abstr. *Schw.* 63, 101. *J. Pharm.* 21, 464.
 GUIBOURT. *J. Pharm.* 17, 360.
 ED. SIMON. *Pogg.* 43, 651; 51, 383.
 BUSSY. *J. Pharm.* 26, 39; also *Ann. Pharm.* 34, 223.
 BOUTRON & FREMY. *J. Pharm.* 26, 48; also *Ann. Pharm.* 34, 230; also *J. pr. Chem.* 19, 230; *J. Pharm.* 26, 112.
 WINCKLER. *Jahrb. pr. Pharm.* 3, 93.
 LEPAGE. *J. Chim. med.* 22, 171.

Oil of mustard does not exist ready formed in cruciferous plants, at least not in their dry parts, as in the seeds, especially in the seed of black

mustard. (The seed of white mustard does not yield oil of mustard, but owes its sharpness to sulphosinapine; it likewise contains myrosin.) The production of the oil requires the presence of water, by which the mutual action of two substances contained in black mustard is brought about. One of these substances is, according to Bussy, *Myronic acid*, (p. 53,) which is present in the form of a potash-salt; the other is *Myrosin*, (p. 54,) a substance closely allied to emulsin, which, in presence of water, acts as a ferment on the myronic acid, and forms oil of mustard out of it. These propositions are deduced from the following experiments, which, on the other hand, are thereby explained.

The dry powder or flour of black mustard, is inodorous. (Guibourt,)

When dried over the water-bath, it exhibits the mustard odour only at first, so long indeed as it contains moisture. The inodorous residue tastes sharp, and when treated with cold water, immediately gives off the strong odour of mustard. (Fauré.)

The fat oil expressed from dry mustard-flour is mild; that obtained from the wet powder has a strong mustard-odour. (Fauré.) Mustard-flour moistened either with cold or with luke-warm water, soon exhibits its sharpness, the more quickly indeed as the water is warmer. (Fauré.)

Scurvy-grass loses all its odour when dried, and if distilled with water, yields an insipid distillate; but when distilled, even after the lapse of a year, with the cold aqueous infusion of white mustard (or with $\frac{1}{2}$ pt. of the powder of white mustard), it yields an acrid oil. It, therefore, contains myronic acid, even after drying; but its emulsion-like substance must have lost its power by drying. (Simon.) — With recently dried parts of plants, the addition of white mustard-flour is by no means necessary. If dried horse-radish, scurvy-grass, or cress, after fourteen days' keeping, be immediately heated with water, an insipid distillate is obtained; but if before distillation, it be macerated in water for 24 hours, the distillate is as strong as that obtained from the fresh plant. But if the plant be subjected to the same treatment after half a year's drying, the distillate obtained from horse-radish and scurvy-grass is less powerful, unless an emulsion of white mustard be added before the distillation. (Lepage.)

Mustard-flour heated till it begins to roast, no longer exhibits any sharpness on being mixed with water. (Fauré.) — So likewise the strongly heated seeds of various kinds of *Lepidium*. (Pless.)

The cold aqueous infusion of mustard-flour smells strongly of mustard, tastes sharp and bitterish, reddens litmus, and deposits a coagulated albuminous substance when heated. (Fauré.) — The coagulation takes place at 70° to 80°. (Boutron & Fremy.)

When mustard-flour is introduced into a tubulated retort, containing water at 75° to 80°, no mustard-oil is obtained by distillation, but an insipid distillate; if the water be at 60°, a tolerably large quantity of oil is obtained; but water under 50° yields the entire quantity. Hence mustard-paste prepared with boiling water, is inactive, the emulsion-like matter being coagulated by the hot water, and thereby losing its power of producing mustard-oil. (Fauré.)

If the mustard-flour be macerated for some hours in cold water before distillation, till the myrosin is dissolved, and has eliminated the mustard-oil from the myronate of potash, the whole of the mustard-oil is obtained by distillation; but the more quickly the water is heated to the boiling point in contact with the mustard-flour, and the myrosin thereby coagulated before it has time to act on the myronate of potash, the smaller is the

quantity of oil obtained; hence also no oil is obtained by distilling mustard-flour in Beindorf's apparatus with the vapour of boiling water. (Hesse, *Ann. Pharm.* 14.41.)

Entire mustard-seeds distilled with water, yield no mustard-oil; but if they are boiled with water for five minutes, then dried and bruised, they no longer exhibit any sharpness when treated with cold water. (Fauré.)

The aqueous decoction of black mustard-flour does not emit any odour of mustard when mixed with white mustard-flour or its cold aqueous infusion. (Robiquet & Bussy.) Similarly with the decoction of horse-radish, scurvy-grass, or cress, when mixed with an emulsion of white mustard. (Lepage.)

Chlorine-water, dilute sulphuric acid, and other mineral acids, coagulate the emulsion-like substance, and consequently neither produce sharpness nor yield any acrid distillate. (Boutron & Robiquet; Fauré.)—But the sharpness of mustard-flour macerated with cold water, is by no means removed by dilute sulphuric acid. (Fauré.)

Dilute solutions of alkali-salts evolve the sharpness from mustard-flour. (Fauré.) Aqueous solutions of copper and mercury-salts (and of silver-salts, according to Lepage,) produce no sharpness with mustard-flour. (Fauré.)

With dilute carbonate of potash, mustard-flour emits, not a sharp odour, but an odour like that of *melilot*, and afterwards an hepatic odour; it does not yield any acrid distillate. (Boutron & Robiquet.) Aqueous caustic alkalis likewise emit no sharpness; and the mustard-flour, which is thereby coloured dark yellow, does not yield mustard-oil, if subsequently washed with water and distilled. (Fauré.)

Mustard-flour forms with vinegar neither a sharper nor a milder paste than with water. (Boutron & Robiquet.) Vinegar almost wholly prevents the development of the acrid quality. (Guibourt.)

Mustard-flour, mixed with at least twice its weight of powdered nutgalls, does not exhibit any sharpness on addition of water, because the emulsion-like substance is coagulated by the tannin. (Fauré.) Mustard-flour does not form an acrid paste with alcohol. When exhausted with alcohol, it yields a slightly bitter but not acrid tincture, and an insipid powder, which no longer exhibits any acidity when mixed with water. (Boutron & Robiquet, Fauré.) But after immersion in water for a day or two, the tasteless powder again emits the sharp mustard-odour. (Bussy.) [The myrosin which has been coagulated by the alcohol, is, probably, restored to activity by long contact with water.] When the mustard-flour which has been exhausted with alcohol, is well boiled with water, a bitter decoction [containing myronate of potash] is obtained, which, after cooling, yields a large quantity of mustard-oil with the emulsion of white mustard [containing myrosin], but not with the emulsion of sweet almonds or linseed. (Boutron & Fremy.)—The seed of various species of *Lepidium*, after exhaustion with alcohol, no longer exhibits any acidity when treated with water. (Pless.) When horse-radish, scurvy-grass, or cress is exhausted, after drying, with cold 85 per cent. alcohol, and the alcoholic extract is dissolved in water, the solution yields, with emulsion of white mustard, a certain quantity of mustard-oil; and the plant, after exhaustion with alcohol, still yields, with the same emulsion, a large quantity of oil. (Lepage.) [The alcohol probably dissolves only part of the myronic acid.]

Ether does not deprive mustard-flour of the capability of producing mustard-oil with water. (Fauré.)

Myronic Acid.

Myronsäure, Acide myronique; from *μύρον*, sweet-smelling ointment!—Occurs in black mustard, in combination with potash.

Preparation. Black mustard-flour is dried at 100°, the fat oil pressed out as completely as possible, and the residue exhausted first in the strainer, at the temperature of the air, and then with 85 per cent. alcohol at 50° or 60°. The alcohol removes a certain quantity of foreign matter, which would impede the crystallization of the myronate of potash, and likewise a very small quantity of myronate of potash, which may, however be recovered by evaporating the alcoholic infusion, exhausting the extract with water, and evaporating the filtrate. The mustard which has been exhausted with alcohol, if freed from alcohol under the press, and treated with water, either warm or cold, gives up to the water the myronate of potash, which may then be obtained in the colourless state by evaporating the filtrate to a thin extract at a gentle heat, exhausting with weak alcohol, which separates a viscid substance, evaporating the alcoholic filtrate, and washing the resulting crystals with weak alcohol. The acid may be obtained from the potash-salt, either by mixing the aqueous solutions of 100 pts. myronate of potash and 38 pts. tartaric acid, evaporating to a certain extent, and extracting the myronic acid with alcohol; or, which is better, converting the potash-salt into a baryta-salt, and precipitating its aqueous solution with an equivalent quantity of sulphuric acid. (Respecting this preparation, compare E. Simon, *Pogg.* 51, 383, and Winckler, *Jahrb. pr. Pharm.* 3, 93).—Lepage did not succeed in preparing myronate of potash from horse-radish.

The colourless aqueous acid thus obtained, leaves, on evaporation, an inodorous, bitter, and sour, uncrystallizable syrup, which reddens litmus strongly.

It contains C, N, H, S, and O.

It decomposes when more strongly heated, yielding various volatile products. — Its dilute solution, when boiled for some time, gives off sulphuretted hydrogen. — With aqueous myrosin it yields oil of mustard.

The *Myronates* are inodorous. They likewise yield oil of mustard with aqueous myrosin. They are all, even the baryta, lead and silver-salts, soluble in water. The ammonia, potash, soda, and baryta-salts are crystallizable. The potash-salt forms large, transparent, colourless crystals, which are neutral, permanent in the air, have a cooling and bitter taste, neither give off water nor undergo any other change at 100°, but fuse at a stronger heat, swelling up, giving off an odour like that of burnt gunpowder, and leaving first a tumefied charcoal, and then sulphate of potash. Hot nitric acid acts upon the potash-salt with evolution of red fumes, and forms sulphate of potash. Weak alcohol dissolves a small quantity of the potash-salt, absolute alcohol none at all.

Myronic acid dissolves in alcohol, but is not perceptibly soluble in ether. (Bussy.)

Myrosin.

The emulsion-like substance in black and white mustard-seed. The seed of *Raphanus sativus*, *Brassica Napus*, *oleracea* and *campestris*, *Erysimum Alliaria*, *Cheiranthus Cheiri*, *Draba verna*, *Cardamine pratensis* and *amara* and *Thlaspi arvense*, likewise contain myrosin. (Lepage.)

Pulverized white mustard is exhausted with cold water; the filtrate evaporated to a syrup, at a temperature below 40°; the syrup precipitated by a moderate quantity of alcohol; the precipitate dissolved in water after the alcohol has been poured off, and the solution evaporated to dryness, at a temperature below 40°.

Myrosin, as thus obtained, resembles other protein-compounds. When incinerated, it leaves sulphate of lime.

In the state of aqueous solution, it is coagulated by heat and also by alcohol, and loses its power of eliminating oil of mustard from myronic acid; but it recovers this power after immersion in water for 24 to 48 hours.

The solution of myrosin mixed with myronates, gives off, after five minutes, a faint odour of mustard-oil, which gradually grows stronger; and if the liquid, which has become turbid and perceptibly sour, be then distilled, the mustard-oil passes over. The turbidity proceeds from a protein-compound, which, when collected on a filter, appears like a white cream, and under the microscope is seen to consist of small globules like those of beer-yeast; this substance does not eliminate mustard-oil from myronate of potash. — Myrosin does not eliminate hydrocyanic acid from amygdalin: neither, on the other hand, does synaptase (the emulsion of almonds), evolve mustard-oil from the myronates.

The aqueous solution of myrosin is transparent, colourless, and gummy, and froths when agitated. (Bussy, *J. Pharm.* 26, 44; *comp.* Winckler, *Jahrb. pr. Pharm.* 3, 93).

2. Oils related to Oil of Mustard.

Many of the oils obtained from cruciferous plants by distillation with water exhibit, to a certain extent, the same chemical relations as oil of mustard, the slight differences of odour perhaps arising from the presence of small quantities of other oils. In several oils obtained from cruciferæ, considerable quantities of garlic-oil may be detected. Others again exhibit quite peculiar chemical characters. But they all appear to agree with mustard-oil in containing nitrogen and sulphur.

A. Oils nearly identical with Oil of Mustard.

a. Oil of Horse-radish. — Obtained from the root of *Cochlearia Armaria*, by making it into a paste and distilling it *per se*. (Einhof.) — The oil exists in the root ready formed, and exhibits its odour immediately on triturating the root. If the distillation be performed in a copper still with a tin head, only a small quantity of oil is obtained, in consequence of the formation of metallic sulphide; hence it is best to distil 3 pts. of the finely chopped root with 2 pts. of water in a glass vessel; 100 pts. of the root thus treated, yield about 0.05 pts. of crude oil, which must be rectified with water, and dried over chloride of calcium.

The purified oil is colourless or very pale yellow; has a density of 1.01; smells like oil of mustard; and contains 48.41 p. c. C and 5.26 H. (Hubatka.) The crude oil is light yellow, of the consistence of cinnamon-oil, and sinks in water; it evaporates quickly, and has an intolerable odour of horse-radish, so strong indeed that a drop of it is sufficient to fill a room with the odour; tastes sweet at first, afterwards sharp and burning, and inflames the lips and tongue. (Einhof.)—When the oil is kept for a year under water in a closed vessel, it disappears, and silvery needles are formed, which smell like horse-radish, excite irritation in the throat, melt when heated, exhaling an odour, first of horse-radish, then of peppermint, then of camphor, and volatilize at the same time completely; they dissolve but slowly in alcohol. (Einhof.)—The pure oil acquires, after a time, a deeper yellow colour. When it is treated with nitric acid, a violent evolution of nitric oxide takes place, and a porous substance [nitrosinapylic acid?] separates out; but long-continued action is required to convert the sulphur completely into sulphuric acid. Oil of vitriol acts violently on the oil, with evolution of sulphurous acid. Chlorine gas converts the oil, with formation of hydrochloric acid and chloride of sulphur, into a thick dark mass, which melts at 100°, and when treated with alcohol, leaves a viscid insoluble residue, smelling like melted sulphur. Horse-radish oil not only yields sinapoline with hydrated oxide of lead, but likewise thiosinamine with ammonia. (Hubatka.)—The solution of horse-radish oil in water is neutral, forms a brown precipitate with neutral acetate of lead, and black with nitrate of silver. The oil dissolves readily in alcohol. (Einhof, *N. Gehl.* 5, 365.) Hubatka, *Ann. Pharm.* 47, 153; see also Tingry, *Crell. Ann.* 1790, 2, 68; Gutret, *Crell. Ann.* 1792, 2, 180.

b. Oil of Scurvy-grass.—Obtained from the fresh herb of *Cochlearia off.* The dry herb does not yield any oil by distillation with water, unless it be previously mixed with white mustard-flour. The oil is exactly like oil of mustard, but does not boil below 156° to 159°. (E. Simon, *N. Br. Arch.* 29, 185; *Pogg.* 50, 377.) The oil is yellowish, heavier than water, has a transient penetrating odour, and a very sharp taste. (Bucholz.) It is brownish yellow and lighter than water. (Reybaud, *J. Pharm.* 20, 453.) By 2 pts. of fuming nitric acid it is converted into a soft resin. (Hasse.) This oil, like oil of mustard, yields sinapoline with hydrated oxide of lead, and thiosinamine with ammonia, and the thiosinamine thus formed likewise yields hydrosulphocyanic acid by distillation with dilute sulphuric acid, and sinnamine when treated with hydrated oxide of lead. (E. Simon.)—The solution of the oil in alcohol, the *Spiritus Cochleariæ*, deposits, when kept for some time, colourless, inodorous, warm-tasting, very delicate needles, which, when heated, emit a strong odour of horse-radish, and blacken a silver needle; are decomposed by nitric acid, giving off, first nitrous fumes with effervescence, and then an odour of bitter almonds; and dissolve in oil of vitriol, hydrochloric acid and potash. (Riem. *Jahrb. prakt. Pharm.* 1, 327.) The *Spiritus Cochleariæ comp.* deposits crystals of sulphur. (Lepage, *J. Chim. méd.* 17, 293.)

c. Oil from the root of Erysimum Alliaria (Alliaria off.) The root in spring, before the leaves are developed, smells like horse-radish, and, when fresh cut and distilled with water in a glass retort, yields 0.03 p. c. of an oil resembling oil of mustard, and forming thiosinamine with ammonia.—The leaves of this plant, on the contrary, smell of

garlic, and yield by distillation with water, a watery liquid, having the smell and taste of garlic. Perhaps many cruciferous plants first produce oxide of allyl, which is subsequently transformed, in the roots into sulphocyanide of allyl (oil of mustard), and in the leaves into sulphide of allyl (oil of garlic). (Wertheim, *Ann. Pharm.* 52, 52.)—The seed of *Erysimum All.* from sunny situations, yields only oil of mustard; that from other situations 0.6 p. c. of a mixture of 90 p. c. mustard oil, and 10 p. c. garlic-oil. (Pless. *Ann. Pharm.* 58. 38.)

d. *Oil from the herb and seed of Iberis amaru.*—Behaves like oil of mustard. (Pless.)

B. *Mixtures of the Oils of Mustard and Garlic.*

Already mentioned (ix., 372, 373).

C. *Peculiar Oils.*

a. *Oil of Cress.*—The herb of *Lepidium ruderalis* and the inodorous seed of *Lepidium ruderalis*, *sativum*, and *campestre*, bruised and macerated in water, yield by distillation a milky water, from which, by repeated fractional rectification in glass vessels, (inasmuch as copper exerts a decomposing action), a yellow oil may be obtained. This oil, after further rectification, is colourless, but turns yellow again on exposure to light. It is heavier than water, neutral, exhibits the refreshing but somewhat alliaceous odour and biting taste of water-cresses, and, when its vapour is inhaled in rather large quantity, produces dryness in the throat and head-ache. It cannot be distilled undecomposed without water. By oxidation with nitric acid, it yields sulphuric acid. With mercurous nitrate it forms a black precipitate of sulphide of mercury; with corrosive sublimate a white precipitate; with nitrate of silver, sometimes white, sometimes black; with bichloride of platinum in alcoholic solution, an orange-yellow precipitate after a while. Aqueous potash and ammonia have no action on this oil. It dissolves with red colour in oil of vitriol, and may be separated again by water. It dissolves slowly in water, readily in alcohol and ether. (Pless, *Ann. Pharm.* 58, 36.)

The fresh leaves of *Lepidium latifolium* yield by distillation with water, a neutral oil heavier than water, together with a milky, strong-smelling and sharp-tasting water, which loses its sharpness by exposure to the air, and likewise in a few hours after being mixed with chlorine (whereupon it precipitates chloride of barium); it gradually forms a black precipitate with nitrate of silver; blackens metallic silver after a while; and is deprived of its taste and odour by charcoal powder. (Steudel, *Diss. de Acredine nonnull. Vegetab. Tübing.* 1805.)

b. *Oil of Radish.*—The root and seed of *Raphanus sativus* yield with water a milky distillate, from which a small quantity of oil may be obtained by rectification. This oil is colourless, heavier than water, and has the taste but not the smell of radishes. It contains sulphur. It forms a white precipitate with corrosive sublimate and yellow with bichloride of platinum. It dissolves with tolerable facility in water. (Pless.)

The same oil is obtained by distilling with water the seeds of *Brassica Napus*, *Cochlearia Draba*, and *Cheiranthus annuus*. (Pless.)

3. *Peculiar Acid obtained from Mustard.*

Black mustard, whether previously exhausted with alcohol or not, or scurvy grass, or horse-radish, is digested in water containing a small quantity of carbonate of soda, the liquid distilled with sulphuric acid, the distillate neutralised with soda, and again distilled with sulphuric acid after sufficient evaporation.

The aqueous acid thus obtained precipitates silver from the solution of the nitrate, like formic acid. But its salts crystallize less easily and less soluble than the formiates; the lead-salt dissolves in 4 or 5 pts. of water.

β . *Nitrogen-nucleus.* C^8NAH^4 .

Thiosinamine.

DUMAS & PELOUZE; ASCHOFF; ROBIQUET & BUSSY; LÖWIG & WEIDMANN: in the memoirs cited under oil of mustard.

ED. SIMON. *Pogg.* 50, 377.

Senf öl-ammoniak, Rhodullin.—Discovered by Dumas & Pelouze in 1834.

Formation. Oil of mustard absorbs ammoniacal gas in large quantity, and forms with it thiosinamine without separation of any substance whatever; it behaves in the same way with aqueous ammonia, in which indeed it is converted into a crystalline mass of thiosinamine. (Dumas & Pelouze.)



The formation of a small quantity of sulphocyanide of ammonium in this reaction is merely accidental. Since oil of mustard cannot be recovered from thiosinamine by the action of either acids or alkalis, and as thiosinamine does not give off ammonia when treated with cold potash, and but slowly when treated with boiling potash, the arrangement of the atoms must have been altered in its formation, and an amidogen-compound produced. (Dumas & Pelouze.) This supposition is corroborated by the fact that whereas oil of mustard, when treated with hydrated oxide of lead, &c., loses carbon and sulphur, thiosinamine is by the same reagents deprived of sulphur only. (Will.)

^f *Preparation.* 1. By saturating oil of mustard with ammoniacal gas. (Dumas & Pelouze.)—By placing oil of mustard together with excess of ammonia in a closed bottle, till it is completely converted into a crystalline mass; dissolving this mass in water; decolorizing it with animal charcoal; then filtering; and bringing it to the crystallizing point by evaporation and cooling. (Dumas & Pelouze.)—To 1 vol. oil of mustard, 3 or 4 vol. strong ammonia may be taken. If the non-rectified oil be used, the mother-liquor decanted from the crystalline mass is coloured by a resinous substance; but, when freed from this impurity by boiling with animal charcoal, it yields crystals of thiosinamine to the last drop. If it be not decolorized, the crystals obtained are less pure, but larger and more developed. (Will.) The two liquids need not be agitated

together. As soon as the crystals are completely formed, the excess of ammonia should be left to evaporate in the air. (Robiquet and Bussy.)—The crystals first obtained are yellowish, and contaminated with a large quantity of sulphocyanide of ammonium: they may be purified by repeated crystallization from water and by animal charcoal. If the ammonia be allowed to act gradually and in small portions on the oil of mustard, the quantity of thiosinamine obtained is smaller, especially if the mixture be frequently heated; and there remains an oil, having no longer a sharp, but rather a sulphurous odour. (Aschoff.)

Properties. White shining rhombic prisms. (Dumas & Pelouze.) Prisms belonging to the right prismatic system, exactly similar to those of formiate of baryta. (Will.) Oblique rhombic prisms often having the base very much developed, and the obtuse edges of the rhomboidal faces replaced by several planes parallel to the diagonal of the base which joins the acute edges of the prism. (Berthelot & De Luca. *N. Ann. Chim. Phys.* 44, 498.)—Melts at 70° (Dumas & Pelouze), at 74° (Wertheim), to a colourless liquid (Will), which on cooling solidifies in a white enamel-like mass (Aschoff), or in a radiating mass (Wertheim).—Cannot be volatilized without decomposition. (Will.)—Inodorous and bitter. (Dumas & Pelouze.) In moderate doses, it does not exert a poisonous action on the human organism, but nevertheless produces palpitation of the heart, sleeplessness, &c. (Wöhler & Frerichs, *Ann. Pharm.* 65, 342.) Neutral to vegetable colours. (Aschoff, Robiquet & Bussy, Will.)—Thiosinamine prepared from artificial oil of mustard (p. 42) exhibits the same properties as that which is obtained from the natural oil. (Berthelot & De Luca; Zinin.)

	<i>Crystallized.</i>	Will.	Dum. & Pel.	Wertheim.	Hubatka.	Berthel. & De Luca.
8 C	48	41·38	40·74	42·75	41·65	41·02
2 N	28	24·14	23·88	24·62	24·00	23·86
8 H	8	6·89	6·91	6·90	7·20	6·99
2 S	32	27·59	26·50	16·84	28·0
O	8·89
$C^{\alpha}N^{\alpha}H^{\alpha}S^{\alpha}$	116	100·00	98·03	100·00	98·9

Wertheim analysed the thiosinamine prepared from *Erysimum Alliaria*; Hubatka, that obtained from *Cochlearia off.*; Berthelot & De Luca, that obtained from the artificial mustard-oil prepared from iodopropylene.

Decompositions. 1. Thiosinamine is decomposed when somewhat strongly heated, leaving a residue of charcoal, and giving off white, pungent-smelling, alkaline fumes, from which drops of oil and hydro-sulphocyanic acid condense. (Aschoff.)

2. The concentrated aqueous solution mixed with *chlorine-water* exhibits a turbidity which disappears after a while, but is reproduced by the addition of more chlorine, then disappears again, and afterwards contains hydrochloric, and sulphuric, but no hydrosulphocyanic acid.—In like manner, *bromine* forms with the solution, a white precipitate which quickly disappears, and is reproduced on the addition of more bromine. When the bromine has been added to the solution till a yellowish colour is produced, the liquid deposits a red-brown oil, no longer smelling like mustard-oil, while hydrobromic and sulphuric acids remain in solution.—A small quantity of *iodine* dissolves in the concentrated solution of thiosinamine without colour, a larger quantity with yellowish colour, depositing a red-brown oil; and the litmus red-

dening liquid filtered therefrom deposits on boiling a white powder, containing sulphur and iodine. (Aschoff.)

3. *Nitric acid* decomposes thiosinamine with formation of sulphuric acid. (Dumas & Pelouze.)

4. When thiosinamine is distilled with dilute *phosphoric* or *sulphuric acid*, hydrosulphocyanic acid passes over. (Aschoff, E. Simon.)

5. *Mercuric oxide* or *lead-oxide* decomposes thiosinamine, forming sinamine, a metallic sulphide, and water (Robiquet & Bussy, Will):



One pt. of thiosinamine triturated with 5 pts. of mercuric oxide, quickly becomes heated above its melting point, and from the resulting black mixture, water or ether extracts sinamine. (Robiquet & Bussy). Similarly with oxide of lead anhydrous or hydrated. After the extraction of the sinamine by ether, there remains sulphide of mercury or sulphide of lead, mixed with the excess of the metallic oxide, but free from carbonic acid and sulphocyanogen. (Will.)—According to E. Simon, there is formed, besides sinamine, another alkaloid, which likewise dissolves in water, alcohol and ether, but is of unctuous consistence; but, according to Will's suggestion, this supposed alkaloid is probably nothing but basic acetate of lead, inasmuch as the hydrated oxide of lead used by Simon may have contained acetic acid. According to Marchand & Simon also (*J. pr. Chem.* 19, 235), thiosinamine, freed from part of its sulphur by the action of hydrated lead-oxide and water, yields a filtrate which reddens ferric salts, crystallizes with difficulty, and again yields oil of mustard by distillation with sulphuric acid.

6. Thiosinamine boiled with *fixed alkalis* gives off ammoniacal gas but slowly. (Dumas & Pelouze.)—When boiled for some time with baryta-water, it slowly deposits carbonate of baryta, while the liquid slowly takes up sulphide of barium, and gives off a small quantity of ammonia only when the baryta-water becomes somewhat concentrated. The remaining liquid, freed from baryta by carbonic acid, yields by evaporation, a very bitter but scarcely alkaline syrup, which appears to contain an alkaloid different from sinamine. (Will.)

7. Thiosinamine, heated with *potassium* till it melts, assumes a brown colour; at a higher temperature it detonates slightly, with emission of black smoke, and forms sulphide and sulphocyanide of potassium. (Aschoff.)

Aqueous sesquichloride of iron is gradually deprived of its yellow colour and acid reaction by thiosinamine, and deposits black flakes when boiled. Sulphate of copper is decolorized by thiosinamine if not too dilute, and alcohol added to the solution throws down light blue flocks. (Will.)—Aqueous thiosinamine forms with acetate of copper a scanty whitish precipitate, which afterwards turns brown; and the liquid filtered therefrom assumes, when mixed with protochloride of iron, a reddish colour, and yields a copious white precipitate insoluble in hydrochloric acid. (Aschoff.)

Combinations. Thiosinamine dissolves in cold and much more readily in hot water (Dumas & Pelouze, Will); after fusion, it dissolves less easily. (Aschoff.)—¶. When thiosinamine (prepared from natural

mustard-oil) is dissolved in boiling water, the solution rarely crystallizes on cooling; it may even be kept in capsules exposed to the air, without depositing crystals; but on stirring the liquid briskly with a glass-rod, it solidifies in a mass. Moreover, when thiosinnamine is melted under a small quantity of water, it remains at the bottom after cooling in the form of a viscous layer which preserves its liquid form for a long time if left at rest, but solidifies immediately on agitation. These phenomena are sufficiently marked to interfere with the regular crystallization of thiosinnamine; hence to effect the crystallization it is advisable to introduce into the tepid liquid a glass rod, having crystals of thiosinnamine already attached to it, and so placed that the crystals may be just at the upper surface of the liquid or even a little above. (Berthelot & De Luca, *N. Ann. Chim. Phys.* 44, 499). ¶.

Hydrochlorate of Thiosinnamine. — 116 pts. of pulverized thiosinnamine exposed to the action of a stream of hydrochloric acid gas, and gently heated towards the end of the action till fusion takes place, absorb 64·82 pts. of hydrochloric acid. The compound, when exposed to moist air, gives off vapours of hydrochloric acid. (Will.)

Thiosinnamine does not appear to combine with *sulphuric, nitric, oxalic, or acetic acid.* (Will.)

Mercury-compound. — The hydrochloric acid solution of thiosinnamine forms with aqueous corrosive sublimate a white curdy precipitate soluble in acetic acid; it must be pressed between paper, and dried at a gentle heat. (Will.)

				Will.
8 C	48·0	7·30	7·92	
2 N	28·0	4·26	4·64	
8 H	8·0	1·21		
2 S	32·0	4·87		
4 Hg	400·0	60·83	60·57	
4 Cl	141·6	21·53	21·22	

$C^6N^2H^8S^2, 4HgCl$. 657·6 ... 100·00

Aqueous thiosinnamine forms with mercurous nitrate a grey precipitate, and with mercuric nitrate, after a while, a white precipitate. (Aschoff.)

Silver-compound. — *a.* A warm aqueous solution of thiosinnamine dissolves a large quantity of recently precipitated chloride of silver, and becomes milky on cooling, with separation of a turpentine-like compound of thiosinnamine and chloride of silver. (Will.)

b. The thick white crystalline precipitate obtained with concentrated aqueous solution of thiosinnamine and nitrate of silver, after being washed with water, and dried at 100°, is greenish white, and in the dried state is but little altered by exposure to light. When decomposed by aqueous sulphuretted hydrogen, it yields sulphide of silver and a solution of thiosinnamine and nitric acid; hence no mustard-oil is reproduced. (Löwig & Weidmann.)

	Dried at 100°.		Löwig & Weidmann.
8 C	48	16·78	16·57
3 N	42	14·69	15·19
8 H	8	2·80	2·67
2 S	32	11·19	11·62
Ag	108	37·76	36·58
6 O	48	16·78	17·37

$C^6N^2H^8S^2, AgO, NO^2$ 286 ... 100·00 100·00

Aschoff formerly made the following statements regarding this compound: Thiosinamine forms with nitrate of silver, if concentrated solutions be used, a copious white crystalline coagulum, soluble in excess of either reagent. The precipitate turns brown even in the dark, and glimmers when heated, evolving a large quantity of cyanogen and leaving sulphide of silver. If it be suspended in water and slowly decomposed by sulphuretted hydrogen (too rapid decomposition causes rise of temperature and evolution of nitrous fumes), and the liquid then distilled, a light yellow oil having the odour of mustard-oil passes over, together with an acid liquid. —The precipitate dissolves when slowly washed with water, leaving however a black powder probably consisting of sulphide of silver; the aqueous solution does not redden ferric salts. The precipitate dissolves in warm dilute nitric acid, and separates again on cooling, provided the liquid be not too dilute, and has not been heated too long. Very dilute solutions of thiosinamine and nitrate of silver remain clear when first mixed, but turn brown after a while and yield a black precipitate. (Aschoff.)

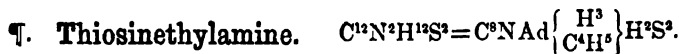
Aqueous thiosinamine forms a yellow-brown precipitate with *terchloride of gold*. (Aschoff.)

Platinum-compound. — Thiosinamine saturated with hydrochloric acid gas and dissolved in water forms with bichloride of platinum — which may contain a certain quantity of free hydrochloric, but no nitric acid — at ordinary temperatures, a yellow-red precipitate, which fuses and blackens at a gentle heat, and leaves sulphide of platinum when more strongly heated. (Will.)

If the precipitation be performed with warm solutions, or if the chloride of platinum be precipitated by thiosinamine dissolved in water and mixed with hydrochloric acid, the precipitate exhibits the somewhat different composition given under *b*. (Will.)

Dried at 100°.		Will.	
		<i>a</i> .	<i>b</i> .
8 C	48.0	14.90	16.8
2 N	28.0	8.69	
3 H	9.0	2.79	1.72
2 S	32.0	9.93	
Pt	99.0	30.73	37 to 43
3 Cl	106.2	32.96	19 to 20
$C^8N^2H^9S^2.HCl + PtCl^2$		322.2	100.00

Thiosinamine dissolves very readily in *ether* and *alcohol*, whence it is partially precipitated by water. (Dumas & Pelouze.)



HINTERBERGER. *Wien, Akad. Ber.* 9, 249; *Ann. Pharm.* 83, 346; *J. pr. Chem.* 58, 263; abstr. *N. Arn. Chim. Phys.* 38, 107; *Pharm. Centr.* 1852, 956. *Jahresber.* 1852, 629.
 WELTZIEN. *Ann. Pharm.* 94, 103.

Formation. 1. By the action of ethylamine on mustard-oil, (Hinterberger.) — 2. By the action of iodide of ethyl on thiosinamine (Weltzien.)

Preparation. Oil of mustard absorbs gaseous ethylamine with considerable rise of temperature. Liquid ethylamine hisses when dropt into mustard-oil; and on adding the oil to liquid ethylamine, it is thrown out by the violence of the action. When ethylamine was passed in excess into mustard-oil cooled with ice, a thin syrupy liquid was formed having the odour of ethylamine, and a bitter aromatic taste. This liquid, after standing for some time, became red-brown but did not yield crystals or form crystallizable salts with acids; when heated, it gave off white fumes, which condensed to oily, alkaline drops, exhibiting a blood-red colour with sesquichloride of iron. (Hinterberger.)

Hydriodate of Thiosinethylamine or Iodide of Thiosinethylammonium. — When thiosinnamine and iodide of ethyl are heated together in alcoholic solution and the liquid evaporated, a white feathery crystalline mass resembling sal-ammoniac is obtained, which turns yellow in the air from separation of iodine, and dissolves in water, alcohol, and ether. (Weltzien.)

			Weltzien.
12 C	72	26.57	25.51
2 N	28	10.33	
13 H	13	4.80	4.94
2 S	32	11.81	
I	126	46.49	46.55
<hr/>			
C ¹² N ² H ¹³ S ² .HI	271	100.00	

Hydrochlorate. — Obtained by decomposing the iodide with oxide of silver, precipitating the excess of the silver from the filtrate with hydrochloric acid, and evaporating the filtered solution. The residue is a syrupy uncrystallizable mass, soluble in water and alcohol. (Weltzien.)

Platinum-salt. — By saturating the syrupy liquid obtained by the action of ethylamine on mustard-oil with dry hydrochloric acid gas, dissolving the resulting viscid mass in absolute alcohol, and adding an alcoholic solution of bichloride of platinum, yellow needle-shaped crystals of the platinum-salt quickly separated; the mother-liquid, when left to itself for some time, yielded crystals of more definite shape. (Hinterberger.) — Weltzien's hydrochlorate mixed with chloride of platinum yielded a yellow, easily soluble, indistinctly crystalline mass.

			Hinterberger.
12 C	72.0	20.56	
2 N	28.0	8.00	
13 H	13.0	3.71	
2 S	32.0	9.14	
3 Cl	106.2	30.33	
Pt	99.0	28.26	28.28
<hr/>			
C ¹² N ² H ¹³ S ² .HCl.PtCl ²	350.2	100.00	

The salt is sparingly soluble in water and alcohol. (Hinterberger.)

Hinterberger has also endeavoured to prepare compounds of mustard-oil with methylamine, propylamine and amylamine, but has hitherto obtained nothing but syrupy liquids which refuse to crystallize. The platinum-salts of these compounds appear however to be crystallizable. ¶.

γ. Nitrogen-nucleus. C⁸N²H⁴.

Sinnamine. C⁸N²H⁸=C⁸N²H⁴,H⁴.

ROBIQUET & BUSSY; WILL. In the memoirs cited under oil of mustard.

Discovered by Robiquet & Bussy in 1839.

Formation. In the decomposition of thiosinnamine by mercuric oxide or lead-oxide (p. 58).

Preparation. 1. One part of thiosinnamine and 5 pts. of mercuric oxide are rubbed together, without application of heat; the mass when cold exhausted with ether; the filtrate evaporated; the viscid residue dissolved in hot water; and the solution left to crystallize. (Robiquet & Bussy.) — 2. Pulverized thiosinnamine is triturated with recently precipitated, still pasty, and well washed hydrated oxide of lead; the mixture heated in the water-bath till a sample diluted with water and filtered, no longer produces a black colour with fresh oxide of lead and potash; the entire mass then repeatedly boiled, first with water and then with alcohol, because the sinnamine is obstinately retained by the sulphide of lead; the whole of the decoctions evaporated to a syrup; and the crystals which form after several months taken out, and freed from the syrup by gentle pressure between paper. (Will.) The syrup is distinguished from the crystals by its smaller amount of water; if the hydrated oxide of lead obtained from the acetate was not well washed, the syrup contains also basic acetate of lead. (Will.)

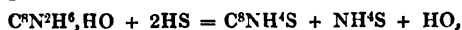
The crystals are freed from their water of crystallization by fusion at 100°.

Properties. Sinnamine dehydrated by fusion is a white, slightly crystalline, opaque mass. It is inodorous and tastes strongly and persistently bitter. (Will.) Its aqueous solution has a strong alkaline reaction. (Robiquet & Bussy.)

	<i>Dried at 100°.</i>			<i>Will.</i>
8 C	48	58.54	57.66	
2 N	28	34.15	33.79	
6 H	6	7.31	7.49	
C ⁸ N ² H ⁸	82	100.00	98.94	

Decompositions. 1. Sinnamine heated in a retort in the oil-bath, gives off ammonia from 160° to 200°, without blackening, and leaves a yellow resinous body [C⁸NH³?]. This body is almost insoluble in water, but dissolves sparingly in alcohol, forming an alkaline solution. Its solution in hydrochloric acid becomes milky when mixed with ammonia, and if subsequently heated, again deposits resinous matter; the hydrochloric acid solution forms a white precipitate with corrosive sublimate and yellow with bichloride of platinum. (Will.) — 2. A cold mixture of aqueous sinnamine and hydrochloric acid does not give off ammonia or become turbid on the addition of potash; but after the hydrochloric acid has been boiled, potash eliminates ammonia from it, and throws down a basic substance, which behaves like the resinous body remaining when sinnamine is heated. (Will.) *Hydrochloric acid gas*, passed over the crystals is absorbed without fusion; the resulting mass when gently heated suddenly emits thick white fumes of sal-ammoniac, and leaves a

tumefied residue. (Will.) — 4. The hydrated crystals exposed to a stream of sulphuretted hydrogen gas, quickly assume a sulphur-yellow colour, without losing water, and if then gently heated, melt to a transparent liquid, which takes up an additional quantity of sulphuretted hydrogen and becomes liver-coloured, but if still subjected to the action of heat, not however rising to 100°, gives off the water of crystallization, together with hydrosulphate of ammonia. Ultimately there remains a transparent, liver-coloured, inodorous mass, amounting in weight to 94·88 p. c. of the crystals. This mass forms with water or alcohol, a solution, which colours lead-salts light-red, and does not precipitate sulphide of lead till it is boiled. (Will.) — If this decomposition by sulphuretted hydrogen took place according to the equation,



the liver-coloured mass would amount to only 90 p. c. of the crystals. (Will.)

Combinations. With water.

a. Syrup. 3C⁸N²H⁶, HO? Remains when the aqueous solution is evaporated over the water-bath, or when the crystals are heated for a short time.

	Will.	Or:	Will.
24 C	144	56·47	56·13
6 N	84	32·94	33·24
19 H	19	7·45	7·61
O	8	3·14	3·02
3 C ⁸ N ² H ⁶ , HO ...	255	100·00	100·00
		255	100·00

b. Crystals. — Separate from the syrup when it is set aside for some time (*vid. sup.*). White, shining, hard, rhombic prisms belonging to the doubly oblique prismatic system. Acute angle of the prisms about 36°. The crystals placed in vacuo over oil of vitriol gradually lose their lustre; they melt at 100°, and gradually part with their water, being converted first into the syrup, and then into anhydrous sinnamine. (Will.)

Air-dried crystals.

C ⁸ N ² H ⁶	82	90·11	90·66
HO	9	9·89	9·34
C ⁸ N ² H ⁶ , HO	91	100·00	100·00

c. Sinnamine dissolves in water.

Sinnamine-salts. — Sinnamine expels ammonia from ammoniacal salts (Robiquet & Bussy, Will); it also precipitates the salts of lead, iron, and copper. (Will.) Nevertheless it does not form solid salts with any acid except oxalic acid with which it slowly forms crystals. (Will.) The acid solutions impart a yellow colour to fir-wood. (Hofman, *Ann. Pharm.* 47, 55.)

Sinnamine with Mercuric Chloride. — The solution of sinnamine in aqueous hydrochloric acid forms with excess of aqueous corrosive sublimate a precipitate, which on account of its tendency to decompose in washing, must be merely collected on a filter, strongly pressed, and dried in vacuo over oil of vitriol. As it contains 14·89 p. c. C, 55·48 Hg and 17·06 Cl, its formula is C⁸N²H⁶, 2HgCl. (Will.)

Sinnamine forms with nitrate of silver a soft resinous precipitate. (Will.)

Platinum-compound.—Aqueous sinnamine mixed with a small quantity of hydrochloric acid, forms with bichloride of platinum, yellowish white flakes, which settle down slowly, so that the liquid filtered after standing for several hours, yields a fresh precipitate, and the filtrate from that yields another, &c. All the precipitates exhibit about the same amount of platinum, viz. about 39.6 p. c. after drying in a current of air at 115°; hence the precipitate is perhaps $C^8N^2H^6$, $2HCl + 2PtCl^2$. (Will.) [The much more probable formula: $C^8N^2H^6$, $PtCl^2$ gives 39.3 p. c. platinum.]

Sinnamine dissolves in *ether* and in *alcohol*. (Robiquet & Bussy, Will.)

Its aqueous solution is precipitated by *tannin*. (Robiquet & Bussy, Will.)



HINTERBERGER. *Ann. Pharm.* 83, 348.

Formation and Preparation. By decomposing thiosinethylamine with hydrated oxide of lead. When the two substances are heated together till a filtered sample no longer blackens on the addition of hydrated lead-oxide and potash, the resulting mass boiled with water and then with alcohol, and the solutions evaporated,—a dark yellow syrupy residue is obtained, which becomes almost wholly crystalline after a few months, and when pressed between bibulous paper and recrystallized from ether, yields pure sinethylamine.

Properties. Sinethylamine crystallizes in needles arranged in dendritic groups; tastes very bitter. At 100° it melts into a colourless liquid, which when touched with a cold body, quickly solidifies in a crystalline mass, the crystallization spreading from the point of contact.

Mercury-compound. A solution of sinethylamine forms with aqueous mercuric chloride a white flocculent precipitate, which, when heated over the water-bath, melts to a yellow resinous mass, solidifying in the crystalline state on cooling.

				Hinterberger.
12 C	72.0	13.95 13.63
2 N	28.0	5.44
10 H	10.0	1.93 1.82
3 Cl	106.2	20.57
3 Hg	300.0	58.11 58.65
<hr/>				
$C^{12}N^2H^{10}, 3HgCl$	516.2	100.00	

Platinum-compound. $C^{12}N^2H^{10}, HCl + PtCl^2$.—A solution of sinethylamine in hydrochloric acid forms with bichloride of platinum, reddish yellow feathery crystals, yielding by analysis 31.55 p. c. platinum; the preceding formula requires 31.24 p. c.

Sinethylamine is insoluble in water, but dissolves in alcohol and ether, forming solutions which have an alkaline reaction. (Hinterberger.) ¶

BUTYLENE SERIES.

A. PRIMARY SERIES.

Primary Nucleus. Butylene. C^4H^8 .

FARADAY (1825). *Phil. Trans.* 1825, 440; also *Schw.* 47, 340 and 441; also *Pogg.* 5, 303.
 KOLBE. *Ann. Pharm.* 69, 258.

Bute, Butyren, most volatile oil of oil-gas, Ditetryl, Butyrene, Tetrylene.

Formation. 1. By the dry distillation of glycerides. (Faraday.) Butylene is also produced, together with caoutchene, and other still less volatile oils, in the dry distillation of caoutchouc. (Bouchardat.)—2. In the decomposition of valerate of lime by the galvanic current. (Kolbe.)—3. In the decomposition of valerianic acid vapour at a red heat. (Hofmann.)—4. In the decomposition of butylic alcohol by oil of vitriol or by chloride of zinc. (Wurtz, p. 72.)—5. In the decomposition of iodide of butyl by potassium. (Wurtz, p. 72.)

Preparation. 1. Oil-gas, prepared on the large scale for illumination; by passing fixed oils and other fats through moderately red-hot iron tubes, and consisting of a mixture of several gases, deposits under a pressure of 30 atmospheres, a thin oily mixture composed almost entirely of butylene, benzin ($C^{12}H^8$), and an oil ($C^{12}H^8?$), which boils at 85.5° . (Faraday.)—1000 cubic feet of oil-gas yield about a gallon of the mixture. It is transparent and colourless; sometimes however green by reflected, and yellow-brown by transmitted light; neutral; of sp. gr. 0.821 at -18° . It burns with a bright flame; is but slowly decomposed by nitric acid; and is scarcely soluble in water or in aqueous alkalis, but dissolves readily in alcohol and ether. It boils for some time, even at ordinary temperatures, as soon as the increased pressure is removed. (Faraday.)—When this oil is gradually heated to 38° in a distillatory apparatus provided with a cooled receiver, and the distillate several times partially rectified at a continually lower temperature, the benzin and the oil $C^{12}H^8$ are left behind more and more completely, and butylene in the pure state is obtained as the most volatile distillate. Sometimes a few delicate needles, which have not been further examined, condense together with the butylene; they melt and volatilize at -13° to -12° .—After the butylene has been removed by distillation, there remains a mixture of benzin and $C^{12}H^8$, which does not boil below 85.5° ; and when this mixture is cooled to -18° , the benzin crystallizes out, and may be separated by stirring and pressure from the oily $C^{12}H^8$, which may then be poured off. (Faraday.)—2. Aqueous valerate of potash is decomposed by the current of a Bunsen's battery (see *Valerianic acid*), and the evolved gas is passed through a tube surrounded with a frigorific mixture and through alcohol, to condense and absorb the admixed vapour of valyl [butyl], then through water to take up the alcohol, and then through strong potash-solution and over hydrate of potash to abstract carbonic acid and water. There then remains a mixture of 27.8 vol. butylene-gas (which may be absorbed by oil of vitriol) and 72.2 vol. hydrogen.

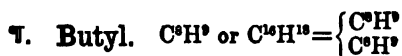
Properties. Thin, transparent, colourless oil, whose specific gravity at + 12·2° would be 0·627. Boils between - 18° and 0°. Its vapour or gas is 27 or 28 times as heavy as hydrogen. [Therefore, vapour-density = 1·8711 to 1·9404]. Its tension at 15·5° is equal to 4 atmospheres. (Faraday.) Vapour-density = 1·993. (Kolbe.)

Calculation, according to Faraday :				Vol.		Density.
8 C.....	48	85·71	C-vapour....	8 3·3280
8 H.....	8	14·29	H-gas.....	8 0·5544
<hr/>						
C ² H ⁶	56	100·00	Butylene-gas	2 3·8824
					1 1·9412

Decompositions. 1. The oil burns with a brilliant flame. 1 vol. of the gas exploded with excess of oxygen, consumes 6·3 vol. oxygen and produces 4·3 vol. carbonic acid gas. Kolbe obtained very nearly the same results. [The 8 vol. hydrogen contained in 2 vol. butylene gas consume 4 vol. O-gas; the 8 vol. carbon vapour therein consumed 8 vol. O-gas, and produce 8 vol. carbonic acid]— 2. One vol. oil of vitriol absorbs 100 vol. butylene-gas very quickly and with great rise of temperature. If however too much heating takes place, the absorption is incomplete and there remains a gas which burns with a pale blue flame. No sulphurous acid is evolved. Oil of vitriol charged with the gas is very much darkened, exhibits a peculiar odour, and generally becomes turbid on addition of water, without however giving off any gas, and is converted into a conjugated acid which forms peculiar salts. [C²H⁶.2SO³?]. (Faraday.)— 3. Butylene gas unites with an equal volume of chlorine gas, quickly condensing to chloride of butylene C²H⁴Cl², and other products richer in chlorine. (Faraday, Kolbe.) Pentachloride of antimony acts in a similar manner. (Kolbe.)— 4. When the gas obtained by decomposing valerianic acid vapour at a red heat (ix, 395) is mixed with bromine vapour, an oily liquid is obtained, the least volatile portion of which appears to consist of bromide of butylene C²H⁴Br². (Hofmann, *Chem. Soc. Qu. J.* 3, 121.)— By the action of bromine on butylene, Cahours has also obtained the compound C²H⁴Br. (*Compt. rend.* 31, 291.)

Combinations. Water shaken up with the gas absorbs it in small quantity. — Aqueous hydrochloric acid and alkalis have no action upon it.

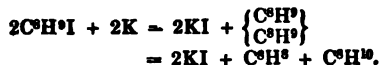
Alcohol absorbs a very large quantity of the gas, acquiring a peculiar odour, and afterwards effervesces when mixed with water. — *Oils*, both *fixed* and *volatile*, likewise absorb the gas; olive-oil six times its volume (Faraday.)



KOLBE. *Chem. Soc. Mem.* 3, 278; *Phil. Mag. J.* [3], 31, 348; abstr. *Ann. Pharm.* 64, 339; — more fully: *Chem. Soc. Qu. J.* 2, 157; *Ann. Pharm.* 69, 257.
WURTZ. *N. Ann. Chim. Phys.* 42, 144; *Ann. Pharm.* 93, 112.

Butyle, *Butylum* (Wurtz); *Valyl* (Kolbe); *Tetryl* (Gerhardt.)—Discovered by Kolbe in 1847.

Formation and Preparation. 1. By the action of potassium on iodide of butyl,—butylene and hydride of butyl, C⁴H¹⁰, being formed at the same time (Wurtz):



The two substances enclosed together in a sealed glass tube and heated in the water-bath for several days, act slowly on each other, the potassium swelling up considerably, and being converted into a mass of iodide of potassium saturated with a colourless liquid. To ensure complete decomposition the potassium must be in excess. On opening the tube after cooling, butylene gas escapes; and the remaining liquid, when gently heated, gives off vapours of hydride of butyl, which may be condensed by a frigorific mixture. The boiling point then rises quickly to 100°, and at 105°, the butyl distils over. (Wurtz.)

2. *By the electrolysis of Valerianic acid:*



When an electric current from four Bunsen's cells is passed through a cold saturated solution of valerate of potash, hydrogen, carbonic acid, and butylene gases are evolved, and an oily liquid rises to the surface consisting of butyl and valerate of butyl (*vid. Valerate of Potash*). On boiling this liquid with an alcoholic solution of potash, valerate of potash gradually separates, while the butyl remains dissolved in the alcoholic liquid, and may be purified by washing with water, drying over chloride of calcium, and rectification.

Properties. Colourless, oily liquid, lighter than water, and having a faint odour. (Wurtz.) Light ethereal oil, having an agreeable ethereal odour, and a density of 0.694 at 18°. (Kolbe.) Boils at 105° (Wurtz); at 108° (Kolbe.) Vapour-density 4.053. (Kolbe.)

		Wurtz.		Kolbe.	
8 C	48	84.21	84.26	84.1	84.0
9 H	9	15.79	16.15	15.9	15.8
C ⁴ H ⁸	57	100.00	100.41	100.0	99.8
	Vol.	Density.		Vol.	Density.
C-vapour	8	3.3280	Or:	16	6.6560
H-gas	9	0.6237		18	1.2474
Butyl-vapour	1	3.9517		2	7.9034
				1	3.9517

[Respecting the vapour-volume of the alcohol-radicals, *vid. vii.*, 171—174.]

Decompositions. Butyl is very inflammable and burns with a strongly luminous flame. (Kolbe.) Under certain circumstances, as in the decomposition of iodide of butyl by potassium (p. 101), it splits up into butylene and hydride of butyl. According to Kolbe also, it is resolved by the influence of nascent oxygen, during the electrolysis of valerate of potash, into butylene and water [C⁴H⁸ + O = C⁴H⁸ + HO]. It is not oxidized by ordinary nitric acid, or by a mixture of chromate of potash and sulphuric acid; but strong fuming nitric acid, especially if mixed

with sulphuric acid, oxidizes it completely after long boiling, forming apparently a mixture of butyric and nitrobutyric acids. — Dry chlorine gas appears not to act on butyl in the dark, but the faintest ray of light is sufficient to induce the formation of hydrochloric acid vapours and of chlorinated substitution-products, the liquid being finally converted by an excess of chlorine, into a viscid mass. — Bromine acts in a similar manner, but less strongly. — Iodine dissolves in butyl, without decomposing it.

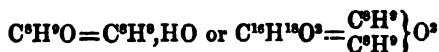
Combinations. Butyl does not appear to combine *directly* with any element excepting iodine; but according to the radical theory, it exists in a great number of compounds homologous with the ethyl compounds. It is insoluble in water, but dissolves in all proportions in alcohol and ether. (Kolbe.)

Hydride of Butyl. $C^4H^{10}=C^4H^9,H$. — This compound has not yet been obtained perfectly pure, but is evolved, together with butylene, by the action of chloride of zinc on butylic alcohol. When butylic alcohol is heated with excess of anhydrous chloride of zinc, and the evolved gases are passed, first through a tube surrounded with ice and inclined upwards to condense the less volatile hydrocarbons formed at the same time and allow them to flow back again — then through a tube surrounded with a freezing mixture, a very volatile, mobile, colourless liquid condenses in this tube, and on being removed from the freezing mixture, quickly evaporates, yielding a mixture of about equal volumes of butylene and hydride of butyl. The butylene may be absorbed by a coke-ball saturated with anhydrous sulphuric acid, and hydride of butyl then remains nearly pure —

Calculation :			Vol.	Density.
8 C	48	82.76	C-vapour....	8 3.2480
10 H	10	17.24	H-gas	10 0.6930
C^4H^{10}	58	100.0	Vap. of C^4H^{10} ...	2 3.9410
				1 1.9705

1 vol. of the gas which remained after absorption of the butylene yielded by explosion with oxygen, 4.26 vol. CO_2 , consuming 7.21 O, and exhibiting a condensation of 3.95 vol. Now 1 vol. hydride of butyl (regarded as diatomic) contains 4 vol. C-vapour, which consume 4 vol. O, producing 4 vol. CO_2 , and 5 vol. H, which consume 2.5 vol. O, making together 6.5 vol. O, and exhibiting a condensation of 3.5 vol. The difference probably arises from the vapour of hydride of butyl being at a temperature only a few degrees above its boiling point, and therefore not having attained its full amount of expansion. (Wurtz.)

7. Oxide of Butyl, or Butylic Ether.



WURTZ. *N. Ann. Chim. Phys.* 42, 152; *Ann. Pharm.* 93.

Obtained: 1. By the action of iodide of butyl on butylate of potassium:



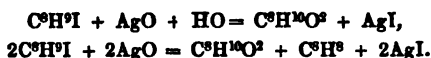
The product however is difficult to purify from butylic alcohol, the boiling points of the two liquids differing but little from each other. The portion which distilled over between 100° and 104° had a very agreeable odour, but contained only 71 p. c. carbon, whereas the calculated quantity is 73·8. If the excess of butylic alcohol be saturated with potassium and the resulting liquid treated, while still hot, with iodide of butyl, a very energetic action takes place, resulting in the formation of butylic alcohol and butylene:



2. By the action of iodide of butyl on oxide of silver —

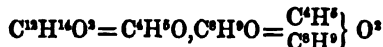


Dry oxide of silver is completely decomposed by iodide of butyl at 100°, with formation of iodide of silver and butylic ether, accompanied however with small quantities of butylene, water, butylic alcohol, and carbonate of butyl:



The formation of water and carbonic acid is probably due to the oxidizing action of the excess of oxide of silver. (Wurtz.)

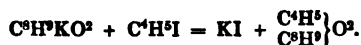
¶. Vinobutylic Ether.



WURTZ. *N. Ann. Chim. Phys.* 42, 118; *Ann. Pharm.* 93.

Ethylobutylic ether, Butylate of Ethyl, Ethylate of Butyl.

Obtained by the action of iodide of ethyl on butylate of potassium, in the cold:

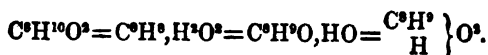


On distilling the mixture after two days' standing, the excess of iodide of ethyl passes over first, then the vinobutylic ether, then (above 95°) the excess of butylic alcohol. The last portion was again treated with potassium, the first portion added to it, in order to form a fresh quantity of vinobutylic ether, and the whole product rectified, the portion which passed over between 78° and 80° being collected apart.

Colourless liquid, of sp. gr. 0·7507; has an agreeable odour.

		Wurtz.	
12 C	72	70·58	70·15
14 H	14	13·72	14·04
2 O	16	15·70	15·81
C ¹² H ¹⁴ O ²	102	100·00	100·00

¶. Butylic Alcohol.

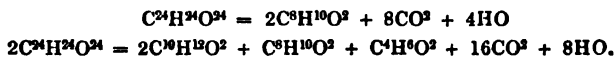


WURTZ. (1852.) *Compt. rend.* 35, 310; *Instit.* 1852, 277; *Arch. ph. nat.* 21, 147; *Ann. Pharm.* 85, 197; *J. pr. Chem.* 57, 305; *Pharm. Centr.* 1852, 798. Further and more fully: *N. Ann. Chim. Phys.* 42, 1; *Ann. Pharm.* 93, 107.

Hydrate of Butyl, Hydrated Oxide of Butyl, Tetrylic Alcohol, Hydrate of Tetryl.

Sources. In some kinds of fusel-oil, viz., in potato-fusel-oil, and in that which is obtained in the rectification of the alcohol produced from the molasses of mangold-wurzel. Different samples of the latter, however, contained very different quantities of butylic alcohol, and some samples none at all. (Wurtz.)—From the experiments of Medlock also (*Ann. Pharm.* 69, 217), and from others made in the Giessen laboratory, it appears that this alcohol does not always exist in potato-fusel-oil.

Formation. By the fermentation of grape-sugar, whereby it may be produced either alone or in conjunction with vinic and amylic alcohols, as shown by the following equations (Wurtz):



Preparation. Fusel-oil obtained in the rectification of mangold-wurzel molasses is subjected to fractional distillation, the portions which distil over between 80° and 105°, 105° and 115°, 115° and 125°, being collected apart. The first portion is washed with water, and the separated oily layer repeatedly rectified, the portion which passes over at 104° being each time collected apart. The latter is mixed with the portion which distilled over between 105° and 115°, and with that part of the last fraction (between 115° and 125°) which, when the latter was repeatedly rectified, passed over below 115°. The whole of the distillates obtained between 105° and 115° are then mixed together and boiled for 48 hours with a concentrated solution of caustic potash, in such a manner that the vapours may be condensed and allowed to run back again; the impure butylic alcohol then distilled over; separated from the water which passed over with it; afterwards mixed with half its weight of quick lime to dehydrate it more completely, and distilled off after standing for 24 hours; this distillate repeatedly rectified; and the portion which passes over between 108° and 110° collected apart: if the boiling point remains within these limits during the distillation, the butylic alcohol thus obtained is very nearly pure. The process of rectification may be considerably abridged by interposing between the flask and the condensing apparatus an upright tube with two bulbs and having a thermometer inserted into its upper part; the less volatile portions then condense on the sides of the tube and run back into the flask, whereby the separation of the more volatile portions is greatly facilitated.—Wurtz first obtained butylic alcohol from potato-fusel oil. When this liquid was distilled, the thermometer remained stationary for a

long time between 108° and 118° ; the liquid which passed over between these temperatures was collected apart, set aside for 48 hours in contact with caustic potash, and repeatedly rectified, the portion which passed over at 112° being collected apart. (*Compt. rend.* 35, 310.)

For complete purification, the butylic alcohol is converted into iodide of butyl (p. 100), which boils at 121° , and is easily separated by fractional distillation from iodide of ethyl, boiling at 73° , and iodide of amyl at 146° ; the iodide of butyl converted into acetate by treating it with acetate of silver; the acetate of butyl decomposed by continued boiling with strong solution of potash, the vapours being condensed and made to run back; and the butylic alcohol thereby separated, decanted and rectified over caustic baryta. (Wurtz.)

Properties. Transparent, colourless liquid, more mobile than amylic alcohol, and having an odour similar to that of the latter, but less pungent and more vinous. Does not turn the plane of polarization of light. Sp. gr. = 0.8032 at 18.5° . Boiling point 110° . Vapour density 2.589. (Wurtz.)

		Wurtz.		
		a.	b.	c.
8 C	48	64.86	64.55	64.49
10 H	10	13.51	13.90	13.53
2 O	16	21.63	21.55	21.98
$C^6H^{10}O^2$	74	100.00	100.00	100.00
		Vol.	Density.	
C-vapour		8	3.3280	
H-gas		10	0.6930	
O-gas		1	1.1093	
Vap. of Butylic Alcohol		2	5.1303	
		1	2.5651	

The analyses *a* and *b* were made with butylic alcohol purified merely by fractional distillation (p. 71); and boiling at 110° ; *c*, with the purer product obtained by decomposing butylic acetate with potash, and boiling at 109° .

Decompositions. 1. Butylic alcohol takes fire on the approach of a burning body, and burns with a bright flame. — 2. Potassium decomposes it with evolution of hydrogen, forming butylate of potassium $C^6H^8KO^2$. — 3. Caustic potash in a state of fusion converts it into butyric acid, with evolution of hydrogen and formation of a butyrate. When dropt upon soda-lime heated to 250° , it is likewise decomposed with evolution of hydrogen and formation of a butyrate. — 4. Hydrochloric acid heated in a sealed tube with butylic alcohol, converts it into chloride of butyl (p. 102). — 5. Pentachloride and oxychloride of phosphorus likewise convert it into chloride of butyl. — 6. Bromine and phosphorus added alternately in small portions convert butylic alcohol into bromide of butyl, with evolution of hydrobromic acid (p. 101) — 7. Similarly, iodine and phosphorus give rise to the formation of iodide of butyl (p. 100). — 8. Oil of vitriol acts violently on butylic alcohol, the mixture becoming very hot and strongly coloured, while sulphurous acid is evolved, and an oily layer separates out, consisting chiefly of hydrocarbons polymeric with butylene. When the alcohol is rapidly mixed with excess of oil vitriol, great heat is produced, and gas is given off in small quantity, which may however be increased by external heating; it consists chiefly of butylene, together with sulphurous and carbonic acid. — When butylic alcohol is gradually

mixed with an equal volume of oil of vitriol, and the vessel kept cool, sulphobutylic acid is produced — 9. Butylic alcohol heated with excess of chloride of zinc is decomposed, with formation of butylene, hydride of butyl, and other less volatile hydrocarbons (p. 66). The butylene is formed by simple abstraction of water: $C^8H^{10}O^2 = C^8H^8 + 2HO$; the excess of hydrogen which the hydride of butyl contains more than the butylene appears to be derived from the liquid hydrocarbons formed at the same time. The mixture of these hydrocarbons which remained in the retort began to boil a little above 100° ; but the boiling point gradually rose to 300° or even higher. The portion which distilled over between 240° and 280° exhibited the following composition :

	Würtz.		Calculation.	

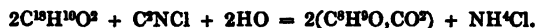
C.....	86.49	86.11	85.72	86.33
H.....	13.95	13.91	14.28	13.67
	100.44	100.02	100.00	100.00

The formation of the hydride of butyl may possibly take place as represented by one of the following equations: $4C^8H^8 = C^8H^{10} + C^8H^2$; $-6C^8H^8 = C^8H^{10} + C^8H^{12}$ (Würtz.)

10. With Chloride of Cyanogen, butylic alcohol forms chloride of butyl and butylic urethane :



If the butylic alcohol, as is generally the case, contains a little water carbonate of butyl and sal-ammoniac are formed at the same time:



(E. Humann, *N. Ann. Chim. Phys.* 44, 437; *Ann. Pharm.* 95, 256; *Chem. Soc. Qu. J.* 8, 274.)

Combinations. Butylic alcohol dissolves in $10\frac{1}{2}$ times its weight of water at 18° , and is precipitated therefrom as an oily layer on addition of chloride of calcium, chloride of sodium, or any other easily soluble salt. — It dissolves *chloride of calcium*, forming a crystallizable compound. — It also dissolves recently fused *chloride of zinc* at ordinary temperatures, forming a syrupy liquid. (Würtz.) — ¶.

Butyral. $C^8H^8O^2$.

CHANCEL. (1845.) *N. J. Pharm.* 7, 113.

GUCKELBERGER. *Ann. Pharm.* 64, 52.

Butyric Aldide, Butyric Aldehyde, Butalidid, Butyrale, Butyraldehyde. [*Nebute.*]

Formation. 1. By the dry distillation of butyrate of lime. (Chancel.) — 2. By the distillation of casein, fibrin, albumin, or gelatin with manganese and dilute sulphuric acid. (Guckelberger).

Preparation. 1. Butyrate of lime in considerable quantity is subjected to dry distillation, and the butyral, which boils at 95° , separated by repeated fractional distillation from the butyrene which boils at 144° , and an oil whose boiling point is 225° , the fractionation being continued till the boiling point becomes constant. (Chancel.) — 2. By the same process as for the preparation of propylic aldehyde (ix. 400, 401).

After the latter has passed over between 65° and 70°, butyric aldehyde is obtained as the principal product between 70° and 100°, and being less soluble in water than the propylic aldehyde, may be separated therefrom by agitation with water. (Guckelberger.) To obtain it perfectly pure, crystalline butyral-ammonia (*q. v.*) is prepared from it, and suspended in water; a concentrated solution of alum added in sufficient quantity to cause the mixture to redden litmus; the liquid distilled, and the butyral separated from the distillate, dehydrated over chloride of calcium, and rectified. (Guckelberger.)

Properties. Thin transparent, colourless oil, which does not solidify when surrounded with a mixture of solid carbonic acid and ether. (Chancel.) Sp. gr. 0·821 at 22° (Chancel); 0·80 at 15° (Guckelberger). Boils steadily at 95° (Chancel); at 68° to 75° (Guckelberger). Vapour-density = 2·61. (Chancel.) Has a brisk penetrating odour, a burning taste, and is neutral (Chancel); it has an ethereal somewhat pungent odour and a burning taste. (Guckelberger.)

				Guckelberger.		Vol.		Density.			
8 C	48	66·67	66·23	C-vapour	8	3·3280
8 H	8	11·11	11·23	H-gas	8	0·5544
2 O	16	22·22	22·54	O-gas	1	1·1093
C ⁴ H ⁸ O ²	72	100·00	100·00	Butyral-vapour	2	4·9917
									1	2·4958

Chancel's analyses likewise agree with the formula.

Decompositions. Butyral is very inflammable and burns with a bright flame slightly tinged with green at the edges. (Chancel.)—2. In the air or in oxygen gas, especially in presence of platinum-black, it absorbs oxygen and soon turns sour, but without colouring, in consequence of the formation of butyric acid, which may be extracted by a small quantity of water; in a stoppered bottle completely filled, it remains unaltered. (Chancel.) It quickly turns acid on exposure to the air. (Guckelberger.)—3. With chlorine or bromine it rapidly gives off hydrochloric or hydrobromic acid, and yields products containing chlorine or bromine, such as C⁶Cl²H⁷O², C⁶Cl²H⁶O², C⁶Cl³H⁵O², C⁶Cl⁴H⁴O² (Chancel.)—4. In contact with crystallized chromic acid, it takes fire with slight detonation. (Chancel.)—5. With dilute nitric acid, it gives off nitrous fumes and yields nitropropionic acid (*ix.* 430). (Chancel.)—6. Heated with water and oxide of silver, it easily reduces the metal, without evolution of gas, and the water takes up a silver-salt containing butyric acid, or perhaps a butyrous acid C⁴H⁸O². (Chancel.) According to Guckelberger's analysis of the silver-salt thus formed, it appears to be butyrate of silver. An aqueous solution of butyral mixed with ammonia and then with nitrate of silver till the alkaline reaction disappears, silvers the vessel very beautifully on the application of a gentle heat. (Chancel, Guckelberger.)—7. Butyral gradually added, with agitation, to twice its bulk of fuming oil of vitriol, yields, with evolution of heat, a dark red solution, which at 100°, gives off a very small quantity of sulphurous acid and turns brown, but does not blacken, and if subsequently diluted with water, yields a very small quantity of butyric acid, but not any trace of a conjugated sulphuric acid. (Chancel.) Consequently the sulphuric acid converts a portion of the butyral into butyric acid by oxidation (Chancel):



8. When 2 parts of butyral are distilled with 3 pts. of pentachloride of phosphorus, chlorobutylene (= Butak = C⁶ClH⁷) is obtained (Chancel):



9. Butyral coats hydrate of potash with a brown crust, and when gently heated with aqueous potash forms a brown lumpy mass. (Guckelberger.)

Combinations. Butyral on the one hand takes up a certain quantity of water; and on the other, dissolves sparingly in water, imparting its peculiar odour. (Chancel.)

BUTYRAL-AMMONIA — Butyral prepared by (2) forms with strong ammonia a crystalline mass, and with very dilute ammonia a milky liquid, which soon deposits crystals and becomes transparent. — If the butyral is contaminated with propylal (propylic aldehyde) — which is the case when it is prepared by (2), — and if it be then mixed, first with water, and then with dilute ammonia, the butyral-ammonia is completely precipitated in the crystalline form, so that the filtrate, when distilled with sulphuric acid, yields pure propylal. — The resulting crystals are collected on a filter, washed with dilute ammonia, pressed between paper, and dried over lime in an atmosphere of ammonia. — The crystals thus formed are very small acute rhombic octohedrons; the alcoholic or ethereal solution yields by spontaneous evaporation, large tables having their acute edges truncated. The crystals after drying remain unaltered in a dry atmosphere, but in damp air, or if they have not been dried, they turn brown like aldehyde-ammonia, and acquire an empyreumatic odour. — When gently heated, they melt without loss of ammonia; if the heat be then slowly raised, the liquid boils, and at a temperature somewhat above 100°, yields a sublimate of transparent and colourless drops, which solidify on cooling, and perhaps consist of the unaltered compound; at a still higher temperature, ammonia is given off. — Aqueous acids decompose butyral-ammonia, separating the butyral which rises to the surface in oily drops; cold potash does not eliminate ammonia from it. When sulphuretted hydrogen gas is passed through the alcoholic solution of butyral-ammonia, an empyreumatic odour is evolved like that of thialdine (ix. 313); and from the resulting liquid, which does not deposit crystals, ether extracts, on agitation, a sulphuretted oil, which immediately forms a crystalline compound with hydrochloric acid. — Butyral-ammonia is nearly insoluble in water, but dissolves readily in ether and alcohol; the alcoholic solution becomes turbid on the addition of water, and in a few hours deposits the greater part of the compound. (Guckelberger.)

	<i>Crystallized.</i>		<i>Guckelberger.</i>
8 C	48	26·82	26·69
1 N	14	7·82	7·81
21 H	21	11·73	11·87
12 O	96	53·63	53·63
<hr/>			
NH ³ , C ⁸ H ⁸ O ² + 10HO	179	100·00	100·00

Chancel's butyral prepared by (1) does not according to Chancel and Henneberg, absorb ammoniacal gas; neither does it appear to be altered by aqueous ammonia. This difference and the higher boiling-point lead to the suspicion that the products (1) and (2) are not identical but isomeric compounds (Guckelberger).

Butyral mixes in all proportions with *wood-spirit, alcohol, ether, and fusel-oil.* (Chancel.)

Butyric Acid. C⁴H⁸O².

- CHEVREUL. *J. Pharm.* 3, 80. — *Ann. Chim. Phys.* 23, 23; also *Schw.* 39, 179. — *Recherches sur les corps gras.* 115 and 209.
 PELOUZE & GÉLIS. *N. Ann. Chim. Phys.* 10, 434; abstr. *Ann. Pharm.* 47, 241; abstr. *J. pr. Chem.* 29, 453.
 WURTZ. *N. Ann. Chim. Phys.* 11, 253; also *Compt. rend.* 18, 704; also *J. pr. Chem.* 32, 501.
 LERCH. *Ann. Pharm.* 49, 217.

Acide butyrique; Buttersäure. — Discovered by Chevreul in 1814—1818.

Sources. 1. Butyric acid has been found, either in the free state or combined with bases: In many samples of gastric juice (Tiedemann & Gm.); also in a liquid discharged in a case of cancer of the stomach (Buchner, *Repert.* 52, 155); once in human urine (Berzelius, *Pogg.* 18, 84); in the liquid expressed from the chopped flesh of man and of various animals (Scherer. *Ann. Pharm.* 69, 196); in the fruit of *Ceratonia Siliqua*, which, when distilled with dilute sulphuric acid, yields 0.6 p. c. butyric acid (Redtenbacher, *Ann. Pharm.* 57, 177); also in the old fruit of *Sapindus Saponaria* and *Tamarindus indica* (Gorup-Besanez, *Ann. Pharm.* 69, 369); in the milk of the cow-tree after it has turned sour (Marchand, *J. pr. Chem.* 21, 48). ¶ Also in cod-liver oil (R. Wagner, *J. pr. Chem.* 46, 155); in flesh-juice (Scherer, *Ann. Pharm.* 69, 196); in crude oil of amber (Marsson, *Arch. Pharm.* [2], 62, 1); in liquid from the spleen (Scherer, *Verhandl. der phys-med. Gesellsch. zu Würzburg*, 2, 298); in perspiration (Schotten, *Archiv. f. physiol. Heilkunde*, 11, 73; Brendecke, *Arch. Pharm.* [2], 70, 34). — 2. Combined with glycerine in the form of butyrin and mixed with other fats; in the butter of the cow and of other mammalia. (Chevreul.)

Formation. 1. By the dry distillation of various substances. In that of tobacco for example; whence the liquid which collects in the smoking of tobacco contains butyric acid. (Zeise, *J. pr. Chem.* 29, 386.) — 2. In the *Butyric acid Fermentation*, which takes place sometimes in sugar, starch, and similar bodies in contact with protein-compounds, sometimes in the latter when alone, and appears to be always preceded by a lactic acid fermentation.

The aqueous solution of common sugar, grape-sugar, gum-sugar, milk-sugar, or dextrin, mixed with an equal weight of powdered chalk and 10 p. c. of ordinary cheese either new or old, or fresh, moist, coarse gluten, and set aside for some weeks in a warm place, either in an open vessel, or in a vessel provided with a cork and gas-delivery tube, becomes turbid and viscid; acquires the odour of sour milk; gradually loses its sweet taste; and finally becomes so thick, that the vessel may often be inverted without the contents running out. At about this stage of the process, the solution, which also contains a little alcohol, yields on addition of alcohol, a white, pasty precipitate, possessing all the properties of gum, so that the solution then precipitates neutral acetate of lead. After the solution has stood for a somewhat longer time, its viscosity diminishes;

carbonic acid is evolved; and crystals of lactate of lime are formed in such quantity that the whole becomes solid. Gradually, however, these crystals disappear; the liquid recovers its transparency; and, after the lapse of 6 to 12 weeks (reckoned from the beginning of the experiment) when the evolution of gas has ceased, contains nothing but butyrate of lime, with a very small quantity of lactate, and traces of acetate of lime, alcohol, and a volatile, odoriferous substance. Mannite cannot be detected at any stage of the fermentation.— Sometimes, however, these phenomena are less sharply defined, namely when the formation of butyric acid takes place simultaneously with that of lactic acid. At the commencement of the process, the hydrogen in the evolved gaseous mixture does not exceed 10 to 15 per cent., but in the later stages, it amounts to between 55 and 60 per cent. The sugar appears therefore first to be converted into a gum; then into lactic acid, which combines with the lime and expels the carbonic acid; and finally into butyric acid. (Pelouze & Gélis.)

[Since lactic acid is $C^3H^5O^3$, and butyric acid $C^4H^7O^4$, the evolution of hydrogen together with the carbonic acid, which proceeds first from the chalk, and afterwards from the decomposing lactic acid, is explained by the following equation: $C^3H^5O^3 = C^4H^7O^4 + 4CO^2 + 4H.$]

Respecting the formation of lactic acid in this process, see *Lactic acid*.

Diabetic urine, which contains grape-sugar, together with animal matters, likewise exhibits the butyric acid fermentation. This liquid, set aside between 15° and 35°, with or without beer-yeast, ferments the more quickly as the temperature is higher; exhibits a continually increasing white turbidity, from separation of globules which appear transparent under the microscope, and look like globules of beer-yeast; gives off carbonic acid and hydrogen gases, first in the proportion of 1 : 2 to 2½, and ultimately in that of to 1 : ¾ to ½. After 5 to 28 days, when the evolution of gas has ceased, the urine is turbid; has a rancid odour; reddens litmus; and no longer contains sugar or urea, but a larger quantity of ammoniacal salts and butyric acid, which passes over together with an odoriferous principle on distilling the liquid with tartaric acid. The fermented urine does not contain either alcohol or acetic acid. A few drops of sulphuric acid stop the fermentation of the diabetic urine, but a small quantity of alkali accelerates it. Boiling the urine suspends the fermentation for a while; so that the urine, if boiled every 3 or 4 days, may be kept for a month. Healthy urine mixed with grape-sugar behaves like diabetic urine. (Fomberg, *Ann. Pharm.* 63, 360.)

If into an aqueous solution of grape-sugar, which does not ferment by itself, pieces of white paper, previously exhausted by potash and water, be introduced, the solution begins to ferment between 17° and 40°, a large quantity of carbonic acid [and hydrogen?] being evolved, and butyric acid formed, but no alcohol. (Döpping & Struve, *Ann. Pharm.* 41, 275.)

Starch in contact with animal matters, likewise passes into the butyric acid fermentation. The fibrous residue of the preparation of potato-starch, which still contains a large quantity of starch and a small quantity of animal matter, if left for two or three days in a pot, at a temperature above 30°, gives off carbonic acid, and forms butyric and acetic acids. (Scharling, *Ann. Pharm.* 49, 213.)— When starch paste or boiled potatoes, stirred up with water, are mixed with flesh, a large quantity of butyric acid is formed in six days, with evolution of gas. (Schubert, *J. pr. Chem.* 36, 47; *comp. Liebig, Ann. Pharm.* 57, 125.)—

Wheat accidentally spoiled and saturated with sea-water in ships, smells strongly of butyric acid, and when distilled with water, yields this acid, together with valerianic acid. (L. L. Bonaparte, *Compt. rend.* 21, 1076.) — ¶ Butyric acid is also formed in the fermentation of wheat-flour, when that substance is stirred up with water, and left to ferment in contact with $\frac{1}{2}$ pt. carbonate of lime; the addition of cheese accelerates the formation of the butyric acid, but likewise gives rise to the formation of lactic acid. (H. Schulze, *Arch. Pharm.* [2] 57, 272.) ¶

When fresh or dry marsh-mallow roots, coarsely bruised, or exhausted with ether and alcohol, and thereby freed from sugar, are placed together with 8 or 12 times their quantity of water, at a temperature of 15° to 25° in a flask provided with a gas-delivery tube, and left for about six weeks, till the evolution of gas ceases and the pieces of root sink to the bottom, the liquid is afterwards found to contain butyric acid, together with small quantities of alcohol and acetic acid. During the fermentation, the water becomes turbid and deposits yellowish-white flocks. At the same time, nitrogen gas is first evolved, and afterwards a mixture of that gas with a very large excess of carbonic acid and with hydrogen. The latter amounts in the mixture at first to 70, then to only 33 to 25 per cent., and does not yield any trace of carbonic acid when exploded with oxygen. After the fermentation, the root is found to be dissolved in the form of a pasty mass, the gum has disappeared, and the asparagin is converted into aspartate of ammonia.— The fermentation takes place, even if the liquid be constantly maintained in a slightly alkaline state.— The bulbs of lilies behave like marsh-mallow roots, excepting that the liquid must be neutralized with chalk. At first a very small quantity of nitrogen gas is evolved, then carbonic acid and hydrogen, and butyrate and acetate of lime are formed. Quince-seeds immersed in water, likewise evolve carbonic acid and hydrogen gases, and yield butyric and acetic acid.— On the other hand, the roots of *Symphytum off.* and the seed of *Plantago Psyllium* yield the same gases, but no butyric acid, only acetic. (Larocque.)

A butyric acid ferment may also be obtained from marsh-mallow roots, lily bulbs, and from *Semen Cydoniorum*, *Psyllii* and *Lini*. Thus, when fresh marsh-mallow roots are bruised and fermented for 8 or 10 days with a six-fold quantity of water, the liquid strained through linen, yields with alcohol a viscid coagulum, which may be washed with water, and preserved under water. This substance is elastic like gluten. It diffuses itself in water, and is partially dissolved thereby. If 1 pt. of it together with a small quantity of water, be exposed to the air for two or three days, and a solution of 5 pts. sugar in 33 pts. water be then added, together with 2 pts. of chalk, nitrogen gas is evolved at first, but after 48 hours carbonic acid and hydrogen are given off with only a small quantity of nitrogen, and, in the course of four weeks, lactate and butyrate of lime are formed, but no alcohol. If the chalk be left out, nothing but nitrogen gas is evolved for the first 9 days, and it is only when the chalk is subsequently added, that the other two gases are given off, and the two acids formed. (Larocque, *N. J. Pharm.* 6, 352.) That the acid produced by the fermentation of marsh-mallow roots, lily-bulbs, and quince-seeds, is really butyric and not valerianic acid, is shown by Larocque's analysis of the silver-salt. (*N. J. Pharm.* 10, 107.)

Tan, when brought to a state of fermentation, is usually exhausted with water, and in the *sour tan-liquor* thus produced the hides are soaked. This liquor yields butyric acid by distillation. (Jul. Chautard, *N. J.*

Pharm. 7, 455, and *J. pr. Chem.* 36, 43.) According to later analyses of silver-salts, Chautard & V. Dessaignes (*N. J. Pharm.* 13, 244; also *J. pr. Chem.* 45, 49) suppose the acid of sour tan-liquor to be a variable mixture of propionic and valerianic acids. [But to judge from the boiling point, which ranges from 140° to 160°, the acid appears to be chiefly butyric acid. The gum and pectic acid of the oak-bark are probably converted into butyric acid by the action of the animal skins.]

Pure protein substances, even when not in contact with sugar, starch, &c. likewise yield butyric acid by putrefaction. — Moist fibrin, left to putrefy in summer, deliquesces, with formation of butyrate and acetate of ammonia. (Wurtz, *N. Ann. Chim. Phys.* 11, 253; also *J. pr. Chem.* 32, 501; compare Bopp, *Ann. Pharm.* 69, 16.)

Pure casein, putrefying under water in summer, yields butyrate and valerate of ammonia, together with other products. (Iljenko, *Ann. Pharm.* 63, 364); hence also the strong-smelling Limburg cheese contains butyrate, valerate, caproate, caprylate, and caprate of ammonia. (Iljenko & Laskowsky, *Ann. Pharm.* 55, 78.)

¶ When 2 oz. of fibrin prepared from ox-blood and free from fat, were mixed with 2 drachms of bicarbonate of ammonia, the mixture stirred up with water to a thin paste, carbonic acid gas passed through it at a temperature of 37° to 44°, during the day for a month, the flask containing the mixture being closed at night, the gas, after passing through had a cheesy odour, in fact that of butyric acid; it likewise contained sulphuretted hydrogen at one stage of the process. The putrefied mass yielded nothing soluble in ether, but was found to contain acetic, butyric, and valerianic acid. Six ounces of fibrin mixed with 3 oz. of chalk, stirred up to a thin paste with water, and left for some months at 37°, yielded acetic, butyric, valerianic, and capric acid. Cassein gave similar results. (Brendecke, *Arch. Pharm.* [2] 70, 26.)

Butyric acid is likewise found among the products of the putrefaction of yeast. (A. Müller, *J. pr. Chem.* 57, 162, 447.) It is also formed, together with succinic and valerianic acids, by the fermentation of malate of lime. (Rebling, *Arch. Pharm.* [2] 67, 300.) Certain kinds of fuci, viz. *Fucus vesiculosus* and *Fucus nodosus*, fermented in contact with lime, yield acetic acid together with a small quantity of butyric. (Stenhouse, *Phil. Mag.* [4], 1, 24.) According to Salvétat, safflower yields butyric acid by spontaneous decomposition. (*N. Ann. Chim. Phys.* 25, 337.) ¶

3. Fibrin heated to 160°—180°, in contact with potash-lime, also yields butyrate of ammonia. (Wurtz.)

4. Many organic compounds distilled with nitric acid, or with a mixture of sulphuric acid and peroxide of manganese, or chromic acid, yield a distillate containing butyric acid.

Maynas resin (from *calophyllum*) treated with nitric acid, yields butyric acid. (B. Lewy, *N. Ann. Chim. Phys.* 10, 283.) — Oleic acid, similarly treated, yields butyric acid, together with several other acids. — When casein, albumin, fibrin, or gelatin is distilled with dilute sulphuric acid and oxide of manganese or chromate of potash, a mixture of acids passes over, the most abundant of which is butyric acid. (Guckelberger, *Ann. Pharm.* 64, 39, and 79.) — ¶. Gluten of wheat distilled with manganese and sulphuric acid, also yields butyric acid, together with other volatile fatty acids. (F. Keller, *Ann. Pharm.* 72, 24.) ¶. The more volatile portion of the empyreumatic oils, obtained by distillation of rape-oil, yields a small quantity of butyric acid when it is heated with strong nitric acid, or when its vapour is passed over

heated soda-lime. (Schneider, *Ann. Pharm.* 70, 109.) — ¶. Oil of turpentine oxidized with nitric acid, yields butyric acid, together with propionic and acetic acid. (F. C. Schneider, *Wien. Akad. Ber.* Nov. and Dec. 337; *Jahresber.* 1849, 447.) — Caprylic alcohol, oxidized with dilute nitric acid, yields butyric acid, together with other acids. (Bouis, *Compt. rend.* 33, 141. — Butyl (obtained by electrolysis of valerianic acid) oxidized with nitric acid, yields an acid liquid which smells of butyric acid, and appears to be a mixture of butyric and nitrobutyric acids. (Kolbe, *Ann. Pharm.* 69, 275.) ¶.

Preparation. A. *From the Butter of Cow's-milk.* — This substance is a mixture of glycerine-fats, by whose saponification, the volatile butyric, caproic, caprylic, and capric acids, and the fixed oleic and margaric acids are produced.—1. Butter is saponified in a still with potash-ley; the product supersaturated with dilute sulphuric acid; half the liquid distilled off; the water decanted from the residue; and the liquid again distilled till the water which passes over no longer reddens litmus. The resulting milky distillates, on which a fat greasy mass floats, consisting of caprylic, and capric acids, are immediately saturated with baryta-water; preserved, till the distillation process is finished, in well stoppered bottles; the united baryta-liquids then boiled down to $\frac{1}{8}$ in the open body of the still, after it has been cleaned; and the remaining liquid transferred to a retort, and evaporated to complete dryness. The residue, which amounts to about 10 per cent. of the butter, consists of a portion more soluble in water (amounting to 95 p. c. of the residue), and composed sometimes of butyrate and caproate, sometimes of vaccinate of baryta, and a less soluble portion (5 per cent.), composed of caprylate and caprate of baryta. The entire residue is boiled with six times its weight of water, the liquid filtered from the sparingly soluble portion, and the filtrate evaporated to the crystallizing point. If the first crop of crystals consists of silky needles of caproate of baryta, permanent in the air and having the appearance of benzoate of lime, then the butyrate of baryta will be found in the mother-liquor. If, on the contrary, small, quickly efflorescing crystals are obtained, arranged in geodes of the size of nuts, such crystals consist of vaccinate of baryta, and it may then be concluded, that the butter used in the preparation did not contain either butyric or caproic acid. (A sample of butter obtained in the very dry summer of 1842, during which the cows were fed to a great extent upon straw, and also butter of the following winter, yielded nothing but vaccinic acid; a sample obtained in the summer of 1843, yielded nothing but butyric and caproic acid.) — If the above-mentioned filtrate yields needles of caproate of baryta, this salt separates out almost completely at the proper degree of concentration, in crystals which may be purified by pressing and recrystallization; and the mother-liquor evaporated in the sunshine, yields at first a few more needles of the caproate, but afterwards pearly laminae of butyrate of baryta, which may likewise be purified by crystallization. (Lerch.) (For the preparation of the acid from the baryta-salt, *vid. inf.*)

2. Four parts of butter are heated to 100° with 1 pt. hydrate of potash and 4 pts. water, till the mass becomes translucent and uniform, and yields a clear solution with water; the solution diluted with so much water that it will no longer draw out into threads at the temperature of 50°, then decomposed by an exactly equivalent quantity of tartaric acid; the solidified mixture of margaric and oleic acid separated, after cooling, from the lower liquid, and washed with water: the greater part of the potash precipitated from the lower liquid by further addition of tartaric acid; that liquid decanted from the cream of tartar; and distilled, toge-

ther with the wash-water of the margaric and oleic acid and the risings of the cream of tartar. The distillate is neutralized with baryta-water, and evaporated to dryness. The residue, which as a mixture of butyrate, caproate, and caprate of baryta, is treated for 24 hours with 2·77 pts. of cold water, the undissolved portion again with 2·77 pts. of water, &c. till nothing but carbonate of baryta remains undissolved. As butyrate of baryta requires 2·77 pts. of cold water to dissolve it, the first solution contains that salt, with but small quantities of the other salts, whereas the following solutions consist chiefly of caproate, and the last of caprate of baryta, which is the least soluble of the three. These solutions abandoned separately to spontaneous evaporation, leave eight kinds of crystals, viz. (1), butyrate of baryta; (2), laminar, and (3), needle-shaped caproate; (4), caprate; (5), transparent laminæ, united in cockscomb-like groups, soluble in 2·7 pts. of water, and yielding by spontaneous evaporation, besides the mother-liquor: partly, (6), transparent crystals (which by a second solution in water and recrystallization, are resolved into butyrate of baryta, octohedrons consisting of butyrate of baryta and lime, [the lime proceeding from the filter,] and delicate transparent needles, which are a mixture of butyrate of baryta and the octohedral salt,)—partly, (7), enamel-white crystals, which by repeated solution and crystallization, are also resolved into caprate and caproate of baryta; and (8), opaque laminæ of capro-caproate of baryta: the latter, when treated with small quantities of water, impart to that liquid, at first, principally the caproate, afterwards the caprate. (Chevreul.)

From the butyrate of baryta after purification by repeated solution in a small quantity of water and crystallization, the acid is separated in two ways: By gradually adding to 100 pts. of the baryta-salt contained in a glass tube, 135 pts. of phosphoric acid of sp. gr. 1·12: the butyric acid thereby separated dissolves gradually in the liquid, whereupon 12 pts. more of phosphoric acid, sp. gr. 1·66 are added; the separated butyric acid decanted; 59 pts. of phosphoric acid of sp. gr. 1·12 then added; and the additional quantity of butyric acid thereby separated also removed. [The watery acid liquid still contains butyric acid, and when saturated with baryta-water, filtered, and evaporated, again yields butyrate of baryta]. The butyric acid obtained by decantation, which is somewhat yellow, and solidifies to a white mass at -7° , is distilled, first in the water-bath, then in the sand-bath. [There then remains a black residue containing acid phosphate of baryta]. The distillate is freed from the water, which passes over, especially at the commencement of the process, by digestion and subsequent distillation with 4 pts. of chloride of calcium.—2. By decomposing 100 pts. of butyrate of baryta with a mixture of 63·36 pts. of oil of vitriol and 63·36 water; decanting the butyric acid, which is colourless and free from sulphuric acid, from the sulphate of baryta (from which a small additional quantity of butyrate of baryta may be obtained by treating it with baryta-water, filtering and evaporating), and distilling it carefully in the sand-bath. There then remains a brown residue of decomposed butyric acid. The transparent and colourless distillate is dehydrated by distillation with an equal weight of chloride of calcium. (Chevreul.)

B. By Butyric acid Fermentation.—To a solution of 100 pts. of starch-sugar (or cane or milk-sugar) marking 8 to 10° Bm., 8 or 10 parts of fresh sour cheese or curd are added, — or 100 pts. of starch-sugar are dissolved in 100 or 150 pts. of milk and so much water that the liquid exhibits a density of 10° Bm.; and the mixture, together with 50 parts of

chalk, set aside in an open bottle [frequently shaken] in a warm place, *e. g.* in the sun in summer, till the evolution of gas ceases, that is to say, for 6 to 12 weeks. The greater the quantity of liquid, the more quickly does the fermentation go on; if it be too slow, more cheese must be added. — When the fermentation is ended, the filtered liquid yields by evaporation, a large quantity of crystals of butyrate of lime, which, if they separate while the liquid is still warm, are free from acetate of lime. — 10 pts. of the crystallized butyrate of lime are dissolved in 30 or 40 parts of water, the solution distilled with 3 or 4 pts. of commercial hydrochloric acid, till 10 pts. (consisting of water and butyric acid, with small quantities of hydrochloric and acetic acid) have distilled over. A large quantity of chloride of calcium is then dissolved in the distillate, and the impure butyric acid which rises to the top is decanted off, and distilled in a tubulated retort provided with a thermometer. The first portion of the distillate consists of aqueous butyric acid, which is either used to prepare the butyrates, or dehydrated by contact with chloride of calcium, decantation and distillation. The boiling point soon rises to 164° and remains there, and at this temperature, if the receiver be changed, pure butyric acid is obtained; this must be boiled for some time in an open vessel, to expel traces of hydrochloric acid, and then redistilled. (Pelouze & Gélis.) — The butyrate of lime froths up strongly when distilled with hydrochloric acid, and therefore requires a capacious distillatory apparatus; the butyric acid obtained by this process is difficult to purify from admixed hydrochloric acid. (Bensch, *Ann. Pharm.* 61, 177.)

¶ Butyric acid may also be obtained from the liquid which remains in the preparation of ferrous lactate by Wöhler's process (digestion of iron filings with sour milk, with addition of milk-sugar: *Ann. Pharm.* 48, 149). After that salt has been separated, the liquid is mixed with a sufficient quantity of milk of lime to render it alkaline; set aside for some weeks in a warm place; and the butyric acid separated by distilling with dilute sulphuric acid, neutralizing the distillate with carbonate of soda, evaporating, and again distilling the residue with dilute sulphuric acid. (Bertram, *Zeitsch. Pharm.* 1853, 43; *Jahresber.* 1853, 439.) ¶

Properties. The acid surrounded with a mixture of solid carbonic acid and ether, crystallizes in broad, transparent, colourless laminæ, but remains liquid at -20°. (Pelouze & Gélis.) At ordinary temperatures, it is a thin, transparent, colourless oil, of sp. gr. 0.9675 at 25° (0.963 at 15°: Pelouze & Gélis; 0.9886 at 0°, 0.9739 at 15°: Kopp; 0.9817 at 0°: Pierre.) Forms on sized paper a greasy spot which gradually disappears; evaporates in the air without residue (Chevreul); boils steadily at 164° (Pelouze & Gélis); at 157° under a pressure of 0.76 m. (Kopp, *Pogg.* 72, 223), and passes over undecomposed. (Chevreul, Pelouze & Gélis.) Boils at 163° under a pressure of 0.7506 m. In a closed space, which it fills to $\frac{1}{4}$, it passes completely into vapour at 220°. (Pierre, *N. Ann. Chim. Phys.* 31, 118.) Vapour-density = 3.30 (Pelouze & Gélis); varies with the temperature. (Cahours, vii, 54.) Has a pungent odour like that of butter (rancid butter, according to Pelouze & Gélis), and acetic acid. Has a very strong and pungently acid taste, afterwards sweetish, like nitrous ether, and makes the tongue white. Reddens litmus strongly. (Chevreul.) Attacks the skin like the strongest acids. (Pelouze & Gélis.)

				Pelouze.	Vol.		Density.
8C.....	48	54.55	54.35	C-vapour.....	8	3.8280
8H.....	8	9.09	9.11	H-gas.....	8	0.5544
4O.....	32	36.36	36.54	O-gas.....	2	2.2186
<hr/>							
C ⁸ H ⁸ O ⁴	88	100.00	100.00		2	6.1010
						1	3.0505

The hypothetical anhydrous acid of the radical theory is C⁸H⁷O³ = Bu. — The hydrated acid may be represented by the formula, $\left. \begin{matrix} \text{C}^8\text{H}^7\text{O}^3 \\ \text{H} \end{matrix} \right\} \text{O}^2$.

Decompositions. 1. Butyric acid is inflammable, and burns in the manner of volatile oils (Chevreul), with a blue flame. (Pelouze & Gélis.) — When distilled in a retort containing air, part of the acid is converted into an aromatic substance. (Chevreul.) — 3. Butyric acid dropt into a bottle filled with dry chlorine gas and exposed to strong sunshine, produces a large quantity of hydrochloric acid, crystals containing oxalic acid which condense on the sides of the vessel, and a pale yellow oil of bichlorobutyric acid, C⁶Cl²H⁶O⁴; if on the contrary, chlorine gas be passed through butyric acid contained in a Liebig's potash-apparatus and exposed to the sun, the chlorine is very rapidly absorbed, and the only products are hydrochloric acid gas and bichlorobutyric acid, amounting to 173 to 176 per cent. of the butyric acid. (Pelouze & Gélis.) Calculation gives 178 per cent.:



This bichlorobutyric acid is decomposed by further action of chlorine into hydrochloric and quadrichlorobutyric acid. (Pelouze & Gélis.) — When bromine is cautiously added to aqueous butyrate of potash till a few drops of a bromuretted acid are precipitated, the liquid then evaporated to dryness, the residue exhausted with alcohol, and a few drops of sulphuric acid added to the filtrate, a compound is produced somewhat different from butyric acid, having a fainter odour, likewise soluble in water and alcohol; but no bromobutyric acid, (C⁶Br²H⁶O⁴), appears to be produced. (Cahours, *N. Ann. Chim. Phys.* 19, 507.) — Iodine likewise exerts but a slight decomposing action, even when aided by heat, forming a small quantity of hydriodic acid. (Pelouze & Gélis.)

Cold nitric acid appears to dissolve butyric acid without decomposition. (Chevreul.) Butyric acid heated with nitric acid of sp. gr. 1.40, is slowly oxidized and converted into succinic acid. (Dessaignes, *Compt. rend.* 30, 50.) — Cold aqueous iodic acid dissolves butyric acid without decomposition. (Millon.)

4. Butyric acid dissolves in cold oil of vitriol with rise of temperature but without decomposition; the solution, which has a faint ethereal odour, becomes very slightly coloured at 100°, gives off butyric acid together with a small quantity of sulphurous acid at a higher temperature, and slowly blackens with formation of a small quantity of charcoal. (Chevreul.) The greater part of the butyric acid passes over unchanged. (Pelouze & Gélis.)

5. Pentachloride of phosphorus converts butyric acid into C⁶ClH⁷. (Cahours, *Compt. rend.* 25, 724.)

Combinations. — Butyric acid mixes with water in all proportions. The mixture of 2 pts. acid and 1 pt. water has a sp. gr. of 1.00287. (Chevreul.)

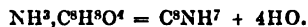
The *Butyrates* in the dry state are inodorous even at 100°, but when moist they have a strong odour of fresh butter. — They are all crystal-

lizable. (Chevreul.)—Several of them yield butyrene by dry distillation. (Chancel.)—Dry butyrate of lime distilled in small quantities at a very slowly increasing heat, is resolved, without any evolution of gas, into white carbonate of lime, and butyrene which passes over:



But when it is more quickly heated and in larger quantity, a considerable quantity of charcoal remains with the carbonate of lime; 3 or 4 per cent. of a gaseous hydrocarbon absorbable by oil of vitriol are given off; and the distillate, which has an unpleasant odour, contains, besides the butyrene which boils at 144°, butyral boiling at 95°, and a yellowish oil boiling at 225° to 230°, which, as potassium remains bright in it, appears to be a hydrocarbon. These products are doubtless produced from the butyrene by the action of too high a temperature. (Chancel.)—Butyrate of potash distilled with an equal quantity of arsenious acid, yields, with evolution of a stinking gas and considerable reduction of arsenic, a distillate consisting of an acid, watery, colourless liquid, and below that, an oily liquid, blackened by arsenic, and smelling like alkarsin; this latter contains either alkarsin, or a corresponding compound of the butylene series. (Wöhler, *Ann. Pharm.* 68, 127.)—The statement of Pelouze & Gélis, that a contamination of butyric acid with acetic acid may be detected by the odour of alkarsin evolved on neutralizing the acid with potash, evaporating, and heating with arsenious acid, is not reconcilable with Wöhler's observation just quoted.—Dry butyrate of soda heated with oxychloride of phosphorus or with chloride of benzoyl, yields anhydrous butyric acid. (Gerhardt; see page 88.)—All butyrates are soluble in water (Chevreul), and many, when thrown on water, rotate like camphor, till they are dissolved. (Chevreul, Pelouze & Gélis.)

Butyrate of Ammonia.—Butyric acid absorbs ammoniacal gas, and is converted into crystals, which by further absorption, deliquesce to a thick, transparent, colourless liquid; but this, when exposed for a still longer time to the action of the ammoniacal gas, ultimately solidifies in needles. (Chevreul.)—The salt is deliquescent. (Pelouze & Gélis.)—Distilled with anhydrous phosphoric acid, it yields butyronitrile=C³NH⁷ (Dumas, Malaguti & Leblanc, *Compt. rend.* 25, 442):



Butyrate of Potash.—Potassium eliminates hydrogen gas with violence from butyric acid. To prepare the salt, potash or carbonate of potash is neutralized with aqueous butyric acid, and the solution evaporated. Crystallizes between 25° and 30° in indistinct, cauliflower-like groups; its taste is sweetish and like that of butter. Very deliquescent; dissolves in 0·8 water at 15°. (Chevreul.) Rotates on water. (Pelouze & Gélis.)

<i>Dried.</i>	Chevreul.
KO	37·96
C ⁸ H ⁷ O ³	62·60
C ⁸ H ⁷ KO ⁴	100·00

A solution of 500 pts. of the salt in 400 pts. water, mixed with 115 pts of butyric acid, does not decompose water without the aid of heat; but after dilution with water, the decomposition takes place at ordinary temperatures. The solution likewise does not redden litmus-

paper till it is diluted. Litmus-paper moistened with it, appears perfectly blue after drying, but becomes red again every time it is moistened, till the excess of acid is evaporated. (Chevreul.)

Butyrate of Soda. — Resembles the potash-salt, but is less deliquescent. (Chevreul.)

Dried.		Chevreul.	
NaO	31·2	28·31	28·78
C ⁶ H ⁷ O ²	79·0	71·69	71·22
C ⁶ H ⁷ NaO ⁴	110·2	100·00	100·00

Butyrate of Baryta. — Baryta-water neutralized with butyric acid, is left to evaporate, and the resulting crystals dried at 100°. The salt may be melted to a colourless glass. In the moist state it smells strongly like fresh butter, has a warm alkaline and buttery taste, and blues reddened litmus slightly. A gramme of the salt subjected to dry distillation, in a bent tube filled with mercury, melts, yields 47·3 cubic centimetres of olefiant gas, and 1·7 of carbonic acid, and a thin, orange-yellow, neutral oil, having the odour of labiate plants (butyrone, according to Chancel), and leaves a mixture of carbonate of baryta with 0·0033 gm. of charcoal. The aqueous solution of the salt does not decompose by keeping: carbonic acid precipitates from it a small quantity of carbonate of baryta, setting butyric acid free. (Chevreul.)

	Dried at 100°.		Chevreul.		Lerch.		Bromeis.
	(a)	(β)	(a)	(β)	(a)	(β)	
BaO	76·6	49·23	49·37	48·71	49·02	49·38	49·38
8C	48·0	30·85		31·34	31·03	31·34	31·34
7H	7·0	4·49		4·72	4·54	3·98	3·98
3O	24·0	15·43		15·23	15·41	15·30	15·30
C ⁶ H ⁷ BaO ⁴	155·6	100·00		100·00	100·00	100·00	100·00

Lerch's salt (α) and (β) is differently crystallized (*vid inf.*) — Bromeis (*Ann. Pharm.* 42, 66) assumed, in accordance with his own analysis, 1At.H more in the salt; but Lerch's analysis is likewise confirmed by Rochleder, who found 4·47 to 4·50 per cent. H.

Crystals with 2 At. Water. — Separate from the concentrated hot-solution; do not melt at 100°; contain 10·07 to 10·50 p. c. water. (Chancel, *N. J. Pharm.* 7, 119.)

Crystals with 4 At. Water. — Obtained by evaporation in the air. Melts below 100°. (Chancel.) Long, flat, compressed prisms, which are permanent in the air, transparent, colourless, and have a fatty lustre; in vacuo over oil of vitriol they remain transparent, but lose 2·25 p. c. of their weight, and then when heated, melt without further loss to a transparent glass. (Chevreul.) The crystals contain 18·83 p. c. of water, and melt without loss to a transparent glass at 100°. (Pelouze & Gélis.)

Lerch constantly obtained anhydrous crystals infusible at 100°, and of the same composition, but sometimes (α) hard granular crusts, which by repeated crystallization passed into the following form, sometimes (β), nacreous laminae or flat flexible prisms. How these observations are to be reconciled with the preceding, remains to be seen.

The salt dissolves in 2·77 pts. of water at 10°, and rotates upon the surface; at 5° it dissolves in 400 pts. of absolute alcohol.

Butyrate of Strontia. — Obtained like the baryta-salt. Long flat needles, similar to those of the baryta-salt; and having the same odour.

When heated, it melts but does not turn brown. Dissolves in 3 pts. of water at 4°. (Chevreul.)

	Dried.		Chevreul.	
SrO	52	39·70	40·58	
C ⁸ H ⁷ O ³	79	60·30		
<hr/>				
C ⁸ H ⁷ SrO ⁴	131	100·00		

Butyrate of Lime. — Obtained in a similar manner. Transparent, very delicate needles, which smell like the baryta-salt. Melts when heated, emitting an aromatic odour, like that of the *Labiatae*. (*comp.* Chancel, p. 84.) The crystals give off their water of crystallization with tolerable facility. They rotate on water. (Pélouze & Gélis.) The salt dissolves in 5·69 pts. of water at 15°, and when the solution is heated, crystallizes out so completely that the whole becomes solid; on cooling, however, it resumes the liquid form. (Chevreul.)

	Dried at 140°.		Chevreul. Pel. & Gélis.	
CaO	28	26·17	26·99	26·27
C ⁸ H ⁷ O ³	79	73·83		
<hr/>				
C ⁸ H ⁷ CaO ⁴	107	100·00		

Butyrate of Lime and Baryta. — The aqueous solution of 2 pts. butyrate of lime and 3 pts. butyrate of baryta yields octohedrons by spontaneous evaporation. 100 pts. of these crystals, ignited with sulphuric acid yield 68 pts. of sulphate. 1 pt. of the salt dissolves in 3·8 pts. of water at 18°.

Butyrate of Magnesia. — Beautiful white laminæ, resembling crystallized boracic acid, containing 5 At. water, which readily escapes; they dissolve very readily in water and rotate upon it. (Pelouze & Gélis.)

Butyrate of Zinc. — Aqueous butyric acid dissolves carbonate of zinc with effervescence, at ordinary temperatures; the solution reddens litmus, even when the base is in excess; the filtrate evaporated in vacuo, leaves shining, fusible laminæ, having the taste and odour of the butyrates. (Chevreul.) Light, snow-white, pearly laminæ, sparingly soluble in water and alcohol. (Larocque & Hurault, *N. J. Pharm.* 9, 430.)

	Dried in vacuo.		Chevreul.	
ZnO	40	33·61	35	
C ⁸ H ⁷ O ³	79	66·39		
<hr/>				
C ⁸ H ⁷ ZnO ⁴	119	100·00		

The aqueous solution, when evaporated, gives off butyric acid, deposits a basic salt, and yields a residue which is still partially fusible, but, when water is repeatedly poured upon it and evaporated, becomes completely infusible, and ultimately retains only 100 pts. of C⁸H⁷O³ to 1525 pts. ZnO. (Chevreul.) [About 30 ZnO + C⁸H⁷O³.]

Butyrate of Lead. — *a. Tribasic.* — Oxide of lead is added in excess to butyric acid, whereupon heat is evolved; the solution is afterwards heated from without; the residue after evaporation exhausted with cold water; and the filtrate evaporated in vacuo over oil of vitriol. The residue is infusible, has but little taste, dissolves sparingly in water, and then absorbs carbonic acid rapidly from the air. (Chevreul.) — Alkaline butyrates form a copious white precipitate with subacetate of lead. (Zeise, *J. pr. Chem.* 29, 287.) — When an aqueous mixture of butyric and acetic acid is saturated with oxide of lead, and the filtrate super-

saturated with ammonia, small rose-coloured needles of basic butyrate of lead separate out; they quickly absorb carbonic acid from the air, and dissolve in water through the medium of the acetate of lead which adheres to them. (Nicklès, *Ann. Pharm.* 61, 349.)

		Chevreul.	
3 PbO	336	80·96	81
C ⁸ H ⁷ O ²	79	19·04	
2PbO, C ⁸ H ⁷ PbO ⁴	415	100·00	

b Monobasic. — The solution of lead-oxide in excess of the aqueous acid, yields fine silky needles by evaporation in vacuo over oil of vitriol. (Chevreul.) The same salt is precipitated by butyric acid from an aqueous solution of neutral acetate of lead, in the form of a colourless, very heavy oil, which solidifies after some time only. (Pelouze & Gélis.) Butyric acid, mixed with acetic acid, does not precipitate neutral acetate of lead. (Nicklès.) The needles distilled in a bent tube filled with mercury, yield 1 vol. olefiant gas to 9 vol. carbonic acid, together with water, and an oil which has a less powerful odour than that which is obtained from the baryta-salt, and a residue consisting of lead-oxide and metallic lead.

<i>Needles.</i>		Chevreul.	
PbO	112	58·64	60·50
8 C	48	25·13	24·81
7 H	7	3·66	2·77
3 O	24	12·57	11·92
C ⁸ H ⁷ PbO ⁴	191	100·00	100·00

Butyrate of Iron. — Aqueous butyric acid exposed to the air in contact with iron forms without effervescence a red solution, from which water throws down a very small quantity of ferric salt, which appears to redissolve on the addition of more water. (Chevreul.)

Butyrate of Copper. — Butyrate of potash (if not too dilute, according to Zeise) forms with cupric salts a blue-green precipitate, which may be obtained in the crystalline form by solution in boiling water. (Pelouze & Gélis.) — The crystals belong to the oblique prismatic system. *Fig.* 104, together with the *m* and *p*-faces. (Haüy.) In vacuo over oil of vitriol, they lose at most 1 per cent. of their weight, and become somewhat turbid. Heated alone to 100°, they retain their form and colour, and do not give off any portion of their acid; but their aqueous solution, when boiled, deposits a blue substance, which changes to pure brown oxide of copper, so that by repeated distillation with water, all the butyric acid passes over and all the cupric oxide is precipitated. (Chevreul.)

<i>Crystals dried in vacuo.</i>		Chevreul.	
CuO	40	29·20	30
C ⁸ H ⁷ O ²	79	57·66	
2 HO	18	13·14	
C ⁸ H ⁷ CuO ⁴ , 2Aq.	137	100·00	

According to Pelouze & Gélis also, the crystals contain 2 Aq., only 1 Aq. of which can be expelled by heat without decomposing the salt: according to Lies however (*Compt. rend.* 21, 321) the crystals contain only 1 Aq.; and since, according to his observations, they agree in form with crystallized verdigris, C⁴H⁴CuO⁴, Aq., he regards this as the first example of the isomorphism of two homologous salts, that is to say, of salts which differ in composition only in the number of atoms of C²H².

[Respecting a butylic acid compound resembling Schweinfurt green (viii, 329), see *Additions to this volume.*]

Mercurous Butyrate. — Butyrate of potash precipitates from mercurous nitrate, white shining scales, resembling those of mercurous acetate. (Pelouze & Gélis.)

Butyrate of Silver. — The potash-salt likewise forms with nitrate of silver, white shining scales, like those of acetate of silver; they must be washed with cold water. (Pelouze & Gélis.) — Butyrate of baryta forms with nitrate of silver, in somewhat concentrated solutions, a curdy precipitate, and but on more dilute solutions only a cloud, — in which case, on leaving the liquid to evaporate, the butyrate of silver crystallizes out in dendrites. (Lerch.) The salt does not deflagrate when heated, but leaves metallic silver mixed with a little charcoal. It dissolves sparingly in water. (Pelouze & Gélis.)

Dried at 100° to 120°.		Pel. & Gél.	Lerch.	J. Genks.
8 C	48	24·62	24·42	24·85
7 H	7	3·59	3·61	3·63
Ag	108	55·38	55·39	55·45
4 O	32	16·41	16·58	16·07
C ⁸ H ⁷ AgO ⁴	195	100·00	100·00	100·00

Butyric acid mixes in all proportions with *wood-spirit* and *alcohol*. (Chevreul, Pelouze & Gélis.)

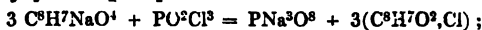
It dissolves *fixed oils* and *tallows*. (Chevreul, Barreswil.)

¶. Anhydrous Butyric Acid. C⁸H¹⁴O² = C⁸H⁷O² } O².

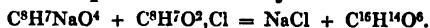
GERHARDT. *N. Ann. Chim. Phys.* 37, 318.

Butyric Butyrate, Butyric Anhydride.

Obtained by treating 4 pts. of dry butyrate of soda with 2 pts. of oxychloride of phosphorus, the oxychloride being added drop by drop to the butyrate, as in the preparation of anhydrous acetic acid (viii. 335). The reaction consists of two stages, the first being the formation of chloride of butyryl and phosphate of soda:



and the second, the formation of anhydrous butyric acid by the action of this chloride on another portion of the butyrate of soda:



As soon as the reaction is complete, the product is distilled; after which it is poured back upon the butyrate of soda, to decompose any portion of butyric chloride that may have remained unaltered, and finally rectified, those portions only being collected which boil at 190°. That which passes over at a lower temperature contains hydrated butyric acid, the formation of which cannot well be avoided, as the butyrate of soda is very deliquescent. — 2. By the action of chloride of benzoyl on butyrate of soda, the decomposition being precisely similar to that which takes place in the formation of anhydrous acetic acid by method 1 (viii. 335), butyric benzoate being first formed, and subsequently splitting up into butyric butyrate and benzoic benzoate. 5 pts. of chloride of benzoyl are mixed in a retort with 8 pts. of dry butyrate of soda, the mixture distilled, and the distillate rectified, first over butyrate of soda, afterwards alone.

Colourless, very mobile, strongly refracting liquid. Sp. gr. 0.978 at 12.5°. Its odour is very strong, but not disagreeable, like that of the hydrated acid, approaching rather to that of butyric ether. Boils at about 190°. — Vapour-density=5.38. (Gerhardt.)

		Gerhardt.	
16 C	96	60.76	60.67
14 H	14	8.86	8.87
6 O	48	30.38	30.46
<hr/>			
$\left. \begin{array}{l} \text{C}^8\text{H}^7\text{O}^2 \\ \text{C}^8\text{H}^7\text{O}^2 \end{array} \right\} \text{O}^2$	158	100.00	100.00
<hr/>			
		Vol.	Density.
C-vapour		16	6.6560
H-gas		14	0.9702
O-gas		3	3.3278
<hr/>			
Vap. of $\text{C}^{16}\text{H}^{14}\text{O}^6$	2	10.9540	
	1	5.4770	

Anhydrous butyric acid exposed to the air, gradually absorbs moisture. When poured into water, it does not mix immediately as the hydrated acid does, but rises to the surface in the form of a colourless oil. — In contact with *aniline* it becomes heated and forms *butyranilide*. $\text{C}^{20}\text{H}^{13}\text{NO}^2 = \text{C}^{16}\text{H}^{14}\text{O}^6 + 2\text{C}^{13}\text{H}^7\text{N} - 2\text{HO}.$

Acid allied to Butyric Acid.

Hircic Acid.

CHEVREUL. (1823.) *Ann. Chim. Phys.* 23, 22; also *Schw.* 39, 179. — *Recherches sur les corps gras*, 151 and 236.

Found (doubtless combined with glycerine in the form of an unknown fat, *Hircin*) in mutton suet, to which, as well as to mutton-broth, it imparts the peculiar taste and smell.

Preparation. 4 pts. of mutton suet are saponified with 1 pt. of hydrate of potash and 4 pts. of water; the whole supersaturated with phosphoric or tartaric acid; the watery liquid separated from the stearic and oleic acid distilled together with the wash-water; the distillate (which must be redistilled, if a sample of it leaves any residue on evaporation) neutralized with baryta-water; the solution evaporated; and the remaining baryta-salt decomposed with a mixture of equal parts alcohol and water.

Properties. Colourless oil lighter than water, not solidifying at 0°, very volatile. Smells like goats and like acetic acid, and reddens litmus strongly.

Combinations. It is slightly soluble in water.

The *Ammonia-salt* smells stronger than the free acid. — The *Potash-salt* is deliquescent. — The *Baryta-salt* is sparingly soluble in water, and contains 43.75 per cent. of baryta.

Hircic acid dissolves very readily in *alcohol*. (Chevreul.)

The distillate obtained by Chevreul's process yields, when neutralized with baryta-water and evaporated, two different salts, viz. crystalline hircate of baryta, which may be purified by washing with cold water and recrystallization, and a very soluble salt, which partly separates out in the form of a salve, partly remains in the mother-liquid, and when smeared on the hand, smells exactly like human fæces.

Hircate of baryta yields, by spontaneous evaporation of the aqueous solution, transparent, colourless pyramids, which are permanent in the air, have an alkaline, bitter taste, an alkaline reaction, and dissolve pretty easily in water. — The hircic acid obtained from this salt is very soluble in water. (Joss, *J. pr. Chem.* 4, 377.)

Conjugated Compounds of Butyric Acid.

Butyrate of Methyl. C¹⁰H¹⁰O⁴ = C³H³O, C⁸H⁷O³.

PELOUZE & GÉLIS. (1844). *N. Ann. Chim. Phys.* 10, 454.

PIERRE. *N. Ann. Chim. Phys.*

Methylic Butyrate, Butterformester.

Formation and Preparation. A mixture of 2 pts. butyric acid with 2 pts. wood-spirit and 1 pt. oil of vitriol, becomes heated and immediately separates into two layers, the upper of which must be taken off, washed with water, dried over chloride of calcium, and distilled. (Pelouze & Gélis.) — The three liquids must be repeatedly shaken up together, and if the mixture has a tendency to cool, it must be kept for some time at 50° to 80°, so that the formation of the butyrate of methyl may take place as quickly as possible; after the compound ether has been repeatedly washed with water, it must be shaken up with chloride of calcium and chalk to remove water and free acid, and rectified two or three times over chloride of calcium. (Pierre.)

Properties. Transparent, colourless liquid of sp. gr. 1·02928. (Pierre.) Boils at 102° (Pelouze & Gélis); at 102·1° under a pressure of 0·7439 met.; but with sudden starts, unless threads of glass or pieces of platinum wire are immersed in it. (Pierre.) Specific heat 0·49176. Latent heat of vapour 87·33. (Favre & Silbermann, *Jahresber.* 1853, 78.) Vapour-density, 3·52. (Pelouze & Gélis.) Its odour is peculiar, but somewhat like that of wood-spirit (Pelouze & Gélis); rather pleasant, like that of pine-apples. (Pierre.)

		Pierre.				Vol.	Density.
10 C.....	60	58·82	58·69	C-vapour	10	4·1600	
10 H	10	9·81	9·99	H-gas	10	0·6930	
4 O.....	32	31·37	31·32	O-gas	2	2·2186	
C ¹⁰ H ¹⁰ O ⁴	102	100·00	100·00		2	7·0716	
					1	3·5358	

Decomposition. Butyrate of methyl is inflammable. (Pelouze & Gélis.)

Combinations. It dissolves sparingly in water, but in all proportions in wood-spirit and alcohol. (Pelouze & Gélis.)

Butyrate of Ethyl. $C^{12}H^{12}O^4 = C^4H^8O, C^8H^7O^3$.

PELOUZE & GÉLIS. (1844.) *N. Ann. Chim. Phys.* 10, 464.
 LERCH, WÖHLEN & BORNTRÄGER, *Ann. Pharm.* 99, 220 and 359.
 PIERRE. *N. Ann. Chim. Phys.* 19, 214.

Butyric Ether, Vinic or Ethylic Butyrate, Buttervinester. The so-called *Ananas oil* used in perfumery consists chiefly of this ether. (Hofmann, *Ann. Pharm.* 81, 87.)

Formation and Preparation. — A solution of butyric acid in alcohol acquires after a while the odour of pine-apples, from formation of butyric ether. (Chevreul.) — 1. Pelouze & Gélis, and likewise Pierre, prepared this compound by a process exactly similar to that above given for butyrate of methyl. — 2. Lerch heats butyrate of baryta with a mixture of alcohol and sulphuric acid to the boiling point, takes off the butyric ether which rises to the surface, washes it with water, dries with chloride of calcium, and rectifies. — 3. Wöhler saponifies butter with strong solution of potash; dissolves the resulting soap in the smallest possible quantity of hot strong alcohol; adds to the solution a mixture of alcohol and oil of vitriol till it acquires a strong acid reaction; distils till the distillate no longer smells of apples; rectifies the distillate several times; and dehydrates it with chloride of calcium. [This product is likely to be contaminated with caproic, caprylic, and capric ether]. — 4. Butyric ether is likewise obtained by the action of alcohol and hydrochloric acid on the butyrins. (Berthelot, p. 94.)

Properties. Transparent, colourless, very thin liquid (Pelouze & Gélis); of sp. gr. 0.90193 at 0°. (Pierre.) Index of refraction 1.3778. (Delfs, *Pogg.* 81, 470.) Boils at 110° (Pelouze & Gélis); at 119° under a pressure of 0.7465 met. (Pierre.) Vapour-density = 4.04. (Pelouze & Gélis.) Has an agreeable odour something like pine-apples (Pelouze & Gélis); and like pippins (Pierre); tastes sweetish, with a somewhat bitter after-taste. (Lerch.)

	Lerch.		Bornträger.		Pierre.	
12 C.....	72	62.07	62.29	61.57	61	93
12 H.....	12	10.35	10.46	10.91	10	45
4 O.....	32	27.58	27.25	27.52	27	62
$C^{12}H^{12}O^4$	116	100.00	100.00	100.00	100	00
			Vol.	Density.		
C-vapour.....			12	4.9920		
H-gas.....			12	0.8316		
O-gas.....			2	2.2186		
Vap. of Butyric ether			2	8.0422		
			1	4.0211		

Decompositions. 1. Butyric ether is very inflammable. — 2. It is but slowly decomposed by aqueous potash, even at a boiling heat, the products being alcohol and butyrate of potash. (Pelouze & Gélis.) — 3. By agitation with aqueous ammonia, it is slowly resolved into butyramide and alcohol (Chance):



4. Heated with glycerine and hydrochloric acid, or even with glycerine alone, it yields a butyrin, probably monobutyryn. (Berthelot, p. 93.)

Combinations. It dissolves very sparingly in water, but in all proportions in alcohol and vinic ether. (Pelouze & Gélis.)

Butyrin.

CHEVREUL. (1819.) *Ann. Chim. Phys.* 22, 371; 23, 27. — *Recherches*, 192, 270 and 476.

Butirine, Butterfett. — Occurs in small quantity in the butter of cows' milk, together with caproin, caprin, olein, and margarin. (Chevreul.)

Preparation. Butyrin has not yet been obtained free from caproin, caprin, olein, and margarin. Butter is freed from adhering butter-milk by melting it at 60° in a tall vessel, decanting the upper transparent layer of fat, filtering it warm, agitating with water at 40°, and again leaving it to subside, decanting, and filtering. It must then be left for several days at 19°; the granules of margarin pressed against the sides of the vessel with a spatula, to extract the oily portion, and the butter filtered. This oily liquid, which does not redden litmus, is a mixture of butyrin, caproin, and olein. As the latter is much less soluble in alcohol than the other fats, the mixture may be shaken up at 19° with an equal quantity of alcohol of sp. gr. 0.796; the solution decanted from the undissolved portion, which consists of a large proportion of olein with a little butyrin; freed from the alcohol by distillation; digested — as it now contains free butyric acid — with carbonate of magnesia and water; the watery liquid containing butyrate of magnesia poured off; and the fat freed from admixed carbonate of magnesia by solution in alcohol, filtration, and careful evaporation.

Properties. The mixture of fats thus obtained [which, as the saponification shows, contains only 16 p. c. butyrin] is, according to the kind of butter used, a colourless, or more frequently but perhaps only accidentally, a yellow oil; has a sp. gr. of 0.908 at 19°; solidifies at about 0°; has the odour of heated butter; neutral.

Decompositions. 1. Butyrin, by the mere boiling of its alcoholic solution, acquires the property of reddening litmus, from liberation of butyric acid. In a warm atmosphere, butyrin acquires by incipient decomposition, the power of reddening litmus, and a strong odour of butyric acid, which may however be removed by magnesia. The odour of butter is likewise due to small quantities of butyric acid gradually eliminated from the butyrin contained in it; a mixture of butyric acid and hog's lard loses the odour of butter much sooner, because in such a mixture all the acids which it contains are in the free state, and are not replaced by fresh quantities as they evaporate. — 2. When heated to 100° with an equal quantity of oil of vitriol, and then left to itself, it gives off an odour of butyric and sulphurous acids. It is saponified with peculiar facility by potash. In this decomposition, 100 pts. of the fat yield (1) a quantity of butyric acid (together with smaller quantities of caproic and capric acid) sufficient to produce 26 pts. of baryta-salt; (2) 80.5 parts of a mixture of a large quantity of oleic and a small quantity of margarinic acid, which solidifies at 32°; and (3) 12.5 pts. of glycerine. [Pure butyrin would probably yield nothing but butyric

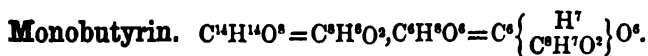
acid and glycerin, and the substance examined as above still contained large quantities of olein, together with margarin, capric, and caproin.]

Combinations. Butyrin mixes in all proportions with boiling alcohol of sp. gr. 0·822. The warm mixture remains clear on cooling if it contains 120 pts. butyrin to 100 alcohol; but a mixture of 20 pts. butyrin to 100 alcohol becomes somewhat turbid. (Chevreul.)

Artificial Butyrin.—When a mixture of butyric acid, glycerin, and oil of vitriol is heated, a yellowish oil rises to the surface. Hydrochloric acid gas may also be passed at ordinary temperatures through a mixture of butyric acid and glycerin, and the separation of the oil effected by addition of water. The oil obtained by either of these processes, amounts, after being washed with a large quantity of water, to 60 or 70 p. c. of the butyric acid used, and has an odour and sharp taste, due perhaps to a foreign product. By saponification, it is reconverted into butyric acid and glycerin. It is insoluble or very sparingly soluble in water, but dissolves in all proportions in ether and alcohol, whence it is separated by water. It remains still to be decided whether this artificial butyrin agrees in composition with natural butyrin, supposing that we can succeed in obtaining the latter in a state of purity. (Pelouse & Gélis, *N. Ann. Chim. Phys.* 10, 455.)

[According to the theory developed in vii, 231, butyrin should be formed from 1 At. glycerine + 4 At. butyric acid — 8 HO, therefore $C^8H^{10}O^2 + 4C^4H^8O^2 = C^{12}H^{14}O^6 - 8HO = C^6H^{14}O^8 = C^{28}H^{28}O^{14}$.]

¶ The three following artificial butyrins homologous with the acetins (ix. 495), have been obtained by the direct action of butyric acid upon glycerine.



BERTHELOT. *N. Ann. Chim. Phys.* 41, 261.

This compound is obtained by exposing a mixture of glycerine and butyric acid, either to sunshine or to diffused daylight for three months, at ordinary temperatures. — 2. By heating butyric acid with excess of glycerine to 200° for three hours—the temperature not exceeding 200°.

1. Neutral, oily, odoriferous liquid, having an aromatic and bitter taste, without any unpleasant after-taste. At — 40° it remains liquid and almost as mobile as at ordinary temperatures. Sp. gr. 1·088 at 17°.

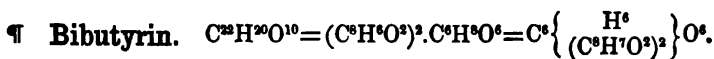
				<i>a.</i>	<i>b.</i>	<i>c.</i>
14 C.....	84	51·8	51·0 50·5
14 H.....	14	8·6	8·9 8·8
8 O.....	64	39·6	40·1 40·7
<hr/>						
$C^{14}H^{14}O^8$	162	100·0	100·0 100·0

a and *b* were prepared at 200°; *c* at ordinary temperatures.

Decompositions. 1. Monobutyryn when exposed to the air, acquires a slight acid reaction. — 2. Saponified with baryta-water, it yields glycerine and butyric acid, the quantity of the latter amounting to about half that of the butyryn, which agrees with the calculated result, [the atomic weight of butyryn being 162, and that of butyric acid, C⁸H⁸O⁴, amounting to 88]. — 3. Treated with alcohol and hydrochloric acid, it is converted, without the aid of heat, into glycerine and butyric ether. — 4. It is decomposed by the pancreatic juice, into butyric acid and glycerine.

Combinations. Monobutyryn mixes with water, and in certain proportions forms a stable emulsion. When 1, 2, and 3 vol. water are successively added to 8 vol. monobutyryn, the water dissolves, and the whole forms a limpid liquid. 2 vol. more water render the mixture slightly opalescent; and 13 vol. more (18 in all) produce an opaque homogeneous emulsion,* which is stable, and remains entire, even after several hours' repose. If this mixture be successively diluted so as to mix with 1 vol. butyryn, first 5, then 32, and at last even 220 vol. water, the liquid still remains in the state of a perfect emulsion, stable and opalescent; 900 vol. water render the liquid almost wholly transparent, without actually forming a true solution. This behaviour of monobutyryn with water serves to distinguish it from the other butyryns.

A butyryn is likewise obtained by the action of hydrochloric acid gas or strong sulphuric acid on a mixture of glycerine and butyric acid (p. 93). Phosphoric and tartaric acid also determine the combination. — Also by heating a mixture of glycerine butyric, butyric ether, and hydrochloric acid to 100° for several hours. On decanting the undecomposed butyric ether, and evaporating, there remains a neutral, inodorous fixed residue which dissolves easily and completely in ether, and when treated with alcohol and hydrochloric acid, is resolved into butyric ether and glycerine. — Butyric ether heated to 100° with glycerine alone, also yields in the course of 102 hours a trace of neutral matter fixed and insoluble in ether. (Berthelot.)



BERTHELOT. *N. Ann. Chim. Phys.* 41, 264.

Dibutyryn. (Berthelot.) — *Preparation.* 1. By heating a mixture of glycerine and butyric acid to 275° for several hours. — Whenever, in the preparation of monobutyryn, the temperature rises above 220°, bibutyryn appears to be formed at the same time. In one experiment, six tubes containing the same mixture of glycerine and butyric acid were heated to 200° for three hours. On opening one of them at the end of that time, it was found to contain a considerable quantity of monobutyryn. The other five, heated to 275° for 12 to 15 hours longer, yielded bibutyryn, but in quantity less than that of the monobutyryn obtained from the single tube previously opened. — 2. By heating to 200° for several hours a mixture of glycerine and butyric acid diluted with water. — 3. By heating to 200° for three hours a mixture of 1 pt. of glycerine with 4 pts. of butyric acid. — Berthelot originally supposed that this last mentioned process yielded another

* This phenomenon is similar to that observed by Chevreul with natural butyryn and alcohol (p. 93).

body, *butyridin* = $C^{14}H^{12}O^7$, — but he now finds this product to be identical with bibutyryn.

Neutral, odoriferous, oily liquid, which volatilizes at 320° , without perceptible alteration. Sp. gr. 1.082 at 17° before distillation, 1.081 after distillation. Sp. gr. of a product obtained by the third process, 1.082. Remains liquid at -40° , but becomes less mobile.

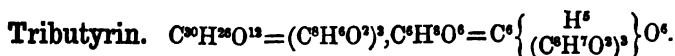
		Berthelot.					
		<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>e.</i>	<i>f.</i>
22 C	132	56.9	53.8	53.1	52.6	54.1	54.3
10 H	10	8.6	9.4	8.9		8.7	9.1
10 O	80	34.5	36.8	35.0		37.2	37.1
$C^{22}H^{20}O^8$	222	100.0	100.0	100.0		100.0	100.0

a. prepared at 275° ; *b.* the same after distillation; *c.* prepared at 200° with the aqueous acid; *d.* prepared by the third process and separated from the watery liquid at the moment of saturation by carbonate of potash; *e.* the portion of the same preparation which remained dissolved in the watery liquid and was extracted by ether; *f.* another preparation.

Berthelot assigns to bibutyryn the formula $C^{22}H^{20}O^{12}$, supposing only 2 At. water to be eliminated in its formation [$C^{22}H^{20}O^{12} = 2C^9H^8O^4 + C^6H^6O^6 - 2HO$]; this formula requires C = 52.8 p. c.; H = 8.8, which agrees with the analyses rather better than the formula $C^{22}H^{20}O^{10}$; but as the formula $C^{22}H^{20}O^{12}$ is altogether anomalous and inconsistent with that of other bodies of the same group (see ix. 492), and as moreover there appears to be considerable difficulty in obtaining this body in a definite state and free from monobutyryn, it is most probable that the correct formula is $C^{22}H^{20}O^{10}$, which supposes the elimination of 4 At. water.

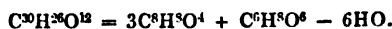
Decompositions. 1. Bibutyryn when heated above 320° , begins to turn acid and yield acrolein. — 2. Heated with water to 220° for some time, it is decomposed, with liberation of butyric acid. This decomposing action of water appears also to be exerted at ordinary temperatures, bibutyryn, as well as the other butyryns, rapidly acquiring a slight acid reaction when exposed to the air. This acidification is not due to oxidation, for monobutyryn and bibutyryn in contact with moist oxygen, with or without addition of brass filings or oxide of lead, do not absorb any perceptible quantity of oxygen in the course of ten weeks. — 3. Bibutyryn (prepared either by the first or the third process) is resolved by baryta into glycerine (slightly saline) and about $\frac{2}{3}$ of its weight of butyric acid, which nearly corresponds with the calculated quantity, [$C^{22}H^{20}O^{10} = 242$; $2C^9H^8O^4 = 176$.] 4. Treated with aqueous ammonia, it yields in five days, crystals of butyramide $C^9H^8NO^2$. — 5. Treated with alcohol and hydrochloric acid at ordinary temperatures, it is resolved, in the course of a few hours, into butyric ether and glycerine. Alcohol alone produces the same decomposition in 48 hours, at 100° in an open vessel.

Combinations. *a.* With Water. — 1 vol. bibutyryn and 1 vol. water form a limpid mixture; the addition of another 1 vol. water precipitates the bibutyryn, which collects quickly at the bottom of the vessel; the addition of 3 vol. more water accelerates the deposition considerably; 150 to 200 vol. water form a transparent solution or emulsion. — *b.* Bibutyryn mixes with alcohol and ether. (Berthelot.)



BERTHELOT. *N. Ann. Chim. Phys.* 41, 267.

Formation. From butyric acid and glycerine, with elimination of 6 At. water:



Preparation. By heating bibutyryn with 10 to 15 times its weight of butyric acid to 240° for four hours.

Properties. Neutral, limpid, oily liquid, of sp. gr. 1.056 at 8°. Has an odour like that of the other butyrins, and a pungent taste with bitter after-taste.

		Berthelot.	
30 C	180	59.6	59.8
26 H	26	8.6	9.1
12 O	96	31.8	31.1
C ³⁰ H ²⁶ O ¹²	302	100.0	100.0

Treated with alcohol and hydrochloric acid at ordinary temperatures, it yields butyric ether and glycerine.

Insoluble in water; very easily soluble in alcohol and ether; sparingly in cold dilute alcohol. (Berthelot.)

Comparison of natural with artificial Butyrins. Butter treated with alcohol yielded an oil containing 6.3 to 6.9 pts. glycerine to 10 pts. butyric acid. — The liquid portion of butter yielded oils containing 3.1, 3.4 and 4.0 pts. glycerine to 10 pts. butyric acid. — On the other hand, monobutyryn should contain 10.5 glycerine to 10 pts. butyric acid; bibutyryn 5.2 to 10; tributyryn 3.5 to 10. The composition of natural butyryn appears therefore to be intermediate between that of the artificial butyrins.

Butyroglyceric Acid? When the liquid obtained in the preparation of the butyrins, as above, is saturated with carbonate of potash, it separates into two layers. — On agitating with a small quantity of ether, the upper layer forms with the ether a stable mixture which admits of filtration; and if this mixture be decanted and ether added to it in large quantity, a watery stratum is immediately precipitated, and an upper ethereal stratum formed containing the neutral compound. The precipitated aqueous stratum retains a considerable quantity of butyryn, which can only be separated by treating it 25 or 30 times with cold ether. The watery liquid then remaining leaves on evaporation a saline mass which, when treated with hydrochloric acid and alcohol, yields butyric ether, glycerine, and chloride of potassium (in one experiment 0.088 grm. of glycerine and 0.133 grm. KCl, corresponding to 0.084 grm. KO.) This result seems to indicate the formation of a butyroglycerate of potash. (Berthelot, *N. Ann. Chim. Phys.* 41, 271.) ¶.



CHANCEL. (1844.) *N. Ann. Pharm.* 12, 146; also *Compt. rend.* 18, 1023; abstr. *J. pr. Chem.* 33, 453; abstr. *Ann. Pharm.* 52, 295. — *N. J. Pharm.* 7, 116, 13, 462.

Chevreul obtained by the dry distillation of various alkaline butyrates, a volatile oil having the odour of the Iabiatæ; this oil was more exactly investigated by Chancel in 1844, and recognised as the ketone of the butyric series.]

Preparation. Dry butyrate of lime in quantity not exceeding a few grammes, is carefully heated in a retort till it is resolved into carbonate of lime and nearly pure butyrene, amounting to 42 or 43 p. c. of the lime-salt (p. 83). The product is distilled in a retort fitted with a thermometer; it begins to boil below 100° , but the boiling point soon rises to 140° ; below 140° , the distillate consists chiefly of butyral; but between 140° and 150° , at which temperature the receiver must be changed, the butyrene passes over; it may be purified by a second distillation. The liquid which passes over above 150° , is a mixture of butyrene with the oil mentioned on page 84.

Properties. Transparent, colourless, oil, of sp. gr. 0.83. When surrounded with a mixture of ether and solid carbonic acid, it solidifies in broad, transparent, and colourless laminae. Boils at about 144° . Vapour-density = 3.99. (*Compt. rend.* 21, 273.) Has a peculiar penetrating odour and burning taste.

Calculation, according to Chancel.			Vol.	Density.	
14 C	84	73.69	C-vapour.....	14	5.8240
14 H	14	12.28	H-gas	14	0.9702
2 O	16	14.03	O-gas	1	1.1093
<hr/>			<hr/>		
C ¹⁴ H ¹⁴ O ²	114	100.00	Vap. of butyrene	2	7.9035
				1	3.9517

Decompositions. 1. Butyrene is very inflammable and burns with a luminous flame. — 2. When exposed to the air, it gradually absorbs oxygen gas, but without acquiring any colour. — 3. Takes fire immediately in contact with crystallized chromic acid. — Mixed with an equal volume of cold moderately strong nitric acid, it rises to the top, turns red, and afterwards green, and when gently heated gives off with violence nitrous vapours mixed with carbonic acid gas and an ethereal liquid smelling like butyric ether, while nitropropionic acid (ix. 430) remains behind. — 5. When butyrene is distilled with pentachloride of phosphorus, phosphoric acid remains behind, and hydrochloric acid passes over, together with a chlorobutyrene, C¹⁴H¹²Cl. — [This product appears rather to be chlorobutylene, C⁸H⁷Cl; *q. v.*]

Combinations. Butyrene is nearly insoluble in water, to which however it imparts its odour. Mixes in all proportions with alcohol.

Odmyl. C⁸H⁸S²?

ANDERSON (1847). *Phil. Mag. J.* 31, 161; also *Ann. Pharm.* 63, 370; also *J. pr. Chem.* 42, 1. .

3 lb. of linseed or olive oil is gradually distilled for a whole day with a small quantity of sulphur, in a flask of 5 times the capacity of the liquid, over a fire which must be kept uniform and can be removed if the mixture threatens to froth over, a piece of sulphur being also added from time to time, so as to keep up a uniform effervescence; the distillate is received in a vessel surrounded with ice and fitted with a bent tube, to conduct the most volatile portion into a bottle containing

alcohol. If the heat be not sufficient, the mass becomes thick and froths over; if it be too great, the evolution of gas becomes too violent. When the mass has decreased to one-third, the residue becomes very thick, and often causes the flask to crack. A large quantity of sulphuretted hydrogen is evolved, and a red-brown sulphuretted oil is obtained together with crystals of margaric acid. By repeated rectification of the oil, the most volatile portion, which is the least abundant, is obtained in the form of a transparent, colourless, very mobile oil, boiling at 71° . This is *impure odmyl*, of variable composition, three analyses of different preparations giving :

C	75.03	...	78.79	...	79.95
H	12.20	...	12.71	...	12.75

But this impure odmyl yields with corrosive sublimate and bichloride of platinum, precipitates of constant composition.

Mercury-precipitate. — The alcoholic solution of impure admyl forms with an alcoholic solution of corrosive sublimate, a white bulky precipitate, which is washed on the filter with a large quantity of ether, (to remove another oil likewise containing sulphur,) then dissolved in a large quantity of boiling alcohol, from which, after filtration and cooling, the pure compound separates as a white nacreous powder, which appears under the microscope to consist of six-sided tables. Even after long washing with ether, it exhibits a slightly unpleasant odour, which increases when the compound is heated.

<i>Calculation according to Anderson.</i>				<i>Anderson.</i>	
16 C	96.0	...	14.48	14.61
16 H	16.0	...	2.42	2.72
4 Hg	400.0	...	60.35	60.01
2 Cl	70.8	...	10.68	10.46
5 S	80.0	...	12.07	12.48
<hr/>			<hr/>		
	662.8	...	100.00	100.28

$C^8H^8S^2, 2HgCl + C^8H^8S^2, Hg^2S$. (Anderson.) Gerhardt (*N. J. Pharm.* 12, 369) prefers the formula $C^{16}H^{16}S^2, 2Hg^2Cl$.

The precipitate gives off when heated, an oil having a disgusting odour. Caustic potash turns it yellow, showing that it contains not dichloride but protochloride of mercury. [What becomes of the disulphide of mercury supposed to exist in the precipitate?] The precipitate, when diffused in water, is immediately blackened by sulphuretted hydrogen; and then yields by distillation a transparent, colourless oil, perhaps pure odmyl, which floats on water, and whose alcoholic solution again forms a white precipitate with chloride of mercury, and yellow with bichloride of platinum. The precipitate is insoluble in water, and is not readily moistened by that liquid; it dissolves in some hundred parts of boiling alcohol, but separates as a crystalline powder on cooling; it dissolves in oil of turpentine at about the same rate as in alcohol; but most abundantly in the most volatile oil of coal-tar.

Platinum-precipitate. — The alcoholic solution of impure odmyl gradually forms a sulphur-yellow precipitate with bichloride of platinum. (The oil which passes over between 150° and 205° , after the impure odmyl, forms an orange-yellow precipitate, containing 49.6 p. c. platinum.) The precipitate, when heated, gives off the same oil as the mercury-precipitate, and leaves black

sulphide of platinum. Hydrosulphate of ammonia converts it into a brown powder.

				Anderson.
16 C	96.0	...	20.83 22.26
16 H	16.0	...	3.47 3.99
2 Pt	198.0	...	42.97 43.06
2 Cl	70.8	...	15.37	
5 S	80.0	...	17.36	
460.8 100.00				

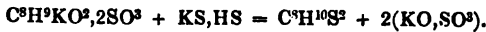
$C^8H^{10}S^2, PtCl^2 + C^8H^8S^2, PtS$. (Anderson.) If the precipitate be regarded as $C^{16}H^{16}S^4Pt^2Cl^2$, odmyl will be $C^{16}H^{16}S^4$. (Gerhardt.)

Impure odmyl dissolved in alcohol produces but a slight cloud with neutral acetate of lead or nitrate of silver; but, on heating the liquid, sulphate of lead or silver is precipitated. (Anderson.)

¶ Butylic Mercaptan. $C^8H^{10}S^2 = C^8H^8, H^2S^2$.

E. HUMANN. *N. Ann. Chim. Phys.* 44, 337; *Ann. Pharm.* 95, 256; *Chem. Soc. Qu. J.* 8, 274.

Formation and Preparation. By distilling at the heat of the water-bath, a mixture of aqueous sulphhydrate of potassium and concentrated aqueous sulphobutylate of potassium, the product being received in a well-cooled flask:



The oily liquid which condenses is decanted, placed in contact with chloride of calcium, and distilled, the portion which passes over between 85° and 90° being collected apart.

Properties. Colourless, very mobile liquid, having the peculiar disagreeable odour which characterises the mercaptans. Sp. gr. 0.848 at 11.5°. Vapour-density 3.10. Boils at 88°. Has no action on vegetable colours.

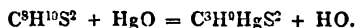
				Humann.
8 C	48	...	53.33 53.52 53.16
10 H	10	...	11.11 11.71 11.32
2 S	32	...	35.56	
$C^8H^{10}S^2$ 90 100.00				

		Vol.	Density.
C-vapour	8	3.3280
H-gas	10	0.6930
S-vapour	1	2.2186
Vapour of $C^8H^{10}S^2$ 2 6.2396			
		1 3.1198

May be regarded as C^8H^8S, HS or as $C^8H^8 \left. \begin{matrix} H \\ S \end{matrix} \right\} S^2$.

Decomposition. 1. Butylic mercaptan is very inflammable, and burns with a pale blue flame. — 2. Dilute nitric acid acts very strongly on it; the liquid turns red from formation of nitric oxide, which dissolves in it, but the colour disappears gradually on heating, and an oily liquid

is found on the surface.—3. Potassium decomposes butylic mercaptan, with evolution of hydrogen and formation of the compound C³H⁹KS².—4. Several heavy metallic oxides in the free state, or dissolved in acids, decompose butylic mercaptan, forming water and a metallic butylmercaptide; *e. g.* with mercury :



Combinations. Butylic mercaptan dissolves very sparingly in *water*. It dissolves *sulphur* and *iodine*.

Butylmercaptide of Potassium. C³H⁹KS².—White granular compound obtained by the action of potassium on butylic mercaptan.

Butylmercaptide of Lead. C³H⁹PbS².—Yellow crystalline precipitate formed on pouring an alcoholic solution of butylic mercaptan into acetate of lead.

Butylmercaptide of Mercury. C³H⁹HgS².—When an alcoholic solution of butylic mercaptan is poured upon red oxide of mercury, a rapid action takes place, attended with considerable evolution of heat; and on dissolving the product in alcohol, and leaving the solution to cool, this compound is deposited in white nacreous scales, which are very fusible and unctuous to the touch. The compound is decomposed by sulphuretted hydrogen, yielding sulphide of mercury and butylic alcohol.

				Humann.
8 C.....	48	25.39 25.78
9 H	9	4.76 5.01
Hg	100	52.91 52.55
2 S.....	32	16.94	
C ³ H ⁹ HgS ²				189 100.00

Butylic mercaptan forms white precipitates with acetate of *copper* and perchloride of *gold*.

Butylic mercaptan dissolves in all proportions in *alcohol* and *ether*. (Humann.)

¶ Iodide of Butyl. C³H⁹I=C³H⁸,HI.

WURTZ, *N. Ann. Chim. Phys.* 42, 129; *Ann. Pharm.* 3, 115.

Preparation. By the action of iodine and phosphorus on butylic alcohol. 1.5 pt. iodine is added to 1 pt. butylic alcohol in a vessel surrounded with cold water, and a quantity of phosphorus, equal to about $\frac{1}{8}$ of the iodine, added in successive small portions, the mixture being heated towards the end of the process, to render the action complete. The dark colour of the liquid then gradually changes to brownish yellow, whilst hydriodic acid is abundantly evolved, which, together with a small quantity of iodide of butyl that passes over with it, is received in a small quantity of cold water. As soon as the colouring produced by the iodine has disappeared, and the liquid is in full ebullition, it is left to cool, and that which remains in the distillation-vessel is washed, first with

the aqueous hydriodic acid previously collected, whereby a small quantity of undecomposed butylic alcohol is dissolved, and then with pure water; it is then dehydrated with chloride of calcium, and freed from the still remaining portion of butylic alcohol, by treating it while warm with pulverized iodide of phosphorus,* till the latter crystallizes out on cooling. The liquid is then distilled, the distillate washed with water, dehydrated over chloride of calcium, and rectified, the portion which passes over between 118° and 122° being collected apart.

Properties. Colourless when recently prepared, but soon turns brown by exposure to light. Refracts light strongly. Boils at 121°, but when a mixture of water and iodide of butyl is distilled, the thermometer, at the beginning of the distillation, when the iodide of butyl chiefly passes over, indicates only 88° to 89°. Sp. gr. 1.604 at 19°. Vapour-density = 6.217.

		Wurtz.				
8 C....	48	26.22	26.04 to 26.59	C-vapour.....	8	3.3280
9 H....	9	4.91	4.92 — 5.13	H-gas	9	0.6237
I	126	68.87	68.68	I-vapour	1	8.7356
<hr/>						
C ⁸ H ⁹ I	183	100.00		Vap. of C ⁸ H ⁹ I	2	12.6873
					1	6.3436

Decompositions. 1. Iodide of butyl burns with difficulty, and only in contact with a burning body; the combustion is attended with evolution of iodine vapours. — 2. It is but slowly attacked by aqueous potash, even when boiled therewith for some time; but alcoholic potash decomposes it with formation of butylic alcohol and iodide of potassium. — 3. Potassium decomposes iodide of butyl, yielding butyl and iodide of potassium. — 4. With butylate of potassium, C⁸H⁹KO², it forms butylic ether and iodide of potassium (p. 69). — 5. With oxide of silver, it forms butylic ether and iodide of silver. — 6. With silver-salts, e. g. the carbonate, sulphate, acetate, &c. it forms iodide of silver and a compound ether, e. g. carbonate, sulphate, acetate, &c. of butyl. A solution of nitrate of silver is immediately precipitated by iodide of butyl. (Wurtz.)

‡ Bromide of Butyl. C⁸H⁹Br = C⁸H⁹,HBr.

WURTZ. *N. Ann. Chim. Phys.* 42, 129; *Ann. Pharm.* 93, 114.

Formation and Preparation. By the action of bromine and phosphorus on butylic alcohol. A few drops of bromine are added to butylic alcohol; a small piece of phosphorus thrown in, the liquid being kept cool and shaken till the colour of the bromine is destroyed; the addition of bromide and phosphorus then repeated; and so on continually till vapours of hydrobromic acid are abundantly evolved, and a quantity of

* Wurtz prepares this compound by adding 8 or 10 pts. of iodine to 1 pt. of phosphorus in a small flask or a glass tube that may be closed, whereupon violent action ensues and the resulting compound fuses. It is then heated for a few seconds till the layer which adheres to the glass on moving the vessel exhibits a dark red colour by transmitted light, and the liquid compound separates from the excess of phosphorus which has passed into the red modification. The iodide of phosphorus separates in the crystalline form on cooling, and may be easily rubbed to a dark-red powder.

bromine has been added, at least equal to that of the butylic alcohol. The liquid is then distilled at a temperature not exceeding 100°, and the resulting vapours passed into a flask containing water, which dissolves the hydrobromic acid, while the impure bromide of butyl collects at the bottom. The latter is washed with water, dried with a little chloride of calcium, and rectified; that which passes over at 89° is pure bromide of butyl.

Properties. Oily liquid, having an ethereal odour, and boiling at 89°. Sp-gr. = 1.274 at 16°. Vapour-density 4.720.

		Wurtz.	
8 C	48	35.03	34.58
9 H	9	6.56	6.67
Br	80	58.41	57.91
<hr/>			
C ⁶ H ⁸ Br	137	100.00	99.55
<hr/>			
C-vapour	8	3.3280	
H-gas	9	0.6237	
Br.-vapour	1	5.5465	
<hr/>			
Vap. of C ⁶ H ⁸ Br	2	9.4982	
	1	4.7491	

Decompositions. 1. *Potassium* decomposes bromide of butyl, slowly at ordinary temperatures, but with violence when heated. When the two substances are heated together in a sealed tube, decomposition begins as soon as the potassium melts, a large quantity of gas, probably butylene and hydride of butyl, being evolved, and the tube explodes with violence. — 2. *Ammonia* acts slowly on bromide of butyl at ordinary temperatures, forming hydrobromate of butylamine. (Wurtz.)

¶ Chloride of Butyl. C⁶H⁸Cl=C⁶H⁸, HCl.

WURTZ. *N. Ann. Chim. Phys.* 42, 129; *Ann. Pharm.* 93, 113.

Formation and Preparation. 1. By the action of hydrochloric acid on butylic alcohol. When the alcohol is saturated with hydrochloric acid gas, and the liquid sealed up in a glass tube and heated in the water-bath, a large quantity of chloride of butyl is produced, and may be obtained pure by washing the product with water, distilling, and separating the portion which goes over between 70° and 75°. — 2. By the action of pentachloride or oxychloride of phosphorus on butylic alcohol. The alcohol is placed in a flask with a long neck, which must be kept very cool, and the chloride of phosphorus added by small portions. Violent action takes place, attended with great evolution of heat, and the pentachloride is converted into oxychloride, which then acts on the last portions of butylic alcohol. The oxychloride may also be used from the beginning instead of the pentachloride, in which case the action is less violent. In either case, the contents of the flask must be left to stand for 24 hours, and then distilled, the portion which passes over below 100° being collected apart; this portion is then washed with water, dried over chloride of calcium, and rectified, collecting separately the portion which distils over at 70°.

Properties. Chloride of butyl is a liquid lighter than water, and having an ethereal odour, recalling also that of chlorine. Boiling point about 70°.

		Wurtz.	
8 C	48.0	51.88	51.21
9 H	9.0	9.72	9.69
Cl	35.4	38.40	38.40
<hr/>			
C ⁸ H ⁹ Cl	92.4	100.00	
<hr/>			
C-vapour	8		3.3280
H-gas	9		0.6237
Cl-gas	1		2.4543
<hr/>			
Vap. of C ⁸ H ⁹ Cl	2		6.4060
	1		3.2030

Chloride of butyl is rapidly decomposed by potassium, with rise of temperature and evolution of gas. (Wurtz.) ¶

Chloride of Butylene. C⁸H⁸Cl².

FARADAY (1825) and KOLBE, in the memoirs cited in connection with Butylene (p. 66).

Butylene-gas mixed with an equal volume of chlorine, condenses quickly and with great evolution of heat, forming a transparent, colourless oil, which tastes sweet at first, but afterwards aromatic and persistently bitter. (Faraday.) When dry butylene-gas mixed with hydrogen, as obtained by the method described on page 66, (2) is brought in contact with dry chlorine in a two-mouthed bottle, the bottom of the bottle, which becomes slightly warm, being at the same time protected from daylight, there is formed, besides the hydrochloric acid proceeding from the hydrogen, an oily liquid which runs down the sides. This liquid is shaken up, first with slightly alkaline, then with pure water, to free it from hydrochloric acid; then dried over chloride of calcium; distilled as long as the boiling point remains below 130° (it afterwards rises to 160°, in consequence of the presence of compounds containing more chlorine and less hydrogen); and the more volatile portion submitted to repeated fractional distillation till the boiling point remains constant at 123°. — In this manner, a transparent, colourless oil is obtained, of sp. gr. 1.1112 at 18°, vapour-density 4.426, and having exactly the agreeably sweet odour of its homologue, chloride of ethylene. (Kolbe.)

		Kolbe.	
8 C	48.0	37.86	38.2
8 H	8.0	6.31	6.8
2 Cl	70.8	55.83	55.5
<hr/>			
C ⁸ H ⁸ Cl ²	126.8	100.00	100.5
<hr/>			
		Vol.	Density.
C-vapour	8		3.3280
H-gas	8		0.5547
Cl-gas	2		4.9086
<hr/>			
Vap. of C ⁸ H ⁸ Cl ²	2		8.7913
	1		4.3956

The oil which distils over at 132° contains 34.6 p. c. C and 5.5 H. (Kolbe.)

Chloride of butylene burns with a bright but sooty flame, forming clouds of hydrochloric acid. (Kolbe.) — When exposed to sunshine in a bottle containing chlorine, it is very slowly converted, with absorption of chlorine and formation of hydrochloric acid, into a viscid liquid consisting of carbon, hydrogen, and chlorine, and not containing any crystals of C^4Cl^6 . (Faraday.) — When heated with alcoholic potash, it deposits a large quantity of chloride of potassium, and the liquid, which then acquires a different odour, becomes milky on addition of water, in consequence of the separation of small drops of a volatile oil which has a peculiar odour, and is probably = $C^4C^1H^7$. (Kolbe.)

When butylene gas mixed with hydrogen is absorbed by pentachloride of antimony, and the resulting mass distilled with addition of hydrochloric acid, it blackens and yields an oil, which, after washing and drying, is found to contain 28·4 per cent. C, 4·2 H and 68·2 Cl. (Kolbe.) [= $C^4C^1H^7, Cl^3$ nearly].

¶ *Bromide of Butylene*, C^4H^8, Br^2 , is formed by bringing together bromine and butylene in the state of vapour. It is a liquid which boils at 160° . When heated to 100° in a sealed tube with an alcoholic solution of ammonia, it yields a deposit of hydrobromate of ammonia, while bromobutylene C^4H^7Br remains in solution. (*Traité de Chimie Organique, par Ch. Gerhardt*, ii, 635.)

¶ *Conjugated Compounds of the Primary Nucleus, C^4H^8 .*

Carbonate of Butyl. $C^4H^8O^2 = C^4H^8O, CO^2$.

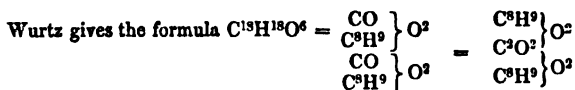
WURTZ. *N. Ann. Chim. Phys.* 42; *Ann. Pharm.* 93, 119.
E. HUMANN. *N. Ann. Chim. Phys.* 44, 337.

Butylic Carbonate, Kohlenbutester.

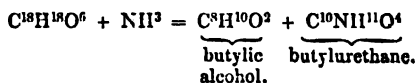
Preparation. 1. By heating equal parts (12 grm.) of carbonate of silver and iodide of butyl enclosed in a strong sealed glass flask, in the water-bath for two days; on opening the tube after cooling, a small quantity of carbonic acid gas escapes, together with a gas (butylene) which burns with a smoky flame. The liquid product is then distilled in the oil-bath, and the portion which passes over above 180° , collected apart and again rectified. (Wurtz.) — 2. When butylic alcohol containing water is treated with chloride of cyanogen, the first portion of the distillate consists of carbonate of butyl, which may be purified by redistilling, and collecting apart the portion which passes over between 180° and 190° . (Humann.)

Colourless liquid, lighter than water, and having an agreeable odour like that of carbonate of ethyl. Boils at 190° .

				Wurtz.	Humann.	
9 C	54	62·07	61·53
9 H	9	10·34	10·65
3 O	24	27·59	27·82
C^4H^8O, CO^2	87	100·00	100·00



Aqueous ammonia converts carbonate of butyl into butylic alcohol and butylurethane. (Humann.)



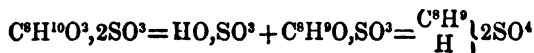
Sulphate of Butyl. $\text{C}^8\text{H}^9\text{O},\text{SO}^2$.

WURTZ, *N. Ann. Chim. Phys.* 42; *Ann. Pharm.* 93, 120.

Butylic Sulphate, Schwefelbutester.—

Formed by the action of iodide of butyl on sulphate of silver at ordinary temperatures, but soon decomposed by the heat evolved in the reaction; the mixture blackens in individual places, and on opening the vessel the odour of sulphurous acid is apparent. The action may be moderated by external cooling, but the sulphate of butyl is so instable that it decomposes in the course of a day, yielding sulphurous acid, a coloured hydrocarbon, and a peculiar conjugated acid which may be extracted by treating the residue with water, and forms with baryta a salt soluble in water and drying up in vacuo to a gummy mass. (Wurtz.)

Sulphobutylic Acid.



WURTZ. *N. Ann. Chim. Phys.* 42, 161; *Ann. Pharm.* 93, 122.

Butylosulphuric acid, Butylätherschwefelsäure.

Formed by the direct action of sulphuric acid on butylic alcohol. May be isolated by decomposing the baryta-salt with sulphuric acid, but has not yet been examined in the free state.

Potash-salt.—Strong sulphuric acid is added to an equal volume of butylic alcohol: the mixture, after 24 hours, diluted with twice its bulk of water; then mixed with solid carbonate of potash; the liquid evaporated to dryness over the water-bath; and the residue exhausted with boiling alcohol. As the filtrate cools, the potash-salt separates in broad laminae with a mother-of-pearl lustre. The salt dissolves readily in water, with tolerable facility in boiling alcohol, sparingly in cold alcohol. The concentrated aqueous solution is precipitated by alcohol. The aqueous solution distilled with caustic potash yields butylic alcohol and sulphate of potash.

		Wurtz.	
KO.....	47·2	24·57	24·11 .. 24·53
8 C.....	48·0	24·97	24·82 .. 24·51
9 H	9·0	4·68	4·94
O	8·0	4·16	
2 SO ²	80·0	41·62	
<hr/>			
C ³ H ⁸ KO ² ,2SO ²	192·2	100·00	

Baryta-salt. — Sulphuric acid and butylic alcohol are mixed as in the preparation of the potash-salt; the liquid diluted with 10 times its bulk of water (it remains almost clear, if it has been kept cool during the mixing); then saturated with carbonate of baryta suspended in water; and the solution of sulphobutylate of baryta filtered and evaporated in the water-bath, till a film appears on the surface. As the liquid cools, the baryta-salt separates in large rhombic laminæ, of a dazzling white colour and unctuous to the touch. The crystals dissolve very readily in water; at 100° or in vacuo they give off 2 At. water.

		Wurtz.	
<i>Crystallized.</i>			
BaO	78·6	32·02	31·74
8 C	48·0	20·01	20·18
11 H	11·0	4·58	4·63
3 O	24·0	10·00	
2 SO ²	80·0	33·39	
<hr/>			
C ³ H ⁸ BaO ² ,2SO ² + 2Aq.	241·6	100·00	

Lime-salt. — Prepared like the preceding salts. By evaporating the aqueous solution, it is obtained in small nacreous crystals, which, under the microscope, present the appearance of six-sided laminæ; they are anhydrous, and dissolve readily in water, forming a solution which quickly effloresces. (Wurtz.)

		Wurtz.	
CaO.....	28	16·18	16·41
8 C.....	48	27·75	
9 H.....	9	5·21	
O.....	8	4·62	
2SO ²	80	46·24	
<hr/>			
C ³ H ⁸ CaO ² ,2SO ²	173	100·00	

Nitrate of Butyl. C³H⁷NO²=C³H⁷O,NO².

WURTZ. *N. Ann. Chim. Phys.* 42; *Ann. Pharm.* 93, 120.

Butylic Nitrate, Salpeterbutester.

Formed by the action of iodide of butyl on nitrate of silver, with addition of urea to prevent the formation of nitrous acid. A few grammes of pulverized nitrate of silver are mixed with a small quantity of urea quite recently fused, the mixture introduced into a small retort, and treated with a quantity of iodide of butyl not quite sufficient to decompose the nitrate of silver. Violent action immediately takes place, attended with evolution of heat, sufficient to cause part of the resulting butylic nitrate to distil over. The remainder is distilled between 140°

and 150°, and the colourless distillate washed with water and dehydrated over chloride of calcium.

Colourless liquid heavier than water; tastes sweet at first, but soon leaves a pungent and aromatic after-taste. Boils at about 130°. (Wurtz.)

				Wurtz.
8 C.....	48	40·34 40·55
3 H.....	9	7·56 7·31
N.....	14	11·76	
6 O.....	48	40·34	

C⁸H⁹O,NO³ 119 100·00

Wurtz writes the formula : $\left. \begin{matrix} \text{NO}^3 \\ \text{C}^8\text{H}^9 \end{matrix} \right\} \text{O}^2$.

Nitrate of butyl burns with a pale flame; its vapour does not detonate. With alcoholic potash, it yields butylic alcohol and nitrate of potash. Sulphuretted hydrogen does not act upon it. (Wurtz.)

Acetate of Butyl. C¹²H¹³O⁴=C⁸H⁹O,C⁴H³O³.

WURTZ. *N. Ann. Chim. Phys.* 42; *Ann. Pharm.* 93, 121.

Butylic Acetate, Essigbutester.

Preparation. 1. By the action of iodide of butyl on acetate of silver. The two salts in equivalent quantities are enclosed in a small sealed flask and heated for several hours in the water-bath; the resulting acetate of butyl separated by distillation; and the distillate washed with water containing a little carbonate of soda, dried over chloride of calcium and rectified. — 2. By distilling equivalent quantities of sulphobutylate of baryta and recently fused acetate of potash.

Pure acetate of butyl is a perfectly colourless ethereal liquid, of sp. gr. 0·8845 at 16°. Has a very agreeable odour. Boils at 114° Vapour-density = 4·073.

				Wurtz.
12 C	72	62·06 61·94
12 H	12	10·34 10·42
4 O	32	27·60 27·64

C⁸H⁹O,C⁴H³O³ 116 100·00 100·00

C-vapour	12	4·9920
H-gas	12	0·8316
O-gas	2	2·2186

Vap. of Butylic acetate 2 8·0422
 1 4·0211

This compound may also be represented by the formula $\left. \begin{matrix} \text{C}^8\text{H}^9\text{O}^2 \\ \text{C}^8\text{H}^9 \end{matrix} \right\} \text{O}^2$. It is metameric with butyrate of ethyl (p. 91) formiate of amyl, valerate of methyl, and caproic acid.

Acetate of butyl boiled for some time with solution of potash, yields butylic alcohol and acetate of potash. (Wurtz.)

Formiate of Butyl, $C^{10}H^{10}O^4 = C^8H^8O, C^2HO^2$, is obtained by distilling equivalent quantities of sulphobutylate and formiate of potash. It is an agreeably smelling liquid which boils at about 100° . (Wurtz) ¶

Secondary Nuclei of Butylene.

a. Oxygen-nuclei.

a. Oxygen-nucleus. $C^8H^8O^3$.

Succinic Acid. $C^8H^8O^4 = C^8H^8O^3, O^1$.

- POTT. *Mém. de l'Acad. des Sciences de Berl.* 1753, 51.
 CARTHEUSER. *Act. Acad. Mogunt.* 1, 281.
 STOCKAR DE NEUFORN. *Diss. de Succino.* Lugd. Bat. 1761.
 J. G. LEONHARDI. *De Salib. succineis.* Lips. 1775.
 WENZEL. In his *Lehre von der Verwandtschaft*, 326.
 RICHTER. *Neuere Gegenst.* 8, 154.
 BERZELIUS. *Ann. Chim.* 94, 187.
 LECANU & SERBAT. *J. Pharm.* 8, 541; also *Ann. Chim. Phys.* 21, 328;
 also *N. Tr.* 8, 1, 280. — *J. Pharm.* 9, 89; also *N. Tr.* 7, 2, 98.
 LIEBIG & WÖHLER. *Pogg.* 18, 162.
 FELIX D'ARCET. *Ann. Chim. Phys.* 58, 282; also *Pogg.* 36, 80; also
J. pr. Chem. 3, 212.
 DÖPPING. *Ann. Pharm.* 47, 253.
 FEHLING. *Ann. Pharm.* 49, 154.

Bernsteinsäure, flüchtiges Bernsteinsalz, Acide Succinique. — Volatile salt of amber was mentioned by Agricola as early as 1657; its acid nature was first recognized by Barchhuseus, Boulduc and Boerhave.

Sources. 1. In amber. That it exists ready formed in that substance has been shown by Gehlen, who obtained a portion of the acid merely by boiling amber-powder with water;—by Funcke (*Br. Arch.* 7, 181), who found that the tincture obtained with 10 pts. amber and 50 pts. alcohol requires 10 pts. of carbonate of potash to neutralize its acid reaction; and when evaporated with water, yields, with separation of resin, an aqueous solution of succinate of potash, whereas the part of the resin which is not dissolved by the alcohol yields, when sublimed with sulphuric acid, only a trace of succinic acid;—and by Berzelius (*Pogg.* 12, 419), who extracted the acid from amber with ether. — 2. In lignite from Muskau (Rabenhorst); in retinasphalt, and to the amount of $\frac{1}{4}$ p. c. in the empyreumatic oil obtained by distilling the lignite of Naumburg, Altenburg, or Camburg, which contains retinasphalt. (Cerutti, *N. Br. Arch.* 22, 286). — 3. In turpentine; Scapoli (*Crell. Ann.* 1788, 2, 102) remarked that, in the distillation of turpentine, an acid liquid is obtained, which contains a crystallizable acid, together with acetic acid. Marabelli found this acid to be very much like succinic acid; Moretti (*Bull. Pharm.* 3, 399) found it to resemble acetic acid; Paolo Sangiorgio (*J. Pharm.* 8, 572) first declared this acid to be really succinic acid, a statement which was fully confirmed in 1822 by Lecanu & Serbat. According to the latter, this acid is deposited in

the neck of the retort in the distillation of turpentine, after the greater part of the oil has passed over, first in colourless crystals, afterwards in crystals coloured brown by resin. Peretti (*Mag. Pharm.* 4, 62) also found this acid in turpentine; Gumbrecht (*Br. Arch.* 14, 168) found it in oil of turpentine; but Fnucke (*Br. Arch.* 15, 173) did not succeed in obtaining it by the distillation of turpentine. — 4. According to a statement of Beissenhirtz, confirmed by John (*Berl. Jahrb.* 1818, 158), succinic acid is likewise obtained by the following process: A mixture of 1½ lb. honey, 2 lb. bread, 1½ lb. *Siliqua dulcis*, 6 lb. vinegar, 6 lb. brandy, and 84 lb. water, is left to undergo the acetous fermentation; the resulting acetic acid neutralised with lime; and the acetate of lime distilled with $\frac{1}{4}$ peroxide of manganese, $\frac{1}{3}$ oil of vitriol, and $\frac{1}{3}$ water; after the acetic acid has passed over, and the heat has been increased, 2 drachms of succinic acid sublime. In this case it is not positively known whether the succinic acid is an educt or a product; in *Siliqua dulcis* John did not find a trace of that acid. — Plümacher (*Schw.* 63, 369) did not succeed in obtaining succinic acid by Beissenhirtz's method. — 5. In the herb of *Lactuca sativa* and *virosa* (Köhnke, *N. Br. Arch.* 39, 153). — 6. In the herb of *Artemisia Absinthium* (Zwenger, *Ann. Pharm.* 48, 122). Luck (*Ann. Pharm.* 54, 112) regards this easily crystallizable acid, which occurs in small quantity in wormwood, as different from succinic acid. — Perhaps also the acid obtained by Kähler (*Br. Arch.* 25, 218) from *Semen Cynæ* is succinic acid. — 7. The mulberry-wcod acid described by Klaproth (*Scher. J.* 10, 3; also *Klaproth's Beiträge*, 3, 114), which sometimes exudes in combination with lime, from the stem of the *Morus alba*, is probably nothing but succinic acid. It crystallizes in needles having the taste of succinic acid, and may be sublimed, with but slight decomposition, in transparent colourless needles. It dissolves readily in water and alcohol. In the free state, it does not precipitate any metallic salt, but in combination with an alkali, it precipitates the salts of oxide of lead, sesquioxide of iron, protoxide of cobalt, oxide of nickel, dioxide of mercury, protoxide of copper, and oxide of silver. (Klaproth.) — Similar results have been obtained by Landerer. (*Repert.* 67, 100). — Another exudation from *Morus alba*, examined by Rouchas (*J. scienc. phys.* 3, 303), exhibited different properties. — 8. According to Vorwerk (*Jahrb. pr. Pharm.* 19, 265), the black carbonaceous matter formed in the preparation of ether contains succinic acid. — 9. Heintz (*Pogg.* 80, 114) found succinic acid in the sacs of echinococci (hydatids) formed in the liver of a woman.

Formation. 1. In the oxidation of organic compounds by exposure to the air. — An acid resembling succinic acid was found in a sample of the volatile oil of *Cuminum Cuminum* which had become sour. (Chevalier, *J. Chim. méd.* 4, 18.) — 2. In the oxidation of organic compounds by nitric acid. — Chevreul (*Recherches*, 28), by continued boiling of stearic acid, margaric acid, stearin, spermaceti, or ethal, with large quantities of nitric acid, obtained an acid resembling succinic acid, and by similar treatment of oleic acid, an acid of somewhat different properties. More recently, Bromeis (*Ann. Pharm.* 35, 90) has shown that stearic acid thus treated really yields succinic acid. This acid was likewise obtained by Sthamer, Radcliff, Ronalds, and Sacc, (*Ann. Pharm.* 43, 346, 349 and 356; 51, 229,) by the action of nitric acid on Japan wax, spermaceti, beeswax, and margaric acid. By boiling concentrated nitric acid with santonin, Heldt (*Ann. Pharm.* 63, 40) obtained needles

of succinic acid. By distilling 1 pt. of starch with 6 pts. of nitric acid of sp. gr. 1.295, till the residue became charred. Tünnermann (*Schw.* 49, 221) obtained a sublimate of soft yellow crystals in the neck of the retort, and a watery distillate, from which an acid was prepared agreeing with succinic acid in every respect, excepting that [on account of impurities?] it was somewhat more soluble in water. — ¶. Butyric acid heated for 10 days with an equal volume of nitric acid of sp. gr. 1.40, the vapours being condensed and made to flow back, and the nitric acid renewed from time to time, yields a crystalline residue of succinic acid, contaminated with a deliquescent substance which may be removed by pressure between bibulous paper (Dessaigues, *Compt. rend.* 30, 50). — Caprylic alcohol, heated for some time with dilute nitric acid, yields succinic acid, together with pimelic, lipic, and butyric acids. (Bouis, *Compt. rend.* 33, 141.) ¶. — 3. In the putrefaction of vegetable juices containing asparagin, succinate of ammonia is formed. (Piria, *Compt. rend.* 19, 576.) — Also in the putrefaction of malate of lime under water. (Dessaigues, *N. Ann. Chim. Phys.* 25, 253; also *N. J. Pharm.* 15, 264; also *J. pr. Chem.* 46, 350; Liebig, *Ann. Pharm.* 70, 104; Blez. *Arch. Pharm.* [2], 62, 13; Gräger, *Arch. Pharm.* [2], 63, 137.) — ¶. Neutral and acid malate of lime, malate of potash, aspartate of potash, aspartate of lime, maleate of lime, and aconitate of lime, are all converted into succinates by the fermentation induced by casein. Asparagin under the same circumstances is converted into aspartate of ammonia, which subsequently passes into succinate. — The peculiar substance in the seed of leguminous plants, which is converted into asparagin during germination, is also capable of passing into asparagin by fermentation. When pea-flour is stirred up with water, the liquid filtered after 12 hours, and left to ferment after being mixed with chalk, a considerable quantity of succinate of lime is formed. The same result is obtained by the fermentation of legumin alone, of the liquid separated from the legumin, and of the nitrogenous substance discovered by Braconnot in leguminosæ, which precipitates tannin. Succinic acid is likewise obtained by the fermentation of an emulsion of sweet almonds, freed from oil and mixed with chalk. (Dessaigues, *Compt. rend.* 30, 50.) Several other seeds treated in a similar manner also yield succinic acid. The bruised seeds are stirred up with water, the filtered liquid mixed with chalk, and left to ferment at 25° to 35°. When the fermentation is complete (in 6 or 7 days), the lime is precipitated by carbonate of soda, the filtrate mixed with excess of hydrochloric acid and evaporated in the water-bath, the residue treated with boiling ether, and the substance left on evaporating the ethereal solution examined for succinic acid. Oats, maize, hemp, mustard, and gourd-seed, treated in this manner, yielded no succinic acid; walnuts and buckwheat, traces; hazel-nuts and acorns (after removal of the tannic acid by lime) yielded considerable quantities. (Dessaigues, *N. J. Pharm.* 25, 27.) Perfectly pure maleate of lime also yields succinic acid when fermented with casein. (Dessaigues.) ¶.

Preparation. A. From Amber. a. By distillation of Amber per se. The amber is heated to the melting point in a distillatory apparatus, till the intumescence and evolution of acid cease, and a thick brown oil begins to pass over. The residue, consisting of *Colophonium Succini*, is used for varnishes. The acid collects in the crystalline form in the neck of the retort and in the receiver, and in small quantity in the watery distillate which must be separated from the oil and evaporated. The

succinic acid thus obtained amounts to about $\frac{1}{3}$ of the amber. — The quantity obtained is greater in glass than in iron vessels. (Funcke.)

b. By Distillation with dilute Sulphuric acid. — 1 pt. of crude amber-powder is moistened with $\frac{1}{3}$ to $\frac{1}{4}$ oil of vitriol diluted with 1 to 3 times its bulk of water, and the process conducted as in *a*. By this treatment, 1 pt. of amber yields about $\frac{1}{8}$ of succinic acid. (Pott, *Crell. N. Archiv.* 5, 177; Bath, *Herbstädt Museum*, 4, 253; J. A. Buchner, *Repert.* 1, 300; Ilisch, *Scher. Ann.* 6, 186; Funcke, *Br. Arch.* 7, 181; Weiss, *Taschenb.* 1826, 37.)

c. By boiling Amber with Nitric acid. — Coarsely pounded amber is heated in a retort with an equal quantity of dilute nitric acid, till the yellow viscid resinous mass which at first rises to the top has disappeared; the clear liquid is then evaporated to a syrup; this syrup repeatedly boiled with fresh, and at last with concentrated nitric acid, to decompose the remainder of the resin; the resulting syrup left in the cold for a few weeks, till it has become crystalline; and the crystals drained on a funnel from the mother-liquor, which, when evaporated with strong nitric acid, again yields crystals and a second mother-liquid, from which, by renewed treatment with nitric acid, an additional quantity of crystals may be obtained. Lastly, the whole of the crystals collected on the funnel are boiled with strong nitric acid, whereby a solution is obtained, which, on cooling yields white crystalline succinic acid amounting to $\frac{1}{3}$ of the amber. Nevertheless this method is not advantageous, as it requires a large quantity of nitric acid, and does not yield any *Colophonium Succini*. From the distillate obtained by heating amber with nitric acid, after the acid has been neutralized with potash, ether extracts a white crystalline matter, which exhibits all the characters of ordinary camphor. (Döpping, *Ann. Pharm.* 49, 350.)

Purification of the acid obtained by a or b. — The acid may be freed from the greater part of the empyreumatic oil by pressure between paper, solution in hot water, filtering through moistened paper, and crystallization. — To remove the last portions of oil and brown colouring matter, it is best to boil the product with nitric acid, which does not exert any decomposing action upon succinic acid. (Morveau, Lecanu & Serbat; Döpping.) — When 1 pt. of still brown and oily succinic acid is boiled for half an hour in a retort fitted with a receiver (because a little of the succinic acid distils over), with 4 pts. of commercial aqua fortis — whereupon only a small quantity of nitrous fumes is evolved at the beginning, arising from decomposition of the oil — and the liquid poured into a basin while still hot, the succinic acid, being but slightly insoluble in nitric acid, crystallizes out almost completely as the liquid cools, and moreover in white inodorous crystals, which may be freed from the nitric acid by recrystallization from water, and are then perfectly pure. The nitric acid mother-liquor does not contain oxalic acid. (Döpping.) Fehling subjects the acid thus purified to a further crystallization from alcohol, whereby the musk-like odour is destroyed.

Less satisfactory modes of purification. — 1. The succinic acid is suspended in water; chlorine gas passed through for some hours; the liquid which has now become inodorous, evaporated to the crystallizing point; and the crystals freed from hydrochloric acid by recrystallization from water. (Liebig & Wöhler, *Pogg.* 18, 163.) — When the aqueous solution

of succinic acid is saturated with chlorine gas, then left for 24 hours in a close vessel, and afterwards filtered and evaporated, it emits a musk-like odour, and yields pale yellow crystals, which cannot be obtained quite colourless, either by recrystallization or by subsequent treatment with chlorine, but only by boiling with nitric acid. (Döpping.) — Tünnermann (*Schw.* 51, 469) boils 1 pt. of succinic acid with 1 pt. of manganese, 3 pts. of strong hydrochloric acid, and $1\frac{1}{4}$ pt. water, filters hot, and purifies the resulting crystals by recrystallization from water. This acid when sublimed does not exhibit the slightest odour of burnt amber. [Is it also colourless?] — 2. Morveau recommends the sublimation of the acid mixed with sand, which however does not remove the oil. — 3. Lowitz recommended the digestion of the aqueous acid with charcoal powder. — This treatment certainly decolorizes the acid, but does not free it from oil. (Berzelius.) Wood-charcoal does not decolorize the acid but absorbs a large quantity of it, which can only be recovered by long continued washing. (Döpping.) — A mode of purification by crystallization from water, then by treatment with wood-charcoal, then by evaporation with a small quantity of nitric acid, then by passing chlorine through the filtered solution, is recommended by Werner (*J. pr. Chem.* 14, 246.) — 4. Berzelius (*Lehrb.*) neutralizes the acid with carbonate of potash not in excess; boils the liquid with a small quantity of the charcoal obtained in the preparation of prussian blue; precipitates the filtrate with neutral acetate of lead; washes the precipitate well with water, which however dissolves a little of the succinate of lead; and decomposes 10 pts. of the dried precipitate with a mixture of 2 pts. oil of vitriol and 30 pts. water.

B. From Stearic acid and other fatty matters by oxidation with nitric acid. — 1 pt. of stearic acid, margarinic acid, stearin, spermaceti, or ethal, is distilled with 100 pts. of nitric acid of 32° Bm., with frequent cohobation, till the distillate forms a clear solution with the residue; this solution evaporated in a basin; the yellowish, tenacious crystalline residue set aside with 26 pts. of cold water for 24 hours; then evaporated; and the resulting crystals separated from the mother-liquor. (Chevreul, *Recherches*, 28.) — 2. Stearic acid is distilled with nitric acid, the liquid being frequently cohobated and the acid renewed, till the whole is dissolved; the solution evaporated to half its bulk; the solidified suberic acid freed after 24 hours from the mother-liquor, by washing on a funnel; and the mother liquor evaporated and cooled, whereupon it yields crystals of succinic acid, which may be freed from the greater part of the still adhering and less soluble suberic acid, by washing with water, and from the remainder by washing with 3 pts. of cold alcohol or 4 pts. of boiling ether, which dissolves but a very small quantity of succinic acid. Finally, the succinic acid is crystallized once more from water. This treatment does not, however, remove the whole of the suberic acid. Hence the succinic acid thus obtained crystallizes, not only in tables, but also in heavy, white, solid granules; melts, after drying at 100° , as low as 170° to 175° ; and exhibits less definite reactions. It is only by sublimation that succinic acid can be completely freed from suberic acid, which is less volatile, and cannot be sublimed without decomposition. — Hence the crude solution of stearic acid in nitric acid, may be evaporated as far as possible, at a moderate heat; mixed with water of 20° to 30° , and set aside; separated from the oil thus set free, which had previously been held in solution by the nitric acid; again evaporated as far

as possible; again mixed with lukewarm water, and separated from a small remaining quantity of oil; then evaporated at a gentle heat till it begins to crystallize, and subsequently cooled; the resulting white, solid, granular mass, pressed between paper, thoroughly dried, and gently heated in a long-necked flask placed in a sand-bath; and the succinic acid which then sublimes in delicate feathery crystals, purified by a second sublimation. The acid thus obtained is very pure, and crystallizes from water, no longer in round granules, but in large tables. (Bromeis, *Ann. Pharm.* 35, 90, 37, 292.) — Japan-wax merely requires to be distilled for a few weeks with nitric acid, with cohobation and frequent addition of fresh acid, in order to yield, when the solution is evaporated and cooled, transparent, colourless tables of pure succinic acid. (Sthamer, *Ann. Pharm.* 43, 346.) — When spermaceti is heated for several days with nitric acid of medium strength, to a temperature short of the boiling point, the resulting solution yields by evaporation and cooling, crystals of succinic acid, which must be purified by recrystallization, first from nitric acid, then from water. The mother-liquor of the first crop of crystals yields an additional quantity by evaporation and cooling; but the last portions are contaminated with a white substance, which appears to be pimelic acid, and is greater in quantity the longer the digestion with nitric acid has been continued. (Radcliff, *Ann. Pharm.* 43, 349.) — From white beeswax, Ronalds (*Ann. Pharm.* 43, 356,) obtained by the same process, transparent laminæ of succinic acid.

C. *By the fermentation of Malate of Lime.* — 12 pts. of crude malate of lime, prepared by Liebig's process, (*vid. Malic acid*), from the juice of mountain-ash berries, are placed, after being three times washed in an earthen jar, together with 40 pts. water and 1 pt. of decayed cheese rubbed to an emulsion with water, and the mixture set aside for 4 to 6 days, at a temperature of 30° to 40°, till the evolution of gas has ceased. The granular precipitate is then collected upon linen, washed several times with water, and mixed with dilute sulphuric acid till it no longer effervesces (from admixed carbonate of lime); another equal quantity of sulphuric acid is then added; the mixture boiled for awhile, till the lime-salt is no longer granular; the liquid strained through linen; the precipitate on the filter thoroughly washed; the whole of the liquid evaporated till a crystalline crust forms on the surface; oil of vitriol then added in small quantities, as long as sulphate of lime is thereby precipitated; the liquid strained off (after dilution with water, if the gypsum forms a paste); the precipitate washed; and the whole of the liquid again evaporated: it then yields on cooling, brownish crystals of succinic acid, still contaminated with gypsum. These crystals are recrystallized, first from pure water, then from water after boiling with a small quantity of animal charcoal, and ultimately freed from all the gypsum by solution in alcohol or by sublimation. By this process, 12 pts. of malate of lime yield from 3.75 to 4 pts of pure crystallized succinic acid: the mother-liquors do not retain a trace of malic acid. (Liebig, *Ann. Pharm.* 70, 104.)

Properties. The acid crystallized from water assumes the form of transparent colourless prisms belonging to the oblique prismatic (monoclinometric) system. *Fig.* 92, often with *f*-faces (formed by truncation of the acute terminal edges; by enlargement of the *m*-faces, the prisms appear like rhombic and six-sided tables. (Wackenroder, *J. pr. Chem.* 23, 204.) Sp. gr. = 1.55. (Richter.) The acid melts at 180°, boils at

235° (D'Arcet), and evaporates without residue in white pungent vapours. It reddens litmus, but not violet-juice. It is inodorous, and has a warm sour taste.

	<i>Crystallized.</i>		D'Arcet.	Zwenger.	Piria.	Bromeis.
8 C.....	48	40·68	41·22	40·62	40·34	41·98
6 H.....	6	5·09	5·33	5·28	5·22	5·37
8 O.....	64	54·23	53·45	54·10	54·44	52·65
C ⁸ H ⁶ O ⁸	118	100·00	100·00	100·00	100·00	100·00

	Sthamer.	Radcliff.	Ronalds.	Dessaignes.	Strecker.
C	40·80	40·89	41·06	40·88	40·3
H	5·15	5·20	5·12	5·25	5·1
O	54·05	53·91	53·82	53·87	54·6
	100·00	100·00	100·00	100·00	100·0

The radical-theory assumes $\bar{S} = C^8H^2O^8$. — D'Arcet analysed the acid obtained from amber; Zwenger, that from wormwood; Piria, (*N. Ann. Chim. Phys.* 22, 167) that from a fermented solution of impure asparagin; Bromeis, that from stearic acid; Sthamer, that from Japan wax; Radcliff, that from spermaceti; Ronalds, that from beeswax; and Dessaignes and Strecker, that from malate of lime. The crystals were in most cases freed from hygroscopic water at 100°.

Decompositions. 1. The acid heated till it volatilizes, sublimes, with evolution of water, in colourless silky needles of sublimed succinic acid, which may be regarded as C⁸H⁶O⁷, and by repeated sublimation, is converted, with further formation of water, into succinic anhydride. (D'Arcet.)



The sublimation takes place even at 140°, though very slowly; the residual portion exhibits the unaltered constitution of C⁸H⁶O⁸, whereas the sublimed portion = C⁸H⁶O⁷. (D'Arcet.)

The *sublimed acid* melts at 160°, and boils at 242°, but begins to sublime even at 140°. Its solution in water again yields crystals of the ordinary acid C⁸H⁶O⁸. (D'Arcet.) [According to the following analyses, the sublimed acid is C⁸H⁶O⁷; but since by 10 sublimations it is gradually but completely converted into C⁸H⁶O⁸, it should perhaps be regarded, not as a distinct compound, but merely as a mixture of C⁸H⁶O⁶ with C⁸H⁶O⁸.]

	<i>Sublimed acid.</i>		D'Arcet.	Liebig & Wöhler.
8 C	48	44·04	44·11	44·38
5 H	5	4·59	4·83	5·00
7 O	56	51·37	51·06	50·62
C ⁸ H ⁶ O ⁷	109	100·00	100·00	100·00

2. Succinic acid, set on fire by a flaming body, burns with a pale blue flame. (Gm.)—3. On heated nitre it deflagrates with a white flame. (Morveau.)—4. Distilled with 2 pts. of sulphuric acid and 3 pts. of manganese, it yields acetic acid. (Trommsdorff.)—5. Heated with excess of caustic potash, it yields oxalate of potash, but no mellitate. (Liebig & Wöhler.) [Perhaps in this manner :



It is not decomposed by chlorine gas, when sublimed therein, or

when the gas is passed through its aqueous solution, even if the solution is hot. (Liebig & Wöhler.)—It is not decomposed by boiling with strong nitric acid (Morveau, Westrumb, and others), or by chlorate of potash and hydrochloric acid (Fehling), not even by aqueous chromic acid. (Winckler, *Repert.* 46, 466.)—For the decomposition of the lime-salt by heat, and of the silver-salt by chlorine, see these salts.—¶ The hydrated acid treated with pentachloride of phosphorus yields anhydrous succinic acid, hydrochloric acid, and oxychloride of phosphorus :



(Gerhardt & Chiozza, *Compt. rend.* 36, 1050; *Ann. Pharm.* 87, 290; *Jahresber.* 1853, 393.)

Combinations. The acid dissolves in 24 pts. of cold, and 2 pts. of boiling water (Neuforn), in 5 pts. of water at 16° and in 2·2 pts. of boiling water. (Lecanu & Serbat.) A solution having a density of 1·01, contains 2·78 p. c., and that of sp. gr. 1·04, contains 10·82 p. c. acid. (Richter.)

The *neutral Succinates*, formed from metallic oxides containing 1 At. metal and 1 At. oxygen, have the formula $C^8H^4M^2O^8$ (according to the radical theory, $MO, C^4H^2O^3$), and the few *acid salts*, which can be formed, have the formula, $C^8H^2MO^8$ (or $MO, C^4H^2O^3 + C^4H^2O^4$). The salts yield by dry distillation, carbonic acid and carburetted hydrogen gas, water, acetic acid, and empyreumatic oil. (Morveau; see especially the lime-salt.) According to Buchner, (*Ann. Pharm.* 88, 203,) the alkaline succinates, under the influence of a ferment, yield, at a certain stage of the decomposition, acetic and butyric acids.—Most succinates are soluble in water; those which are insoluble in water, dissolve in aqueous acetate of potash, so that succinate of potash mixed with acetate does not precipitate any heavy metallic salt. (Lecanu & Serbat.)

Succinate of Ammonia.—*a. Neutral.*—Occurs, contaminated with empyreumatic oil, in *Liquor Cornu Cervi succinatus*.—To prepare this salt, the acid is dissolved in excess of aqueous ammonia, and the solution evaporated to the crystallizing point over lime, within a receiver containing air. (Döpping.)—Since, even by this process, a portion of the ammonia is lost, and an acid salt formed, it is better to precipitate subacetate of lead with excess of neutral succinate of ammonia, evaporate the filtrate in vacuo over oil of vitriol, wash the crystalline mass with a small quantity of cold water, as soon as the greater part of it has separated out, press between paper, and dry under 50°. (Fehling.) [If the acetate of ammonia protects the succinic acid from loss of ammonia, it would be simpler to mix the solutions of the two salts and evaporate.] Transparent, six-sided prisms, having a slight acid reaction, (Döpping,) perfectly neutral. (Fehling.) When exposed to the air, they continually give off ammonia, but without efflorescing. (Döpping.) When heated, they at first give off ammonia and water, and the acid salt, $C^8NH^3O^8$, which then remains, is resolved into bisuccinamide, ($C^8NH^2O^8$), which sublimes together with a small quantity of water, and 4HO. (Fehling.) The salt dissolves readily in water and alcohol; its aqueous solution takes up a large quantity of chloroplatinate of ammonium or potassium, and consequently the ammonia is but imperfectly precipitated from it by bichloride of platinum. (Döpping.) The aqueous solution exposed to the air for half a year, yields a black precipitate and becomes alkaline. (Horst, *Br. Arch.* 1, 257.)

	Crystallized.		Döpping.		Fehling.
8 C	48	31·58	31·71	31·94	
2 N	28	18·42	18·50		
12 H	12	7·90	7·85		7·92
8 O	64	42·10	41·94		
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$C^8H^4(NH^4)O^8$	152	100·00	100·00		

b. Acid Salt. — The aqueous solution of *a* is evaporated by heat to the crystallizing point, or 1 pt. of the acid exactly neutralized with ammonia is mixed with 1 pt. more of the acid, and the liquid evaporated. (Döpping.) Long transparent prisms belonging to the doubly oblique prismatic (triclinometric) system. *Fig. 127*; cleavage easy parallel to *y*, *u*, and *v*; generally with the *y*-face superposed; $y : u = 91^\circ 53'$; $y : v = 93^\circ 25'$; $y : z = 91^\circ 45'$; $y : q = 151^\circ 57'$; y : the face below $u = 151^\circ 7'$; $u : v = 100^\circ 15'$; $u : q = 119^\circ 53'$; u : the face below $u = 117^\circ$; $v : z = 135^\circ 46'$. (Brooke, *Ann. Phil.* 22, 286.) — The salt tastes sharp, bitter, and cooling, and reddens litmus. — It loses scarcely 2 or 3 per cent. at 100° , but at 140° it volatilizes with partial decomposition. (Döpping.) When gently heated for some time, it gives off a large quantity of ammonia together with a small quantity of water, and leaves pure succinic acid together with a small quantity of bisuccinamide. (Bineau, *Ann. Chim. Phys.* 67, 241.) It dissolves readily in water and in alcohol. (Döpping.)

	Crystallized.		Döpping.	
8 C	48	35·55	35·54	
N	14	10·37		
9 H	9	6·67	6·73	
8 O	64	47·41		
<hr/>				
$C^8N^8(NH^4)O^8$	135	100·00		

Succinate of Potash. — *a. Neutral.* — An aqueous solution of succinic acid neutralized with carbonate of potash, and evaporated nearly to a syrup, slowly yields needles united in stellate groups. (Lecanu & Serbat.) Thin rhombic tables, which give off 4·2 to 4·8 p. c. water at 100° . (Fehling.) The crystals are deliquescent; they give off all their water amounting to 6·2 per cent. at 100° , and the residue sustains without further loss a heat of 230° to 240° , and then fuses quietly without decomposition. (Döpping.) The crystals deliquesce in the air (Lecanu & Serbat, Döpping); they are permanent in the air. (Fehling.) They dissolve readily in water and in weak alcohol, but are insoluble in ether. (Döpping, Fehling.)

	Dried at 100° .		Fehling.	
2 KO	94·4	48·56	48·21	
$C^8H^4O^8$	100·0	51·44		
<hr/>				
$C^8H^4K^2O^8$	194·4	100·00		
<hr/>				
	Crystallized.		Döpping.	
2 KO	94·4	40·97	40·39	
$C^8H^4O^8$	100·0	43·40		
4 HO	36·0	15·63	16·20	
<hr/>				
$C^8H^4K^2O^8 + 4 Aq.$	230·4	100·00		

b. Acid Salt. — Prepared by mixing 1 pt. of the acid neutralized with carbonate of potash, with 1 pt. more of acid, and evaporating to the crystallizing point. Transparent, six-sided prisms belonging to the

doubly oblique prismatic system. They redden litmus; gradually become turbid when exposed to the air; give off all their water (17·77 to 18·0 per cent.) at 230° without further decomposition; and melt at a stronger heat, with volatilization of succinic acid and further decomposition. They dissolve readily in water and alcohol. (Döpping.)

<i>Anhydrous crystals.</i>				Fehling.	
KO	47·2	30·22	30·11		
C ⁹ H ⁶ O ⁷	109·0	69·78			
<hr/>					
C ⁹ H ⁶ KO ⁸	156·2				
<i>Hydrated crystals.</i>				Döpping.	
KO	47·2	24·56	24·46		
C ⁹ H ⁶ O ⁷	109·0	56·71			
4 HO	36·0	18·73	18·00		
<hr/>					
C ⁹ H ⁶ KO ⁸ + 4Aq.	92·2	100·00			

Fehling analysed crystals which did not lose anything at 100° after being dried in the air. Hence this salt forms anhydrous as well as hydrated crystals.

c. Hyperacid Salt. — When 1 pt. of the acid dissolved in water is neutralized while hot with carbonate of potash, and 3 pts. more of acid added, the liquid yields on cooling, sometimes an anhydrous salt *a*, sometimes a hydrated salt *β*, which gives off 9·65 p. c. water at 100°. (Fehling.)

						Fehling.	
						<i>a.</i>	<i>β.</i>
						<i>Crystals dried at 100°.</i>	
KO	47·2	17·22	17·48	17·44			
16 C	96·0	35·01	36·18	36·35			
11 H	11·0	4·01	3·99	3·97			
15 O	120·0	43·76	42·35	42·24			
<hr/>							
C ⁹ H ⁶ KO ⁸ , C ⁹ H ⁶ O ⁸	274·2	100·00	100·00	100·00			
<i>Crystals β, air-dried.</i>						Fehling.	
KO	47·2	15·67	16·24				
C ⁹ H ⁶ O ⁷	109·0	36·19					
C ⁹ H ⁶ O ⁸	118·0	39·18					
3 HO	27·0	8·96	9·65				
<hr/>							
C ⁹ H ⁶ KO ⁸ , C ⁹ H ⁶ O ⁸ + 3Aq.	301·2	100·00					

[Fehling reckons 1 At. less of water in the dry salt, because he obtained more carbon; this may however have arisen, partly from his assumption of C=6·12, partly from his supposition that in the combustion with oxide of copper, the residual potash retained $\frac{3}{4}$ of the carbonic acid, which was perhaps too large an allowance.]

Succinate of Soda. — *a. Neutral.* — The acid neutralized with aqueous carbonate of soda, yields on evaporation, transparent, colourless, neutral, rhomboïdal prisms, which are permanent in the air. (Döpping.) Oblique rhomboïdal prisms. (Fehling.) Bitter. They effloresce slightly in the air. (Lecanu & Serbat, Fehling.) They give off all their water = 40·00 per cent. (40·4 p. c. according to Fehling) at 100°, after which they do not lose any more below 230° to 240°. (Döpping.) The dry salt yields by dry distillation, carbonic acid and carburetted hydrogen gases, water containing acetic acid, a brownish yellow oil, and carbonate of soda mixed with a small quantity of charcoal. (Morveau.) The salt dissolves readily

in water, especially in hot water (Lecanu & Serbat), and in hydrated alcohol. (Döpping.)

<i>Dried at 100°.</i>				Fehling.
2 NaO	62.4	38.42	37.85	
8 C	48.0	29.55	29.89	
4 H	4.0	2.47	2.68	
6 O	48.0	29.56	29.58	
C ⁸ H ⁶ Na ² O ⁸				100.00
<i>Crystallized.</i>				Döpping.
2 NaO	62.4	23.08	21.73	
C ⁸ H ⁶ O ⁶	100.0	36.98		
12 HO	108.0	39.94	40.00	40.40
C ⁸ H ⁶ Na ² O ⁸ + 12Aq.				100.00

b. Acid Salt. — Obtained by adding to 1 pt. of the acid neutralized with carbonate of soda, another 1 pt. of the acid, and evaporating the liquid at a gentle heat to the crystallizing point. (Döpping.)

a. In a few cases the solution yields indistinct crystals which do not effloresce; they give off 21.44 p. c. water at 100°, but when recrystallized from water, yield the crystals *β*. (Fehling.)

β. In most cases, transparent prisms are obtained belonging to the doubly oblique prismatic system, *Fig. 128*; indistinctly cleavable parallel to the truncation-face of the edge between *u* and *v*; *y* : *u* = 128°; *y* : *d* = 169° 55'; *y* : *v* = 140° 50'; *y* : the truncation face between *u* and *v* = 99° 30'; *u* : *v* = 117° 6'; *v* : *z* = 133° 20'; *u* : the face between *u* and *v* = 115° 8'; *v* : the face between *u* and *v* = 108° 07' (Brooke, *Ann. Phil.* 22, 286.) [Brooke does not state whether he examined the neutral or the acid salt; but the resemblance of the form with that of the acid ammonia-salt renders the latter the more probable. Moreover, Döpping likewise describes the crystals as six-sided prisms belonging to the oblique prismatic system, and Fehling describes them as large tables formed from shortened oblique rhombic prisms]. — The crystals redden litmus, effloresce slowly in the air (Döpping), under which circumstances they soon lose 4.5 per cent. (Fehling.) They give off all their water at 100°. (Döpping, Fehling.)

The dry salt remains unaltered at 200°, and decomposes at a stronger heat, like the acid potash-salt. (Döpping.) With chloride of benzoyl it yields anhydrous succinic and benzoic acids, together with water and chloride of sodium. (Gerhardt & Chiozza.)



The salt dissolves readily in water and in hydrated alcohol. (Döpping.)

<i>Dried at 100°.</i>				Fehling.
NaO	31.2	22.25	21.83	
8 C	48.0	34.24	34.21	
5 H	5.0	3.56	3.71	
7 O	56.0	39.95	40.25	
C ⁸ H ⁶ NaO ⁸				100.00
<i>Crystals a.</i>				Fehling.
NaO	31.2	17.71	17.76	
C ⁸ H ⁶ O ⁷	109.0	61.86		
4 HO	36.0	20.43	21.44	
C ⁸ H ⁶ NaO ⁸ + 4Aq.				100.00

			Fehl.	Döpping.
NaO	31·2	16·4 15·89
C ⁶ H ⁴ O ⁶	109·0			
6 HO	27·81	27·6 28·06
<hr/>				
C ⁶ H ⁴ NaO ⁸ + 6Aq.	194·2	100·0	

It does not appear possible to prepare either a succinate of soda and ammonia, or a succinate of soda and potash. (Fehling, Döpping.)

Succinate of Baryta. — Neutral. — Succinate of soda, but not the free acid, precipitates hydrochlorate or nitrate of baryta when not too dilute. (John.) From a concentrated solution, a white heavy powder is immediately precipitated which does not redden litmus; a dilute solution deposits crystalline grains after a while, or more quickly when heated. (Döpping, Fehling.) Baryta-water precipitates the same salt from a not too dilute solution of acid succinate of potash or soda, and without forming a double salt. (Döpping.) — The air-dried salt merely gives off a little hygroscopic water at 200°. (Döpping, Fehling.) — It dissolves but very sparingly in water or in succinic acid, with which it does not form an acid salt; it dissolves more readily in acetic acid, still more readily in dilute hydrochloric or nitric acid, but is insoluble in ammonia and in alcohol. (Döpping.)

	Dried at 200°.		Döpping.		Fehling.
2 BaO	153·2	60·50	59·66
C ⁶ H ⁴ O ⁶	100·0	39·50		
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C ⁶ H ⁴ Ba ² O ⁸	253·2	100·00		

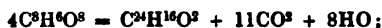
No acid baryta-salt can be formed: the clear aqueous mixture of succinic acid and acetate of baryta, when evaporated to dryness and treated with alcohol to extract the free succinic acid, leaves the neutral salt. The clear mixture of acid succinate of soda and chloride of barium, when heated and evaporated, deposits the neutral salt in the form of a crystalline powder. (Döpping.)

Succinate of Strontia. — Obtained by precipitating a not too dilute aqueous solution of a strontia-salt with neutral succinate of soda. (Bucholz, John, Döpping.) White powder, or, when obtained by evaporating the aqueous solution, crystalline grains. (Lecanu & Serbat.) It is anhydrous after drying in the air, and does not lose anything at 200°. (Döpping.) It is insoluble in alcohol, sparingly soluble in water, but dissolves more readily in acetic acid. (Döpping.) The solution of this salt in aqueous succinic acid yields crystals (of the neutral salt, according to Döpping) by evaporation. (John.)

	Dried at 200°.		Döpping.	
2 SrO	104	50·98 50·21
C ⁶ H ⁴ O ⁶	100	49·02	
<hr/>				
C ⁶ H ⁴ Sr ² O ⁸	204	100·00	

Succinate of Lime. — a. Neutral. — A mixture of chloride of calcium not too concentrated and neutral succinate of soda deposits, after long standing, needles of succinate of lime. (Döpping.) Even when the solution is tolerably concentrated, the precipitate does not appear for some time; on the application of heat, it forms more quickly, but then contains less water. (Fehling.) The dry salt, or a mixture of 2 At. lime with 1 At. succinic acid, yields by dry distillation a strongly empyreumatic, dark brown oil, from which by repeated rectification at 120°, *Succinone*

is obtained (amounting to 0.2 per cent. of the lime-salt). Succinone is a thin colourless liquid, having only a faint empyreumatic odour. It contains 79.86 C, 8.90 H, and 11.24 O. (D'Arcet.) From these numbers D'Arcet deduces for succinone the formula $C^8H^{16}O^2$, and explains its formation by the equation:



nevertheless, he himself admits that succinone may be only a mixture.

a. Crystals with 2 At. Water. — When aqueous succinate of soda is mixed with chloride of calcium at a boiling heat, or when the cold mixture is heated to the boiling point, delicate needles quickly separate, which, after drying in the air, give off only 2.5 p. c. of water at 100° , and do not lose all their water, amounting to 11.2 per cent. till they are heated to 200° . The mother-liquor yields by evaporation a further quantity of the needles *a*; but when these are left in the liquid for 24 hours, they change to the needles *β* . (Fehling.)

β . Crystals with 6 At. Water. — A mixture of succinate of soda and chloride of calcium left in the cold or gently heated, deposits, after several hours,—the more quickly as the solution is more concentrated,—needles which gradually increase in size and hardness. After drying in the air, they give off 22.35 p. c. (5 At.) water at 100° , and at 200° , the entire quantity, amounting to 26.4 p. c. (6 At.) (Fehling.) The air-dried needles give off the greater part of their water at 100° , and the whole between 120° and 130° , so that at 200° , nothing more is evolved. (Döpping.)

The salt dissolves sparingly in water and in acetic acid, better in succinic acid, very easily in nitric or hydrochloric acid, but is insoluble in alcohol.

Dried at 200° .		Fehling.	
2 CaO	56	35.90	36.03
$C^8H^{16}O^2$	100	64.10	63.97
<hr/>			
$C^8H^{16}Ca^2O^8$	156	100.00	100.00
<hr/>			
Air-dried Crystals <i>a</i> .			
2 CaO	56	32.18	32.32
$C^8H^{16}O^2$	100	57.48	
2 HO	18	10.34	11.20
<hr/>			
$C^8H^{16}Ca^2O^8 + 2Aq.$	174	100.00	
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2 CaO	56	26.67	26.78
$C^8H^{16}O^2$	100	47.62	
6 HO	54	25.71	26.40
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$C^8H^{16}Ca^2O^8 + 6Aq.$	210	100.00	

b. Acid Salt. — 1. The solution of the salt *a* in excess of succinic acid, when evaporated to the crystallizing point, yields on cooling, clear, transparent prisms with four-sided summits; they are permanent in the air and redden litmus. (Döpping.) — 2. When the aqueous acid is allowed to act on finely pounded marble, there is formed, together with a small portion of the undissolved salt *a*, a solution of the salt *b*, which crystallizes in long needles on cooling. The saturated solution of the salt *a* in moderately heated dilute nitric acid likewise yields crystals of the same salt, though not so fine. — The crystals give off all their water

at 100°, and nothing further till they are heated to 200°. (Fehling. Their powder gives off vapours of succinic acid at 150°: hot alcohol extracts from it the half of its acid, leaving the salt *a*. The salt *b* is somewhat less soluble in water. (Döpping.)

Dried at 100°.				Fehling.		Fehling.	
Ca	23	20.44	20.88	CaO	28	18.07	18.07
C ⁶ H ⁴ O ⁷	109	79.56		C ⁶ H ⁵ O ⁷	109	70.32	
				2 HO	18	11.61	11.50
<hr/>							
C ⁶ H ⁴ CaO ⁸	137	100.00		+ 2Aq.	155	100.00	

Succinate of Magnesia. — a. Basic. — Precipitated by ammonia from the aqueous solution of the salt *b*, in the form of a white powder, which, after drying in the air, gives off but a small quantity of water at 100°, but the whole at 200°, and then remains unaltered at 230°. (Döpping.)

Dried at 200°.				Döpping.	
6 MgO	120	54.55		54.76	
C ⁶ H ⁴ O ⁶	100	45.45			
<hr/>					
4MgO, C ⁶ H ⁴ Mg ² O ⁸	220	100.00			
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Dried at 100°.				Döpping.	
6 MgO	120	48.58		49.24	
C ⁶ H ⁴ O ⁶	100	40.49			
3 HO	27	10.93		10.71	
<hr/>					
4MgO, C ⁶ H ⁴ Mg ² O ⁸ + 3Aq.	247	100.00			

b. Neutral — The hot aqueous acid readily dissolves carbonate of magnesia, and when evaporated after saturation and set aside in the cold, slowly deposits neutral prisms which are permanent in the air. These crystals give off nearly all their water at 100°, and the rest at 130°. They dissolve readily in water, but are insoluble in alcohol. (Döpping.) — The crystals, which appear to be rhombohedral, become turbid in the air without perceptible loss, give off 40.1 p. c. of water at 100°, 41.9 at 150°, and the whole, amounting to 42.9 per cent. at 200°; after that they suffer no further loss at 250°. (Fehling.) The salt was kept at each of these temperatures for six hours, till it sustained no further loss at that temperature.

Moreover, Fehling distinguishes two salts containing less water, which crystallize from solutions more completely evaporated. One of these salts, *a*, forms clear crystalline crusts which are permanent in the air, give off 30.56 p. c. (8 At.) water at 100°, and 7.2 p. c. (2 At.) more at 200°. — The other salt *β*, forms in the syrupy solution in nodules, which increase till the solution solidifies; are very hard; change to the salt *a* when exposed to the air for some years; dissolve in water more slowly than *a*; give off 10.15 p. c. water at 100°; and suffer no further loss at 250°.

Dried at 200°.				Döpping.		Fehling.	
2 MgO	40	28.57		29.14		28.99	
C ⁶ H ⁴ O ⁶	100	71.43					
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C ⁶ H ⁴ Mg ² O ⁸	140	100.00					
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Ordinary Crystals.				Döpping.		Fehling.	
2 MgO	40	16.13		16.35		16.19	
C ⁶ H ⁴ O ⁶	100	40.32					
12 HO	108	43.55		42.83		43.10	
<hr/>							
C ⁶ H ⁴ Mg ² O ⁸ + 12Aq.	248	100.00					

Succinate of Magnesia and Potash. — 1 pt. of the aqueous acid is saturated with carbonate of magnesia; 1 pt. more of the acid added; and the solution neutralized with carbonate of potash and evaporated, first by heat, afterwards in the air at ordinary temperatures. — Double six-sided pyramids, neutral and permanent in the air. The air-dried crystals give off 20.79 p. c. water at 100° , and leave a residue which deliquesces in the air. They dissolve readily in water, but with difficulty in hydrated alcohol. (Döpping.) — Sometimes, instead of this salt, there is obtained an indistinctly crystallized saline mass containing a much larger quantity of magnesia. (Döpping.)

<i>Crystals.</i>	<i>Döpping.</i>		
KO	47.2	22.24
MgO	20.0	9.42
$C^8H^6O^8$	100.0	47.13
5 HO	45.0	21.21
$C^8H^6KMgO^8 + 5Aq$ 212.2 100.00			

Succinate of Cerium. — Cerous salts form a white, curdy precipitate with alkaline succinates. Succinate of ammonia, however, does not form any precipitate with cerous acetate. The precipitate dissolves very sparingly in water, even on addition of succinic acid, but readily in the stronger acids. (Berzelius.)

Succinate of Yttria. — Alkaline succinates added to concentrated solutions of yttria-salts, throw down succinate of yttria in nodular crystals. (Klaproth.) From concentrated yttria-salts, succinate of soda throws down a crystalline powder in the course of a few minutes; from more dilute solutions, it throws down crystalline granules, after a longer time only. The salt contains 6 At. water, two of which are given off at 100° . It decomposes slowly at a red heat. Dissolves sparingly in cold, more readily in warm water. (Berlin.)

Succinate of Glucina. — Alkaline succinates precipitate glucina-salts (Eckeberg.) The precipitate dissolves with difficulty in water. (Berzelius.)

Succinate of Alumina. — According to Gehlin & Bucholz, succinate of soda precipitates hydrochlorate of alumina (not however according to Bonsdorff, from very dilute solutions); Wenzel obtained by direct combination an insoluble salt, together with a soluble salt which crystallised in prisms.

Succinate of Thorina. — Succinate of ammonia added to neutral thorina-salts throws down white flakes; hydrate of thorina in contact with the aqueous acid, is converted into the same salt, only a trace of which is dissolved by excess of succinic acid. (Berzelius.)

Succinate of Zirconia. — Succinate of ammonia precipitates zirconia-salts.

Succinate of Molybdous Oxide. — Like the acetate. (Berzelius.)

Succinate of Molybdic Oxide. — Like the acetate. (Berzelius.)

Succinate of Molybdic Acid. — The colourless solution obtained by digesting together the two aqueous acids, yields by evaporation, yellow

crystals, from which alcohol separates a yellow powder, dissolving out only the succinic acid. (Berzelius, *Pogg.* 6, 384.)

Aqueous succinic acid dissolves an extremely small quantity of *Hydrated Vanadic Oxide*, forming a pale blue liquid, which, when left to evaporate, leaves a white powder mixed with crystals of the acid. Neutral alkaline succinates do not precipitate vanadous salts. (Berzelius.)

Chromous Succinate. — Succinate of soda forms with protochloride of chromium a scarlet precipitate, which when dried in vacuo becomes lighter and in some places bluish green; the same change of colour takes place immediately on exposure to the air. (Moberg, *J. pr. Chem.* 44, 330.)

<i>Red powder dried in vacuo.</i>		Moberg.	
2 CrO	72	37.89	37.06
8 C	48	25.26	25.37
6 H	6	3.16	3.25
8 O	64	33.69	34.32
<hr/>			
C ⁸ H ⁴ Cr ² O ⁸ + 2Aq.....	190	100.00	100.00

Chromic Succinate? — Neutral succinate of soda forms with sesquichloride of chromium, a pale green pulverulent precipitate, insoluble in water, but soluble in acetic acid. (Hayes.) — The blue precipitate obtained with sesquichloride of chromium dissolves in succinate of soda, and is precipitated from the solution by alcohol. (Berlin.) — According to Fehling, green sesquichloride of chromium is not precipitated by succinate of soda. — When chromic acetate is precipitated with succinic acid, and the precipitate exhausted with water, the filtrate yields on evaporation green-coloured crystals of succinic acid, but no definite salt. (Döpping.) — The green solution of hydrated chromic oxide in warm aqueous succinic acid yields by evaporation, first crystals of green-coloured succinic acid, and then dark violet octohedrons [?]. (Moser.) — The blue solution of the blue hydrate in the acid leaves on evaporation an amorphous mass, which is blue by reflected, red by transmitted light, and from which water extracts nothing but the excess of acid. (Berzelius.)

Uranic Succinate. — Obtained by precipitating a uranic salt with an alkaline succinate; pale yellow, sparingly soluble in water. (Richter.)

Manganous Succinate. — The pale red solution of manganous carbonate in the aqueous acid yields reddish, transparent, highly lustrous, rhombic prisms, double four-sided pyramids, and four-sided tables, which are permanent in the air, and have a slightly acid saline taste. When heated, they become white and like porcelain; by dry distillation, they give off, first water, and then a brown oil, together with carbonic acid and carburetted hydrogen gases. They dissolve in 10 pts. of water at 19°, but are insoluble in alcohol. (John, *N. Gehl.* 4, 439.) — The prisms belong to the doubly oblique prismatic (triclinometric) system; they are of an amethyst colour, neutral, permanent in the air, give off all their water at 100°, and only a trace at 200°. (Döpping.)

	<i>Air-dried crystals.</i>		Döpping.		John.
2 MnO	72	29.51	29.57	30.27	
C ⁸ H ⁴ O ⁶	100	40.98			
8 HO	72	29.51	28.71		
<hr/>					
C ⁸ H ⁴ Mn ² O ⁸ + 8Aq.	244	100.00			

Succinic acid dissolves but a very small quantity of recently precipitated *Antimonie oxide* (Wenzel, Döpping); the acid potash or soda-salt likewise dissolves only a trace of that oxide. (Fehling.)

Succinate of Bismuth. — By digesting succinic acid with hydrated oxide of bismuth, a soluble salt is obtained, containing but a very small quantity of bismuth, and crystallizing in yellow laminæ, together with an insoluble salt. (Wenzel.)

Succinate of Zinc. — When recently precipitated carbonate of zinc is added very slowly and by small portions to a boiling aqueous solution of the acid, which must remain in excess, the salt separates as a white crystalline powder. The air-dried salt gives off a little hygroscopic water at 100° , and nothing more at 200° . It dissolves very slowly in water and succinic acid, readily in mineral acids, acetic acid, ammonia and potash, but is insoluble in alcohol. (Döpping.) — Succinate of soda does not precipitate chloride of zinc. (Bucholz.)

	Dried at 200° .	Döpping.
2 ZnO	80·4	44·57
$C^8H^6O^8$	100·0	55·43
$C^8H^4Zn^2O^8$	180·4	100·00

Succinate of Cadmium. — The metal dissolves very sparingly in aqueous succinic acid, the carbonate very readily. — The solution yields by evaporation, transparent prisms united in spherical groups, which dissolve readily in water, and when treated with alcohol, are resolved into an acid salt, which dissolves in the alcohol, and a more neutral salt easily soluble in water. (John.)

Stannous Succinate. — According to Bucholz, succinate of soda forms a precipitate with stannous hydrochlorate. Wenzel, by digesting 30 pts. of succinic acid with 10 pts. of hydrated stannous oxide, obtained a liquid containing a very small quantity of tin and 11 pts. of residue (neutral salt?).

Stannic Succinate. — By double decomposition. — White, insoluble.

Succinate of Lead. — *a. Polybasic.* — *a.* Remains when the salt *c* is digested with ammonia, in the form of a white anhydrous powder, very sparingly soluble in water. (Berzelius.) It gives off but very little water at 100° , and nothing more at 200° . Hot acetic acid converts it into the salt *e*. It dissolves readily in dilute nitric acid and in potash-ley, but is insoluble in alcohol. (Döpping.) — *β .* A similar salt is obtained by mixing subacetate of lead with a small quantity of ammonia, and precipitating with succinate of ammonia. (Fehling.)

	Dried at 200° .		Berzelius.	Döpping.	Fehling.
			<i>a.</i>	<i>a.</i>	<i>β.</i>
6 PbO	672	87·05	86·93	86·88	85·37
8 C	48	6·22	6·99
4 H	4	0·52	0·52
6 O	48	6·21	7·12
4 PbO, $C^8H^4Pb^2O^8$	722	100·00			100·00

Fehling deduces from his analysis of the salt *β* , the formula $5PbO, C^8H^2O^8$; perhaps it contained a little of the salt *δ* .

b. Basic. — Precipitated on mixing subacetate of lead, with neutral or acid succinate of ammonia, potash, or soda. The precipitate obtained with the acid soda-salt from hot solutions, coagulates to a plastic mass, which hardens as it cools, and when exposed to the air for several days, becomes brittle, and may be rubbed to a powder which no longer bakes together at 100°. The salt dried at 130° gives off 1.13 p. c. more at 230°, but turns brown at the commencement. The salt is converted by ammonia into the salt *a*, and by boiling acetic acid into *c*. It is insoluble in water and alcohol, but soluble in potash. (Döpping.) — Even when 1 pt. of succinic acid is dissolved, together with an equal quantity of oxalic, tartaric, malic, or nitric acid, in 1000 pts. of water, it still forms in hot solutions, this characteristic tenacious precipitate. (Köhnke, *N. Br. Arch.* 39, 153.)

The salt may be obtained in the crystalline form by the following processes: *a*. A boiling neutral solution of succinate of ammonia is added, by small portions, to a boiling and tolerably strong solution of sub-acetate of lead, till the white precipitate just ceases to redissolve, after which the clear liquid is left to cool in a closed vessel. If the inner sides of the vessel be then scratched with a glass rod, the whole of the salt separates in a few minutes, in the form of a white powder; if, on the contrary, the liquid be left at rest, it yields, in two or three days, rosette-shaped crystals, having the same composition; and the decanted mother-liquor yields an additional quantity of the pulverulent salt on scratching the vessel with the glass rod. The air-dried salt, either crystallized or pulverulent, gives off only a trace at 230°, at which point it begins to turn yellow. — *β*. Sometimes, instead of *a*, crystals are obtained having the composition given under *β*; these crystals give off 1.99 p. c. of water at 100°, and nothing more at a higher temperature. — *γ*. When neutral succinate of potash or soda is boiled with moderately strong subacetate of lead, and the liquid decanted from the plastic mass into a flask which can be closed, it yields, after some months, a few large crystals, which after drying in the air, give off 3.35 per cent. of water at 150°, and nothing more at 220°. (Fehling.)

	Döpping.		Fehling.			
	dried at 130°.		<i>a</i> .	<i>β</i> dried over oil of vitriol.	<i>γ</i> air-dried.	
3 PbO.....	336	77.07	76.97	78.33	76.78	75.60
8 C.....	48	11.01		10.71	10.79	9.71
4 H.....	6	0.91		0.83	1.19	1.21
6 O.....	48	11.01		10.13	11.24	13.48
PbO, C ⁶ H ⁴ Pb ² O ⁸	436	100.00		100.00	100.00	100.00

Fehling regards the salt *a* as 3PbO, C⁶H²O⁶; the salt *β* as 3PbO, C⁶H⁴O⁶; and the salt 3PbO, C⁶H⁶O⁷.

c. Neutral. — Obtained by precipitating neutral or basic acetate of lead with the free acid, or nitrate of chloride of lead with an alkaline succinate. (Berzelius, Döpping.) — White crystalline powder, which separates in long narrow laminae from the solution in hot aqueous succinic acid; anhydrous. (Berzelius.) The air-dried salt loses two or three per cent. of hygroscopic water at 100°, and no more at 230°, at which temperature it begins to turn brown. (Döpping.) When more strongly heated, it blackens, and burns away with a glimmering light, leaving a mixture of lead and oxide of lead. (Winckler, *Repert.* 39, 66.) It is converted into the salt *a* by ammonia. (Berzelius.) It is but very

sparingly soluble in water, acetic acid, or even in heated succinic acid, and is insoluble in alcohol. (Döpping.) It dissolves in aqueous neutral acetate of lead. (Winckler.)

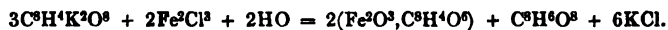
	Dried at 100°.		Berzelius.		Döpping.		Fehling.	
2 PbO	224	69·13	69·10	69·12	70·05			
8 C	48	14·82	14·71		14·81			
4 H	4	1·23	1·39		1·16			
6 O	48	14·82	14·80		13·98			
$C^8H^4Pb^2O^8$	324	100·00	100·00		100·00			

[The salt analyzed by Fehling was obtained by decomposing succinic ether with oxide of lead; he regards it as $2PbO, C^8H^2O^5$; but this formula requires 71·11PbO, 15·24C, 0·95 H and 12·70 O.]

Ferrous Succinate.—Alkaline succinates form with ferrous salts a grey-green precipitate, which oxidizes in the air, and dissolves with difficulty in water, somewhat more readily in aqueous succinic acid. (Berzelius, *Lehrb.*) It dissolves partially in ammonia and ammoniacal salts. (Wittstein.)

Ferric Succinate.—*a. Polybasic.*—*a.* When the recently precipitated salt *b* is treated with warm aqueous ammonia, it becomes gelatinous and darker, and after washing and drying at 200°, appears black-brown and easy friable, and contains 95·88 p. c. ferric oxide, therefore about $= 30 Fe^2O^3, C^8H^4O^6$.—*β.* By treatment in the cold, a salt is obtained, which has a similar appearance, but after drying at 200°, contains 93·21 p. c. ferric oxide, and has, therefore, about the composition $18 Fe^2O^3, C^8H^4O^6$. (Döpping.) According to Bucholz also, a more basic salt is obtained by boiling the recently precipitated salt *b* with water; but according to Döpping, such is not the case.—When a ferric salt is precipitated by succinate of ammonia slightly supersaturated with ammonia, the precipitate contains 80 p. c. of ferric oxide. (Fehling.)

b. Basic.—Neutral alkaline succinates form with susquichloride of iron, a pale brown-red gelatinous precipitate. (Bucholz.)—In this reaction, one-third of the succinic acid is set free. Probably in this manner:



If the iron solution contains a little free acid, the whole of the ferric oxide is indeed precipitated, but redissolves during the washing, unless the precipitate be boiled up and left to cool again. (Berzelius.)—The precipitate settles but slowly, and is difficult to wash on the filter, because it coagulates to a solid paste, which does not readily allow the water to pass through. But if the chloride of iron be mixed with acetate of soda before precipitation with the succinate, the precipitate obtained is not gelatinous, but forms a pale brick-red powder, which settles down quickly, and after addition of 70 per cent. alcohol, easily lets the liquid run through the filter, but becomes gelatinous as soon as an attempt is made to wash it with water, without however altering its composition. (Döpping.)

The precipitate when dry has a dark red-brown colour, (Bucholz,) and is easily rubbed to a dark brick-red powder. (Döpping.)—It requires a heat of 180° to free it from hygroscopic water, and rapidly absorbs water again

from the air. (Döpping.) The dry salt swells and glows when ignited, leaving 38.5 p. c. of dark brown-red oxide. (Bucholz.)—It is insoluble in water. (Bucholz,) and dissolves very sparingly but without alteration in boiling water. (Döpping.)—According to Bucholz, whose statement is contradicted by Döpping, it is resolved by boiling with water into a more acid salt which dissolves, and a residue of basic salt.—The recently precipitated salt dissolves pretty freely in boiling succinic acid; the solution when evaporated, deposits the greater part of the salt in flakes of unaltered composition, and finally yields crystals of succinic acid coloured with a small quantity of salt, from which it may be separated by alcohol. (Döpping.) Wenzel obtained a similar solution by boiling ferric hydrate with excess of succinic acid; this solution is not precipitated by alkalis. (*vid. inf.* Winckler.)—Since, in the precipitation of a ferric salt by neutral alkaline succinates, $\frac{1}{2}$ of the succinic acid is set free, this free acid redissolves a portion of the precipitate when the mixture is boiled, forming a very pale red solution; but the undissolved portion, when dried at 200°, contains 43.9 p. c. ferric oxide, therefore not perceptibly more than before. (Döpping.)—The salt *b* dissolves slowly in cold, readily in hot acetic acid. (Döpping.) It dissolves readily in dilute mineral acids. (Bucholz, *N. Gehl.* 2, 515.) When this salt is precipitated by excess of ammonia or soda, it redissolves therein, forming a liquid which, in the course of 12 hours, solidifies to a light brown-red jelly. (Winckler, *Repert.* 39, 65.)—The statement of Lecanu & Serbat, that this salt *b* is likewise soluble in aqueous acetate or nitrate of soda, is unfounded. (Berzelius, *Jahresber.* 4, 192; Gm.)

	<i>Dried at 200°.</i>		Döpping.	
Fe ² O ³	80 44.44	43.46 to 43.80
C ⁸ H ⁴ O ⁶	100 55.56		
<hr/>				
Fe ² O ³ , C ⁸ H ⁴ O ⁶	180 100.00		

Without further analyses, it is impossible to construct a formula for this salt according to the substitution-theory.

Succinate of Cobalt.—Alkaline succinates form only with concentrated solutions of cobalt-salts, a peach-blossom coloured, somewhat soluble precipitate. (Berzelius, Macaire-Princep, *J. Pharm.* 15, 529.)

Succinate of Nickel.—The pale green solution of hydrated oxide of nickel in hot succinic acid, yields, when evaporated over oil of vitriol in a vessel containing air, small, green, crystalline nodules, which, after being pulverized, may be purified from the free acid by alcohol. The salt does not redden litmus, gives off nearly all its water at 100°, the whole at 130°, and remains undecomposed at 200°. It dissolves in water, acetic acid, and ammonia, but not in alcohol. (Döpping.)

	<i>Dried at 200°.</i>		Döpping.	
2 NiO	75 42.86	42.28
C ⁸ H ⁴ O ⁶	100 57.14		
<hr/>				
C ⁸ H ⁴ Ni ² O ⁸	175 100.00		
	<i>Air-dried crystals.</i>		Döpping.	
2 NiO	75 30.36	30.38
C ⁸ H ⁴ O ⁶	100 40.49		
8 H ² O	72 29.15	29.08
<hr/>				
C ⁸ H ⁴ Ni ² O ⁸ + 8Aq.....	247 100.00		

Cupric Succinate. — Alkaline succinates added to cupric salts throw down curdy flakes of a fine green colour (Macaire-Princep); pale blue flakes. (Winckler.) — By digesting 10 pts. of cupric carbonate with 30 pts. of succinic acid dissolved in water, there is obtained 17 per cent. of undissolved pale green salt, and a solution of succinic acid containing copper. (Wenzel.) When recently precipitated cupric carbonate is added to the boiling aqueous acid, which must remain in excess, the salt is obtained in the form of a soft, bluish green, crystalline powder, which, after drying in the air, gives off only 2 or 3 per cent. of hygroscopic water at 100° , and nothing more at 200° . It dissolves with difficulty in water and succinic acid, forming a pale green solution, more easily in acetic acid, but is insoluble in alcohol (Döpping), and likewise in ether. (Unverdorben.)

	<i>Dried at 200°.</i>	<i>Döpping.</i>
2 CuO	80	44.44
$C^8H^4O^2$	100	55.56
$C^8H^4Cu^2O^8$	180	100.00

Mercurous Succinate. — Alkaline succinates form a white precipitate with mercurous nitrate. (Bucholz, Gehlen.) The precipitate is contaminated with basic mercurous nitrate. — It is insoluble in water, succinic acid, and alcohol, but dissolves readily in nitric acid. (Döpping.) With an excess of succinate of soda, a white precipitate is obtained, which when washed on the filter, begins to dissolve and pass through milky, as soon as all the succinate of soda is removed; turns yellow when further washed with water; and when boiled with that liquid, becomes black from reduction of mercury. The filtrate contains mercuric as well as mercurous oxide in solution. (H. Rose, *Pogg.* 53, 127; *comp.* Harff and Burkhardt, *N. Br. Arch.* 5, 287, and 11, 272.)

Mercuric Nitrate. — Recently precipitated mercuric oxide is partially converted by long boiling with the aqueous acid into a white powder which contains rather more than 2 At. oxide to 1 At. acid; the liquid contains a small quantity of mercuric oxide in solution. — When mercuric acetate is evaporated to dryness with succinic acid, and the excess of acid dissolved out by alcohol, there remains a sparingly soluble white powder, free from acetic acid, but containing mercurous acid. — Neither succinic acid, nor the soda-salt precipitates corrosive sublimate. The latter mixture yields by evaporation, silky needles, apparently consisting of a compound of mercuric chloride with succinate of soda. (Döpping.) — Succinate of soda added to mercuric acetate throws down a fine white powder. (Winckler.)

Succinate of Silver. — Succinate of soda precipitates nitrate but not sulphate of silver. (Bucholz.) Free succinic acid does not precipitate nitrate of silver. (Döpping.) The precipitate is a fine, white, amorphous powder, which settles down rapidly and is easily washed. When dried in the air, it diminishes slightly in weight at 100° ; at 150° it acquires a constantly deepening green-grey colour, without diminishing much in weight. (Döpping.) In dry chlorine gas it is instantly decomposed with evolution of heat. (Liebig.) In a stream of hydrogen gas at 100° , it acquires a lemon-yellow colour, and at a somewhat higher temperature, half of it sublimes, while yellow succinate of suboxide of silver remains behind. (Wöhler, *Ann. Pharm.* 30, 4.) — It dissolves very slowly in

water or acetic acid, readily in dilute nitric acid or ammonia, but is insoluble in alcohol. (Döpping.)

	Dried at 100°.		D'Arcet.		Döpping.		Fehling.	
2 AgO	232	69·88	69·65	69·91	69·53			
C ⁶ H ⁴ O ⁶	100	30·12						
<hr/>								
C ⁸ H ⁴ Ag ² O ⁸	332	100·00						
<hr/>								
	Dried at 100°.		Zwenger.	Bromeis.	Sthamer.	Radcliff.	Ronalds.	
2AgO	232	69·88	69·35	69·27	69·07	69·35	69·16	
8 C	48	14·46	14·49	15·73	14·30	14·34	14·21	
4 H	4	1·20	1·46	1·61	1·50	1·28	1·23	
6 O	48	14·46	14·70	13·39	15·13	15·03	15·40	
<hr/>								
C ⁸ H ⁴ Ag ² O ⁸ 332	100·00	100·00	100·00	100·00	100·00	100·00	100·00	

D'Arcet, Döpping and Fehling analysed a silver-salt, the acid of which was obtained from amber; Zwenger's acid was obtained from wormwood; Bromeis's from stearic acid, Sthamer's from Japan wax; Radcliff's from spermaceti; and Ronalds's from beeswax.

Succinic acid dissolves in 1·37 pt. of boiling highly rectified alcohol. (Wenzel.) — It is but very slightly soluble in ether. (D'Arcet.)

Conjugated Compound of Succinic Acid.

Sulphosuccinic Acid. C⁶H⁴O³·2So².

FEHLING. (1841.) *Ann. Pharm.* 38, 285; 49, 203.

Bernsteinschwefelsäure; Bernsteinunterschwefelsäure.

Formation and Preparation. The vapour of anhydrous sulphuric acid brought in contact with succinic acid contained in a cooled flask, forms, with considerable evolution of heat, a brown, transparent, viscid, mass. It is only when the succinic acid is contaminated with empyreumatic oil, that sulphurous acid is evolved in this reaction and the mass becomes nearly black and opaque. — The mass is left to stand for a few hours at 40° to 50°, or for 24 hours at 15°, so that the action may be complete; then taken up with water; mixed from time to time with carbonate of baryta or carbonate of lead, till a filtered sample no longer precipitates chloride of barium; the liquid filtered; the sulphosuccinate of lead precipitated by acetate of lead, the succinate of lead then remaining in solution; — the well washed precipitate decomposed by sulphuretted hydrogen, and the filtrate evaporated in vacuo over oil of vitriol to a syrup, which gradually yields crystals.

Properties. Nodular crystals having a strongly acid taste. They cannot be obtained in the dry state, but remain gummy, and are therefore not adapted for analysis: they contain 13·62 p. c. sulphur.

Decompositions. The crystals when heated give off suffocating vapours containing succinic acid, and leave a difficultly combustible charcoal. — 2. The aqueous solution suffers partial decomposition when evaporated in the water-bath, a brown mass remaining and a trace of sulphuric acid being set free.

Combinations. The crystals absorb moisture from the air and dissolve readily in water.

Sulphosuccinates. — The acid saturates bases completely and expels acetic acid. [Fehling, in accordance with his analysis of the lead-salt, regards the acid as quadribasic $=C^6H^2O^8, S^2O^8 + 4HO$; Berzelius (*Jahresber.* 22, 246,) regards it as tribasic $=C^6H^3O^8, 2SO^8 + 3HO$, a view which is in accordance with Gerhardt's law (vii. 222); for, $2+2-1=3$. According to this view, the formula of the free acid is $C^6H^4O^8, 2SO^8$; and of the 6H, three may be replaced by metals.] See also remarks in *Rev. Scient.* 6, 285.

Sulphosuccinate of Ammonia. — The acid evaporated to a syrup, and immersed in ammoniacal gas, solidifies in a few seconds from formation of needles, and is converted after some time into a nearly dry solid mass. When dried in vacuo over oil of vitriol, it acquires the power of reddening litmus slightly.

<i>Dried at a gentle heat.</i>				Fehling.
8 C.....	48	17.98 18.19
3 N.....	42	15.73	
17 H	17	6.37 6.34
10 O.....	80	29.96	
2SO ⁸	80	29.96	
$C^6H^3(NH^4)^2O^8, 2SO^8 + 2Aq.$				267 100.00

Sulphosuccinate of Potash. — *a. Tribasic.* — The aqueous acid rendered slightly alkaline by carbonate of potash, and evaporated to a syrup in vacuo over oil of vitriol, yields in a few days only a few very deliquescent crystals; but if it be then mixed with a small quantity of acid, it solidifies almost entirely to a crystalline magma, from which by recrystallization pure crystals may be obtained. The crystallization is greatly accelerated by covering the mother-liquor with a layer of alcohol. The crystals left in vacuo for a few days, give off 5.4 p. c. (2 At.) water, afterwards at 100°, 7.6 p. c. (3 At.) more; nothing further is given off at 150°, but at a higher temperature the crystals are decomposed, leaving a mixture of sulphate and sulphite of potash. The salt absorbs moisture from the air, but without deliquescing, dissolves readily in water with a slightly acid reaction, but scarcely at all in absolute alcohol.

<i>Dried in vacuo.</i>				Fehling.
3 KO	141.6	42.83 41.50
8 C	48.0	14.52 14.99
5 H	5.0	1.51 1.68
7 O	56.0	16.94	
2 SO ⁸	80.0	24.20	
$C^6H^3K^3O^8, 2SO^8 + 2Aq.$				330.6 100.00

b. Bibasic. — The solution of *a* mixed with a larger quantity of acid, yields crystals which have an acid reaction, and separate more easily than those of *a*. They give off 2.78 p. c. (1 At.) water in vacuo, 1 At. more when gently heated, and 11.3 p. c. (4 At.) in all at 100°. The salt remains dry when exposed to the air, but dissolves readily in water, and in almost all proportions in boiling water.

<i>Crystals dried at a gentle heat.</i>				Fehling.
2 KO	94.4	32.28	31.63	
8 C	48.0	16.42		
6 H	6.0	2.05		
8 O	64.0	21.89		
2 SO ³	80.0	27.36	26.85	
<hr/>				
$C^8H^4K^2O^8, 2SO^3 + 2Aq.$	292.4	100.00		
<i>Air-dried Crystals.</i>				Fehling.
2 KO	94.4	30.41	29.93	
8 C	48.0	15.47	15.66	
8 H	8.0	2.58	2.67	
10 O	80.0	25.77		
2 SO ³	80.0	25.77		
<hr/>				
$C^8H^4K^2O^8, 2SO^3 + 4Aq.$	310.4	100.00		

Sulphosuccinate of Soda. — Obtained by precipitating the following baryta-salt with excess of sulphate of soda, evaporating the filtrate to dryness, and dissolving out the sulphosuccinate of soda by alcohol. It crystallizes with difficulty and dissolves readily in water and in ordinary alcohol.

Sulphosuccinate of Baryta. — Acetate of baryta is precipitated even by the free acid; nitrate or hydrochlorate of baryta only by the acid when in combination with ammonia, potash, or soda. The precipitate, after drying at 100°, gives off nothing more at 200°. While still moist it dissolves readily in hydrochloric or nitric acid, sparingly in hot acetic acid; after drying, it is much less soluble in hydrochloric acid, and almost insoluble in acetic. Its solution in aqueous sulphosuccinic acid placed in vacuo yields crystals doubtless containing less baryta.

<i>Dried at 100°.</i>				Fehling.
3 BaO	229.8	57.34	56.90	
8 C	48.0	11.98	11.69	
3 H	3.0	0.74	0.94	
11 O	88.0	21.96	22.49	
2 S	32.0	7.98	7.98	
<hr/>				
$C^8H^3Ba^2O^8, 2SO^3$	400.8	100.00	100.00	

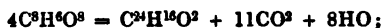
Sulphosuccinate of Lime. — The aqueous acid readily dissolves marble, even in the cold, but retains its acid reaction, and yields by evaporation, a non-crystalline residue, which, after drying at 100°, contains 24.6 p. c. lime, and is therefore $C^8H^4Ca^2O^8, 2SO^3$.

The *magnesia-salt* does not crystallize.

The *potash-salt* does not precipitate the salts of manganese, iron, cobalt, nickel, or copper.

Sulphosuccinate of Lead. — *a. Quadribasic.* — The acid liquid purified from free sulphuric acid by digestion with carbonate of lead (*vid. Preparation of Sulphosuccinic acid*) is mixed with so much ammonia that it retains only a slightly acid reaction, and then precipitated by neutral acetate of lead. The yellowish white precipitate heated to 100°, after drying in the air, gives off 5.57 p. c. (4 At.) water. Boiling acetic acid converts it into the salt *b*, by removing 1 At. oxide of lead. It dissolves with tolerable facility in hydrochloric, nitric, or sulphosuccinic acid.

is obtained (amounting to 0·2 per cent. of the lime-salt). Succinone is a thin colourless liquid, having only a faint empyreumatic odour. It contains 79·86 C, 8·90 H, and 11·24 O. (D'Arcet.) From these numbers D'Arcet deduces for succinone the formula $C^{24}H^{18}O^8$, and explains its formation by the equation:



nevertheless, he himself admits that succinone may be only a mixture.

a. Crystals with 2 At. Water. — When aqueous succinate of soda is mixed with chloride of calcium at a boiling heat, or when the cold mixture is heated to the boiling point, delicate needles quickly separate, which, after drying in the air, give off only 2·5 p. c. of water at 100° , and do not lose all their water, amounting to 11·2 per cent. till they are heated to 200° . The mother-liquor yields by evaporation a further quantity of the needles *a*; but when these are left in the liquid for 24 hours, they change to the needles *β*. (Fehling.)

β. Crystals with 6 At. Water. — A mixture of succinate of soda and chloride of calcium left in the cold or gently heated, deposits, after several hours,—the more quickly as the solution is more concentrated,—needles which gradually increase in size and hardness. After drying in the air, they give off 22·35 p. c. (5 At.) water at 100° , and at 200° , the entire quantity, amounting to 26·4 p. c. (6 At.) (Fehling.) The air-dried needles give off the greater part of their water at 100° , and the whole between 120° and 130° , so that at 200° , nothing more is evolved. (Döpping.)

The salt dissolves sparingly in water and in acetic acid, better in succinic acid, very easily in nitric or hydrochloric acid, but is insoluble in alcohol.

<i>Dried at 200°.</i>		Fehling.	
2 CaO.....	56	35·90	36·03
$C^8H^6O^8$	100	64·10	63·97
$C^8H^4Ca^2O^8$	156	100·00	100·00

<i>Air-dried Crystals a.</i>			
2 CaO.....	56	32·18	32·32
$C^8H^6O^8$	100	57·48	
2 HO.....	18	10·34	11·20
$C^8H^4Ca^2O^8 + 2Aq$	174	100·00	

2 CaO.....	56	26·67	26·74	26·78
$C^8H^6O^8$	100	47·62		
6 HO.....	54	25·71	26·42	26·40
$C^8H^4Ca^2O^8 + 6Aq$	210	100·00		

b. Acid Salt. — 1. The solution of the salt *a* in excess of succinic acid, when evaporated to the crystallizing point, yields on cooling, clear, transparent prisms with four-sided summits; they are permanent in the air and redden litmus. (Döpping.) — 2. When the aqueous acid is allowed to act on finely pounded marble, there is formed, together with a small portion of the undissolved salt *a*, a solution of the salt *b*, which crystallizes in long needles on cooling. The saturated solution of the salt *a* in moderately heated dilute nitric acid likewise yields crystals of the same salt, though not so fine. — The crystals give off all their water

at 100°, and nothing further till they are heated to 200°. (Fehling. Their powder gives off vapours of succinic acid at 150°: hot alcohol extracts from it the half of its acid, leaving the salt *a*. The salt *b* is somewhat less soluble in water. (Döpping.)

Dried at 100°.				Fehling.		Fehling.	
Ca	23	20.44	20.88	CaO	28	18.07	18.07
C ⁸ H ⁴ O ⁷	109	79.56		C ⁸ H ³ O ⁷	109	70.32	
				2 HO	18	11.61	11.50
<hr/>							
C ⁸ H ⁴ CaO ⁸	137	100.00		+ 2Aq.	155	100.00	

Succinate of Magnesia. — *a. Basic.* — Precipitated by ammonia from the aqueous solution of the salt *b*, in the form of a white powder, which, after drying in the air, gives off but a small quantity of water at 100°, but the whole at 200°, and then remains unaltered at 230°. (Döpping.)

Dried at 200°.				Döpping.	
6 MgO	120	54.55		54.76	
C ⁸ H ⁴ O ⁸	100	45.45			
<hr/>					
4MgO, C ⁸ H ⁴ Mg ² O ⁸	220	100.00			
<hr/>					
Dried at 100°.				Döpping.	
6 MgO	120	48.58		49.24	
C ⁸ H ⁴ O ⁸	100	40.49			
3 HO	27	10.93		10.71	
<hr/>					
4MgO, C ⁸ H ⁴ Mg ² O ⁸ + 3Aq.	247	100.00			

b. Neutral — The hot aqueous acid readily dissolves carbonate of magnesia, and when evaporated after saturation and set aside in the cold, slowly deposits neutral prisms which are permanent in the air. These crystals give off nearly all their water at 100°, and the rest at 130°. They dissolve readily in water, but are insoluble in alcohol. (Döpping.) — The crystals, which appear to be rhombohedral, become turbid in the air without perceptible loss, give off 40.1 p. c. of water at 100°, 41.9 at 150°, and the whole, amounting to 42.9 per cent. at 200°; after that they suffer no further loss at 250°. (Fehling.) The salt was kept at each of these temperatures for six hours, till it sustained no further loss at that temperature.

Moreover, Fehling distinguishes two salts containing less water, which crystallize from solutions more completely evaporated. One of these salts, *a*, forms clear crystalline crusts which are permanent in the air, give off 30.56 p. c. (8 At.) water at 100°, and 7.2 p. c. (2 At.) more at 200°. — The other salt *β*, forms in the syrupy solution in nodules, which increase till the solution solidifies; are very hard; change to the salt *a* when exposed to the air for some years; dissolve in water more slowly than *a*; give off 10.15 p. c. water at 100°; and suffer no further loss at 250°.

Dried at 200°.				Döpping.		Fehling.	
2 MgO	40	28.57		29.14		28.99	
C ⁸ H ⁴ O ⁸	100	71.43					
<hr/>							
C ⁸ H ⁴ Mg ² O ⁸	140	100.00					
<hr/>							
Ordinary Crystals.				Döpping.		Fehling.	
2 MgO	40	16.13		16.35		16.19	
C ⁸ H ⁴ O ⁸	100	40.32					
12 HO	108	43.55		42.83		43.10	
<hr/>							
C ⁸ H ⁴ Mg ² O ⁸ + 12Aq.	248	100.00					

Succinate of Magnesia and Potash. — 1 pt. of the aqueous acid is saturated with carbonate of magnesia; 1 pt. more of the acid added; and the solution neutralized with carbonate of potash and evaporated, first by heat, afterwards in the air at ordinary temperatures. — Double six-sided pyramids, neutral and permanent in the air. The air-dried crystals give off 20.79 p. c. water at 100° , and leave a residue which deliquesces in the air. They dissolve readily in water, but with difficulty in hydrated alcohol. (Döpping.) — Sometimes, instead of this salt, there is obtained an indistinctly crystallized saline mass containing a much larger quantity of magnesia. (Döpping.)

Crystals.	Döpping.
KO	22.24
MgO	9.42
$C^4H^6O^2$	47.13
5 HO	21.21
$C^4H^4KMgO^8 + 5Aq$	100.00

Succinate of Cerium. — Cerous salts form a white, curdy precipitate with alkaline succinates. Succinate of ammonia, however, does not form any precipitate with cerous acetate. The precipitate dissolves very sparingly in water, even on addition of succinic acid, but readily in the stronger acids. (Berzelius.)

Succinate of Yttria. — Alkaline succinates added to concentrated solutions of yttria-salts, throw down succinate of yttria in nodular crystals. (Klaproth.) From concentrated yttria-salts, succinate of soda throws down a crystalline powder in the course of a few minutes; from more dilute solutions, it throws down crystalline granules, after a longer time only. The salt contains 6 At. water, two of which are given off at 100° . It decomposes slowly at a red heat. Dissolves sparingly in cold, more readily in warm water. (Berlin.)

Succinate of Glucina. — Alkaline succinates precipitate glucina-salts (Eckeberg.) The precipitate dissolves with difficulty in water. (Berzelius.)

Succinate of Alumina. — According to Gehlin & Bucholz, succinate of soda precipitates hydrochlorate of alumina (not however according to Bonsdorff, from very dilute solutions); Wenzel obtained by direct combination an insoluble salt, together with a soluble salt which crystallised in prisms.

Succinate of Thorina. — Succinate of ammonia added to neutral thorina-salts throws down white flakes; hydrate of thorina in contact with the aqueous acid, is converted into the same salt, only a trace of which is dissolved by excess of succinic acid. (Berzelius.)

Succinate of Zirconia. — Succinate of ammonia precipitates zirconia-salts.

Succinate of Molybdous Oxide. — Like the acetate. (Berzelius.)

Succinate of Molybdic Oxide. — Like the acetate. (Berzelius.)

Succinate of Molybdic Acid. — The colourless solution obtained by digesting together the two aqueous acids, yields by evaporation, yellow

crystals, from which alcohol separates a yellow powder, dissolving out only the succinic acid. (Berzelius, *Pogg.* 6, 384.)

Aqueous succinic acid dissolves an extremely small quantity of *Hydrated Vanadic Oxide*, forming a pale blue liquid, which, when left to evaporate, leaves a white powder mixed with crystals of the acid. Neutral alkaline succinates do not precipitate vanadous salts. (Berzelius.)

Chromous Succinate. — Succinate of soda forms with protochloride of chromium a scarlet precipitate, which when dried in vacuo becomes lighter and in some places bluish green; the same change of colour takes place immediately on exposure to the air. (Moberg, *J. pr. Chem.* 44, 330.)

<i>Red powder dried in vacuo.</i>		Moberg.	
2 CrO	72	37.89	37.06
8 C	48	25.26	25.37
6 H	6	3.16	3.25
8 O	64	33.69	34.32
<hr/>			
C ⁸ H ⁴ Cr ² O ⁸ + 2Aq.....	190	100.00	100.00

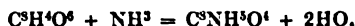
Chromic Succinate? — Neutral succinate of soda forms with sesquichloride of chromium, a pale green pulverulent precipitate, insoluble in water, but soluble in acetic acid. (Hayes.) — The blue precipitate obtained with sesquichloride of chromium dissolves in succinate of soda, and is precipitated from the solution by alcohol. (Berlin.) — According to Fehling, green sesquichloride of chromium is not precipitated by succinate of soda. — When chromic acetate is precipitated with succinic acid, and the precipitate exhausted with water, the filtrate yields on evaporation green-coloured crystals of succinic acid, but no definite salt. (Döpping.) — The green solution of hydrated chromic oxide in warm aqueous succinic acid yields by evaporation, first crystals of green-coloured succinic acid, and then dark violet octohedrons [?]. (Moser.) — The blue solution of the blue hydrate in the acid leaves on evaporation an amorphous mass, which is blue by reflected, red by transmitted light, and from which water extracts nothing but the excess of acid. (Berzelius.)

Uranic Succinate. — Obtained by precipitating a uranic salt with an alkaline succinate; pale yellow, sparingly soluble in water. (Richter.)

Manganous Succinate. — The pale red solution of manganous carbonate in the aqueous acid yields reddish, transparent, highly lustrous, rhombic prisms, double four-sided pyramids, and four-sided tables, which are permanent in the air, and have a slightly acid saline taste. When heated, they become white and like porcelain; by dry distillation, they give off, first water, and then a brown oil, together with carbonic acid and carburetted hydrogen gases. They dissolve in 10 pts. of water at 19°, but are insoluble in alcohol. (John, *N. Gehl.* 4, 439.) — The prisms belong to the doubly oblique prismatic (triclinometric) system; they are of an amethyst colour, neutral, permanent in the air, give off all their water at 100°, and only a trace at 200°. (Döpping.)

	<i>Air-dried crystals.</i>		Döpping.		John.
2 MnO	72	29.51	29.57	30.27	
C ⁸ H ⁴ O ⁸	100	40.98			
8 HO	72	29.51	28.71		
<hr/>					
C ⁸ H ⁴ Mn ² O ⁸ + 8Aq.	244	100.00			

Anhydrous succinic acid immersed in ammoniacal gas, is converted with evolution of heat and formation of water, into bisuccinamide:



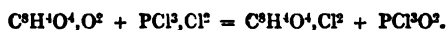
It does not absorb moisture from the air. Dissolves in water, but less quickly than the hydrated acid, and separates out in the form of the latter.

It dissolves in alcohol more readily than in water, but is very sparingly soluble in ether. (D'Arcet.)

¶ Chloride of Succinyl. $C^8H^4O^4.Cl^2$.

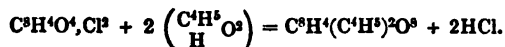
GERHARDT & CHIOZZA. *Compt. rend.* 36, 1050; *Instit.* 1853, 253; *Ann. Pharm.* 87, 293; *Jahresber.* 1853, 394.

Formed by the action of 1 At. pentachloride of phosphorus on 1 At. anhydrous succinic acid:



Hence it is obtained by the action of 2 At. pentachloride of phosphorus on 1 At. hydrated succinic acid. The action then consists of two stages, the first being the formation of anhydrous succinic acid, as shown on page 135; and the second that just given.

Strongly refracting liquid, which fumes in the air, and has a penetrating odour, like that of damp straw. Sp. gr. 1.39. Boils at 190°. When boiled for some time, it suffers partial decomposition, a small quantity of carbonaceous matter being left behind: hence its vapour-density could not be determined. In contact with moist air, it is converted into crystallized succinic acid. Absolute alcohol acts upon it with rise of temperature, hydrochloric acid being copiously evolved and succinic ether formed:



Aniline acts violently on chloride of succinyl, forming succinilide. (Gerhardt & Chiozza.) ¶.

b. Bromine-nucleus. $C^8Br^2H^6$.

Bibromobutyric Acid.



CAHOURS. (1847.) *N. Ann. Chim. Phys.* 19, 495; also *J. pr. Chem.* 41, 67.

Bibrombutterst ure, Acide bromocitronique.

Formation. In the decomposition of itaconate or citraconate (not of butyrate, p. 83) of potash by bromine (vid. *Citraconic acid*).

Preparation. Bromine is added in successive portions, till slightly in excess, to a solution of 1 pt. citraconate of potash in 1½ pt. water, whereupon, carbonic acid is evolved and a heavy oil, amounting to ¼ of the acid, is deposited. From this oil, after washing with water, the acid is extracted by dilute potash; and the alkaline liquid decanted from the small residual quantity of neutral oil, and supersaturated with hydrochloric acid, which sometimes separates an oily acid, sometimes a buttery mixture of this oil with a crystalline modification of bibromobutyric acid more soluble in water than the oily acid.

Oily acid. — The precipitated oil is washed with water, till it no longer produces a cloud in a silver-solution, or till the turbidity disappears on the addition of a small quantity of nitric acid; after which it is dried in vacuo over oil of vitriol.

Crystalline acid. — Often formed spontaneously from the oily acid. Frequently also produced at once when the acid is separated from the neutral oil by potash, as above described, and the alkaline liquid supersaturated with dilute nitric acid; the acid then separates in crystalline flakes, which are washed with the smallest possible quantity of cold water, well dried, dissolved in ether, and left to crystallize by spontaneous evaporation.

Properties. The oily acid is pale yellow, much heavier than water, has a faint odour in the cold, but an irritating odour at higher temperatures and a pungent taste. The crystalline acid forms long silky needles, which melt at a gentle heat, and volatilize at a higher temperature, leaving only a small carbonaceous residue.

		Cahours.							
				<i>a.</i>	<i>b.</i>		<i>c.</i>		
8 C	48	19·51	19·32	19·46	19·66
2 Br.....	160	65·04	64·38	65·14	64·99
6 H	6	2·41	2·41	2·34	2·39
4 O	32	13·01	13·89	13·06	12·96
<hr/>									
C ⁶ Br ² H ⁶ O ⁴	246	100·00	100·00	100·00	100·00

a, oily acid from citraconate of potash; *b*, from itaconate; *c*, crystalline acid.

Decompositions. 1. The oily acid is partially decomposed by distillation, giving off vapours of bromine. — 2. It dissolves in gently heated oil of vitriol: and is but partially precipitated therefrom by water. — 3. Both the oily and the crystalline acid become strongly heated by contact with concentrated potash, and give off a peculiar odour, after which, even concentrated acids separate nothing. — 4. The alcoholic solution of the potash-salt of the oily acid, treated after the manner of Melsens with potassium-amalgam (ix. 211) deposits bromide of potassium, and afterwards on addition of sulphuric acid, yields a crystalline substance, having the odour of the volatile soap-acids, and dissolving very easily in water, especially when hot.

Combinations. The oily acid is but sparingly soluble in water; the crystalline acid dissolves pretty readily.

With *Ammonia* the oily acid forms an acid salt, which crystallizes in yellowish white, unctuous scales, easily soluble in water and alcohol.

<i>Crystals dried in vacuo.</i>		<i>Cahours.</i>	
16 C	96	18·86	18·94
N	14	2·75	2·88
4 Br	320	62·87	63·18
15 H	15	2·95	3·26
8 O	64	12·57	11·74
<hr/>		<hr/>	
C ⁶ Br ² H ⁶ (NH ⁴)O ⁴ , C ⁶ Br ² H ⁶ O ⁴	509	100·00	100·00

The crystalline acid forms soluble crystallizable salts with *potash* and *soda*, sparingly soluble salts with the oxides of lead and silver.

The *ammonia-salt* of the oily acid forms with *nitrate of silver* a curdy precipitate, which is slightly soluble in cold water, and when left to stand for some time, unites into a pitchy mass; after quick drying in vacuo, it forms a white powder, which when ignited leaves 53·57 p. c. bromide of silver, and therefore contains 30·77 p. c. silver, which agrees with the formula C⁶Br²H⁶AgO⁴.

The oily acid mixes in all proportions with *alcohol* and *ether*; and the crystalline acid dissolves readily in those liquids. (Cahours.)

Conjugated Compound.

Bibromobutyric Ether.



Obtained with difficulty, by saturating a solution of bibromobutyric acid in absolute alcohol heated to 70° or 80°, with hydrochloric acid gas, then distilling; mixing the distillate with water; washing the oil thereby precipitated, first with a very dilute solution of carbonate of soda, then with pure water to remove hydrochloric and free bibromobutyric acid; and lastly drying it in vacuo over oil of vitriol.

Nearly colourless oil, heavier than water. Has but a faint odour in the cold, but when heated emits an extremely pungent odour which excites tears. Tastes very sharp, like horse-radish.

It is partially decomposed by distillation and leaves a carbonaceous residue. (Cahours, *N. Ann. Chim. Phys.* 19, 499; also *J. pr. Chem.* 41, 71.)

		<i>Cahours.</i>	
12 C	72	26·28	26·03
2 Br	160	58·39	58·06
10 H	10	3·65	3·63
4 O	32	11·68	12·28
<hr/>		<hr/>	
C ¹² Br ² H ¹⁰ O ⁴	274	100·00	100·00

c. Chlorine-nuclei.

a. Chlorine-nucleus. C⁶ClH⁷.

Chlorobutylene. C⁶ClH⁷.

CHANCEL. (1845.) *N. J. Pharm.* 7, 253; abstr. *Compt. rend.* 20, 865.

Chlorbutyren, Butyrène chloré (Chancel); *Chlorure de Butyriole* (Cahours); *Chlorobutyrase* (Laurent); *Butak* (Gm.)

Preparation (p. 74). $1\frac{1}{2}$ pt. pentachloride of phosphorus is added in successive portions to 1 pt. of butyral in a tubulated retort; a few hot coals placed under the retort as soon as the ebullition and evolution of hydrochloric acid, which soon take place, have slackened; the mixture distilled till the black residue begins to swell up; the resulting distillate rectified three or four times; then washed with water, shaken up with solution of carbonate of potash, and finally distilled over chloride of calcium.

Properties. Colourless, very thin liquid, lighter than water, boiling somewhat above 100° , having a tolerably brisk, peculiar odour and biting taste.

Burns with a green-edged flame.

Insoluble in water, but dissolves in all proportions in alcohol and ether; the alcoholic solution when recently prepared does not produce any turbidity in a solution of nitrate of silver. (Chancel.)

The liquid obtained by distilling butyrene with pentachloride of phosphorus, redistilling several times with fresh pentachloride to ensure complete decomposition of the butyrene, and purifying in the manner adopted for the compound ethers, is a transparent, colourless liquid, lighter than water, boiling at 116° , of peculiar penetrating odour; it burns with a green-bordered flame; is insoluble in water; but dissolves in all proportions in alcohol; and the solution does not produce any turbidity in a solution of nitrate of silver. (Chancel.) — Chancel regards this liquid, according to an unpublished analysis, as C^6H^7Cl , and names it *Chlorobutyrene*. But the agreement of its properties with those of C^6ClH^7 suggests the identity of the two compounds, and renders a repetition of the analysis desirable.

Chlorobutyral. $C^6ClH^7O^2$.

CHANCEL (1845.) *N. J. Pharm.* 7, 350; abstr. *Compt. rend.* 20, 865.

Preparation. Well-dried chlorine gas passed through butyral by daylight, is at first quietly absorbed, with evolution of heat and pale red colouring of the liquid; but afterwards the liquid acquires a yellow colour, gives off abundance of hydrochloric acid gas, and after two hours is found to be saturated with chlorine. The liquid is then heated nearly to the boiling point, and a rapid stream of carbonic acid gas passed through it to expel free chlorine and hydrochloric acid, after which it is rectified once or twice.

Properties. Transparent, colourless liquid, heavier than water, boiling at about 141° , and distilling without decomposition; has a pungent, tear-exciting odour; neutral.

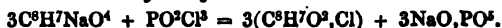
Burns with a green-bordered flame. Does not form an amide with ammonia.

Insoluble in water, but dissolves in alcohol, forming a solution which does not cloud nitrate of silver. (Chancel.)

¶. Chloride of Butyryl. $C^6H^7O^2Cl$.

GERHARDT. *Ann. Pharm.* 87, 71.

Formation and Preparation. By the action of 1 At. oxychloride of phosphorus on 3 At. dry butyrate of soda;



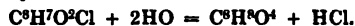
The butyrate of soda must be pulverized, and added by small portions to the oxychloride of phosphorus contained in a tubulated retort; if, on the contrary, the oxychloride were poured upon the butyrate, a large quantity of anhydrous butyric acid would be formed, (p. 88,) in consequence of the oxychloride coming at once in contact with an excess of butyrate of soda. The mixture is then distilled, and the liquid distillate rectified over a very small quantity of the butyrate, the temperature being kept as low as possible, to prevent the anhydrous butyric acid formed during the rectification, from distilling over with the chloride.

Properties. Colourless, very mobile, strongly refracting liquid heavier than water, and fuming slightly in the air. Boils without decomposition at 95° . Has a pungent odour like butyric and hydrochloric acid together.

				Gerhardt.
8 C.....	48.0	...	45.08 44.96
7 H.....	7.0	...	6.57 6.70
Cl	35.4	...	33.32 33.07
2 O.....	16.0	...	15.03 15.27
<hr/>				
$C^2H^7O^2Cl$	106.4	...	100.00 100.00

Metameric with chlorobutyral (p. 139).

Chloride of butyryl is immediately decomposed by water, with formation of butyric and hydrochloric acids :



Distilled with excess of butyrate of soda, it yields anhydrous butyric acid and chloride of sodium, (p. 88.) It acts very strongly upon *aniline*, forming hydrochloric acid and butyranilide, $C^2H^3NO^2$. (Gerhardt.) ¶.

β. Chlorine-nucleus. $C^2Cl^2H^4$.

Bichlorobutyral. $C^2Cl^2H^4O^2$.

When dry chlorine gas is passed, for three hours, in sunshine through butyral, the action is observed to slacken at a certain point; and if a rapid stream of carbonic acid gas be then passed through the heated liquid, and the liquid afterwards rectified, a neutral oil is obtained, which boils at 200° . (Chancel, *N. J. Pharm.* 7, 351.)

Bichlorobutyric Acid. $C^2Cl^2H^4O^4$.

PELOUZE & GÉLIS (1844). *N. Ann. Chim. Phys.* 10, 447.

Formation (p. 83).—*Preparation.* Dry chlorine gas is passed, in bright sunshine, through butyric acid contained in a Liebig's bulb-apparatus, the acid heated to 70° or 80° , as soon as the absorption is complete, and carbonic acid gas passed through it to expel hydrochloric acid.

Properties. Colourless viscid liquid, heavier than water, and having a peculiar odour.

				Pelouze & Gélis.	
8 C	48·0	30·61 30·79
2 Cl	70·8	45·15
6 H	6·0	3·83 4·02
4 O	32·0	20·41
<hr/>				<hr/>	
C ⁸ PH ⁶ O ⁴	156·8	100·00	

The acid may by great care be, for the most part, distilled without decomposition; but a small quantity of hydrochloric acid is always evolved, and the distillate has a different odour. This decomposition takes place above 164°. — The acid burns with a green flame, diffusing a large quantity of hydrochloric acid.

The acid is nearly insoluble in water.

It forms very soluble salts with ammonia, potash, and soda. The potash-salt forms a very sparingly soluble precipitate with nitrate of silver.

The acid dissolves in alcohol in all proportions. (Pelouze & Gélis.)

γ. *Chlorine-nucleus.* C⁸Cl⁴H⁴.

Quadrichlorobutyral. C⁸Cl⁴H⁴O².

Chlorine gas is passed for several days in burning sunshine through butyral, after it has been converted into bichlorobutyral, the liquid being heated towards the end of the process, and the passage of the gas continued as long as hydrochloric acid gas continues to form. When this point is attained, the passage of chlorine, even for weeks and in sunshine produces no further effect.

Thick, neutral, very heavy oil. — Boils at a high temperature, and with decomposition.

Insoluble in water, but dissolves in alcohol and ether. (Chancel, *N. J. Pharm.* 7, 351.)

Quadrichlorobutyric Acid. C⁸Cl⁴H⁴O².

Chlorine gas, as made to act upon butyric acid in sunshine, till the bichlorobutyric acid produced at first, is converted, after some time, into a white solid mass, which may be pressed between paper, and purified by crystallization from ether.

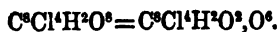
White oblique rhombic prisms, which melt at 140°, distil without decomposition, and smell like butyric acid.

The acid is insoluble in water, but dissolves very readily in ether and alcohol; and its potash-salt forms a white, sparingly soluble precipitate with nitrate of silver. (Pelouze & Gélis, *N. Ann. Chim. Phys.* 10, 447.)

	<i>Crystals.</i>		<i>Pelouze & Gélis.</i>	
8 C	48·0	21·28
4 Cl	141·6	62·76
4 H	4·0	1·77
4 O	32·0	14·19
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C ⁸ Cl ⁴ H ⁴ O ⁴	225·6	100·00

δ. *Chlorine-nucleus.* C⁸Cl⁴H²O².

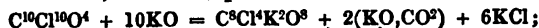
Quadrichlorosuccinic Acid.



PLANTAMOUR: — LAURENT. *Compt. rend.* 26, 36.

Acide bichlorosaltique (Plantamour); *Acide succinique quadrichloré.* (Laurent).

Chlorine forms with citric acid an oil = C¹⁴Cl¹²O⁶, and with succinate of soda an oil = C¹⁰Cl⁸O⁴. Both these oils yield, by distillation with potash, a salt = C⁸Cl⁴K²O⁸. (Plantamour.)—The first oil may be regarded as C¹⁰Cl¹⁰O⁴, and the equation is:



with the second oil the equation is:



it remains to be shown, that formiate of potash is produced in this latter reaction. (Laurent.)

Conjugated Compounds of the Chlorine-nuclei.

Bichlorobutyric Ether.



The solution of bichlorobutyric acid in alcohol deposits, when gently heated with oil of vitriol, an oily compound ether having an ethereal odour; it may be washed with water and distilled. (Pelouze & Gélis.)

	<i>Pelouze & Gélis.</i>			
12 C	72·0	38·96
2 Cl	70·8	38·31
10 H	10·0	5·41
4 O	32·0	17·32
<hr/>				
C ¹² Cl ² H ¹⁰ O ⁴	184·8	100·00

Quadrichlorobutyric Ether.



With a solution of quadrichlorobutyric acid in several times its bulk of alcohol, oil of vitriol immediately forms a crystalline mass, which melts at a gentle heat and separates into two liquids. The

heavier of these liquids is quadrichlorobutyric ether. It has an ethereal odour like that of the preceding compound and of butyric ether; burns with green flame and white fumes, is very sparingly soluble in water, but dissolves abundantly in alcohol and ether. (Pelouze & Gélis, *N. Ann. Chim. Phys.* 10, 449.)

Perchlorosuccinic Ether.



CAHOURS (1848.) *N. Ann. Chim. Phys.* 9, 206; also *Ann. Pharm.* 47 294; also *J. pr. Chem.* 30, 244.

MALAGUTI. *N. Ann. Chim. Phys.* 16, 66; abstr. *compt. rend.* 21, 747; abstr. *J. pr. Chem.* 37, 433.

GERHARDT. *N. J. Pharm.* 9, 307; 14, 238, and 291.

Perchlorbernsteinsäureäther, Perchlorbernsteindäther, éther chlorosuccinique, éther perchlorosuccinique.

Formation and Preparation. Succinic ether exposed to sunshine in a bottle filled with chlorine gas, is converted in a few days into a white crystalline mass, which must be pressed between paper, washed with a small quantity of ether, pressed again, and crystallized from ether. (Cahours, p. 134.)

Properties. Small snow-white needles, which have a strong tendency to interlace. Melts at 115° to 120°, and distills over, partly undecomposed, at a stronger heat. Smells like other similar chlorine-compounds. (Cahours.)

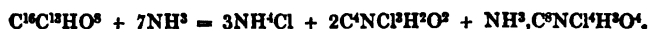
	Cahours.				
16 C	96·0	15·45	15·25
13 Cl	460·2	74·09	74·25
H	1·0	0·16	0·67
8 O	64·0	10·30	9·83
$\text{C}^{16}\text{Cl}^{12}\text{HO}^2$	621·2	100·00	100·00

Laurent (*Compt. rend.* 35, 381,) assigns to this compound the formula $\text{C}^{16}\text{Cl}^{14}\text{O}^2$, which however requires 14·7 p. c. carbon and 75·4 chlorine.

Decompositions. 1. Perchlorosuccinic ether distilled at 290°, continually gives off carbonic acid, and yields a thick, oily, fuming distillate. This distillate, when covered with water, which then takes up hydrochloric, perchloracetic, and chlorosuccic acids, diminishes considerably in a few weeks, and is converted, by crystallization of sesquichloride of carbon, into a solid magma. (Malaguti.) — $\text{C}^{16}\text{Cl}^{12}\text{HO}^2 = 2\text{CO}^2 + \text{C}^4\text{Cl}^4 + \text{C}^4\text{Cl}^4\text{O}^2$ (chloraldehyde, which then, together with 2HO, yields HCl and $\text{C}^4\text{Cl}^4\text{HO}^4$ [perchloracetic acid]) + $\text{C}^8\text{Cl}^8\text{HO}^2$ (a chlorosuccide not known in the separate state, which then, with 2HO, forms chlorosuccic acid, $\text{C}^8\text{Cl}^8\text{H}^2\text{O}^4$). (Gerhardt.)

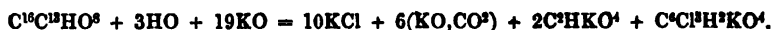
2. When dry ammoniacal gas is passed over the finely pounded ether, the latter becomes hot and cakes together, and at the same time specular scales are deposited from the stream of gas. If the mass be pulverized as often as the gas ceases to act, and ammonia again passed over it as long as heating and absorption take place, a chocolate-coloured crystalline mass is obtained, which, when treated with ether, leaves a residue of sal-ammoniac, together with a small quantity of matter

resembling paracyanogen, the ether at the same time taking up chlorocarbethamide and chlorazosuccate of ammonia, which must be separated by water. (Malaguti.) — According to Gerhardt, the compound ether acquires by the action of ammonia, only a very faint yellowish tint, and yields nothing but sal-ammoniac, chloracetamide (ix. 270), and chlorazosuccate of ammonia. (x. 37.) — Gerhardt's equation is therefore :

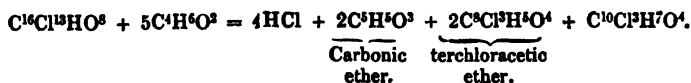


Since Gerhardt has demonstrated the identity of chlorocarbethamide, (prepared from the ether by the action of dry as well as of aqueous ammonia,) with chloracetamide, the more complicated equation given by Malaguti is no longer admissible. — Aqueous ammonia in contact with pulverized and recently prepared perchlorosuccinic ether, becomes so strongly heated as to be thrown out of the vessel; but the ether of older preparation is dissolved by ammonia with the aid of a gentle heat, forming a yellow liquid, which contains the same three products that are obtained by the action of ammoniacal gas. (Malaguti.) That the crystals obtained in this reaction are not chlorocarbethamide, as Malaguti formerly supposed, but chloracetamide, as shown by Gerhardt, has since been admitted by Malaguti himself, (*N. J. Pharm.* 14, 289,) who, however, still maintains that his chlorocarbethamide, prepared with ammoniacal gas, is different from chloracetamide, and now regards it as $\text{C}^{10}\text{N}^2\text{Cl}^7\text{H}^6\text{O}^4 = 2\text{C}^4\text{NCl}^3\text{H}^2\text{O}^3$ (chloracetamide) + $\text{C}^2\text{NCl}^1\text{H}^2$ (unknown compound).

3. Perchlorosuccinic ether, heated with a concentrated solution of three times its weight of hydrate of potash, dissolves quickly, without any evolution of chloroform, producing a liquid which contains chloride of potassium, and carbonate, formiate, and chlorosuccate of potash. (Malaguti.)



4. Perchlorosuccinic ether dissolves in alcohol, but only with aid of heat, and is at the same time completely decomposed. From the solution, which contains hydrochloric acid, water throws down an oily mixture of carbonic ether (viii. 392), terchloraetic ether (ix. 237), and chlorosuccic ether (Malaguti). — Chlorosuccic ether is not known in the separate state. Malaguti supposes it to be $\text{C}^{10}\text{Cl}^3\text{H}^6\text{O}^3$; but according to Gerhardt's formula of chlorosuccic acid (ix. 430), it must be regarded as $\text{C}^4\text{H}^2\text{O}, \text{C}^6\text{Cl}^3\text{H}^2\text{O}^3 = \text{C}^{10}\text{Cl}^3\text{H}^7\text{O}^4$, and then the equation will be:

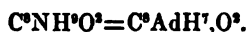


According to Malaguti's formula of chlorosuccic ether, 1HO should be formed at the same time].

a. *Amidogen-nuclei.*

d. *Amidogen-nucleus.* C⁶AdH⁷.

Butyramide.



CHANCEL. *Compt. rend.* 18, 949.

Formation (p. 91). — *Preparation.* 1 pt. of butyric ether is briskly agitated with 6 pts. of aqueous ammonia till it has completely disappeared, which takes place in about eight days, after which the liquid is evaporated down to one-third, and left to crystallize by cooling. (Chancel.)

Properties. Snow-white, nacreous, transparent tables, which melt at 115° to a colourless liquid, and evaporate without residue. Have a sweet and fresh taste with bitter after-taste. Permanent in the air. (Chancel.)

Calculation, according to Chancel.			
8 C	48	55·17
N	14	16·09
9 H	9	10·35
2 O	16	18·39
<hr/>			
C ⁶ NH ⁸ O ²	87	100·00

Decompositions. 1. The vapour of butyramide is inflammable. (Chancel.) — 2. When passed over red-hot lime, it yields butyronitrile (Laurent & Chancel):



3. Butyronitrile is likewise obtained by distilling butyramide with anhydrous phosphoric acid. (Dumas, Malaguti & Leblanc.) — 4. The aqueous solution of butyramide is decomposed by boiling with fixed alkalis, yielding ammonia and an alkaline butyrate (Chancel):



5. With pentachloride of phosphorus, butyramide forms butyronitrile, hydrochloric acid, and chlorophosphoric acid (Cahours, *Compt. rend.* 25, 325):



6. In cold nitric acid through which nitric oxide gas is passed, butyramide is resolved into butyric acid, water, and nitrogen gas (Piria, *N. Ann. Chim. Phys.* 22, 177):



Combinations. Butyramide dissolves readily in water, especially in hot water. (Chancel.)

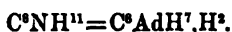
¶ *Mercury-compound,* C⁶NH⁸HgO². — When butyramide and mercuric oxide are boiled together in water, a solution is formed which by evapo-

ration yields this compound in thin nacreous crystals, resembling those of butyramide but having a higher lustre. (Dessaigues, *Ann. Pharm.* 82, 234.)

Dessaigues.				
8 C	48	...	25.81	
N	14	...	7.53	
8 H	8	...	4.30	
2 O	16	...	8.60	
Hg	100	...	53.76 53.89
<hr/>				
$C^6NH^8HgO^2$	186	...	100.00	

This compound is soluble in cold water. (Dessaigues.) ¶
Butyramide dissolves in *alcohol* and *ether*. (Chancel.)

¶. Butylamine.



WURTZ. *N. Ann. Chim. Phys.* 42, 164; *Ann. Pharm.* 92, 124.

Butyramine, Butyriaque, Butyliaque, Butylia.

Formation. By the action of potash on cyanate and cyanurate of butyl.

Preparation. 2 pts. of sulphobutylate of potash are distilled with 1 pt. of recently prepared and perfectly dry cyanate of potash; the pasty mixture of cyanate and cyanurate of butyl which distils over, dissolved in alcohol; and the solution boiled with fragments of caustic potash. Carbonate of potash is then formed, and butylamine distils over, and is condensed in a small quantity of cold water acidulated with hydrochloric acid. The boiling is continued till the residue fuses completely, and no longer gives off alkaline vapours. The resulting solution of hydrochlorate of butylamine is evaporated to dryness; and the residual salt freed by fusion from the water which it retains, pulverized when cold, and quickly mixed with an equal weight of quick lime. This mixture is then introduced into a tube of hard glass, which must be filled with it to about four-fifths; the upper part of the tube filled with fragments of caustic baryta; a gas-delivery tube bent at right angles adapted to the larger tube, and made to pass into a small flask surrounded with ice; and the tube carefully heated in a combustion-furnace, from the closed end onwards. The evolved butylamine is then completely dehydrated by the caustic baryta, and condenses in the cooled flask.

Properties. Transparent, colourless liquid, having a strongly ammoniacal and somewhat aromatic odour, and producing dense white fumes with hydrochloric acid. Boils at 69° to 70° .

Wurtz.				
8 C	48	...	65.75 65.58 65.87
N	14	...	19.19	
11 H	11	...	15.06 14.99 15.26
<hr/>				
C^6AdH^7, H^2	73	...	100.00	

May also be regarded as butylene conjugated with ammonia: C^6H^5, NH^2 ,—or as ammonia in which 1 At. H is replaced by butyl: $N(H, H, C^6H^5)$.

Combinations. Butylamine dissolves in *water* in all proportions; the aqueous solution smells like the pure base, and is very caustic; when concentrated it is somewhat viscid.

Salts of Butylamine. — Most metallic solutions are precipitated by butylamine in the same manner as by ammonia. The *zinc*, *cadmium* and *copper* precipitates dissolve in excess of the reagent; gelatinous *alumina* likewise dissolves in excess of butylamine; the precipitates formed in solutions of *chromium*, *nickel*, and *cobalt*, are insoluble in excess of butylamine. With *nitrate of silver*, butylamine forms a tawny yellow precipitate, easily soluble in excess. — Gelatinous *silica* dissolves in butylamine, and remains in the pulverulent and amorphous state when the solution is evaporated.

Hydrochlorate of Butylamine crystallizes in deliquescent needles, which melt below 100°; when exposed to the air, it gives off thick white fumes and volatilizes without residue.

8 C.....	48.0	43.83	Wurtz.
N	14.0	12.78	43.83
12 H	12.0	10.95	11.05
Cl	35.4	32.44	
<hr/>					
C ^o NH ¹¹ ,HCl	109.4	100.00	

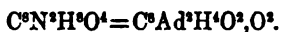
Gold-salt. — Hydrochlorate of butylamine and terchloride of gold may be mixed without separation of a double-salt; but on evaporation the double-salt crystallizes in rectangular tables of a pure yellow colour, but melting and changing to orange-yellow at 100°.

16 C.....	96	18.32	Wurtz.
2 N	28	5.34	18.79
24 H.....	24	4.58	4.84
Au	199	37.98	37.50
5 Cl.....	177	33.78	
<hr/>					
2(C ^o NH ¹¹ ,HCl) + AuCl ³	524	100.00	

Platinum-salt. — Hydrochlorate of butylamine and bichloride of platinum do not form an immediate precipitate when mixed even in the state of concentrated solutions; but on evaporation, the double salt crystallizes in beautiful orange-yellow laminae, which are soluble in water and in alcohol.

8 C.....	48.0	17.18	Wurtz.
N	14.0	5.05	17.18
12 H	12.0	4.30	4.52
Pt	99.0	35.45	35.02
3 Cl	106.2	38.02	
<hr/>					
C ^o NH ¹¹ ,HCl + PtCl ²	279.2	100.00	

Butylamine dissolves in all proportions in *alcohol* and *ether*. (Wurtz) ¶.

β . *Amidogen-nucleus.* $C^6Ad^3H^4O^2$.**Succinamide.**

FEHLING. (1844.) *Ann. Pharm.* 49, 196.

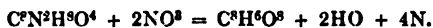
When succinic ether is shaken up with aqueous ammonia, a white deposit is produced, which must be left for a few days till it no longer increases, then washed with alcohol, and crystallized from boiling water. White needles, which do not give off any thing at 100° , and melt when suddenly heated, turning slightly brown, but without further alteration.

				Fehling.
8 C	48	41.38	41.69
2 N	28	24.14	24.13
8 H	8	6.90	7.00
4 O	32	27.58	27.18
$C^8N^2H^8O^4$	116	100.00	100.00

Succinamide slowly heated to 200° , and kept at that temperature for a considerable time, gives off a large quantity of ammonia, and afterwards, when the heat is increased, sublimes in the form of bisuccinamide, leaving a small quantity of charcoal (Fehling):

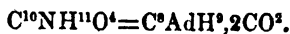


In cold nitric acid, through which nitrous gas is passed, it is resolved into succinic acid, water, and nitrogen gas (Piria, *N. Ann. Chim. Phys.* 22, 177):



The boiling aqueous solution of 1 pt. succinamide mixed with bichloride of platinum, deposits on cooling almost exactly 2 pts. of chloroplatinate of ammonium: hence 1 At. nitrogen is transferred to the platinum-salt. (Fehling.)

Succinamide dissolves in 220 pts. of *water* at 15° , and in 9 pts. of boiling water; it is insoluble in *ether* and in absolute *alcohol*, sparingly soluble in hydrated alcohol. (Fehling.)

γ. Butylic Urethane.

E. HUMANN. *N. Ann. Chim. Phys.* 44, 337; *Ann. Pharm.* 95, 372; *Chem. Soc. Qu. J.* 8, 276.

Obtained by the action of gaseous or liquid chloride of cyanogen on butylic alcohol, its formation being however usually accompanied by that of carbonate of butyl (p. 104). — The best mode of preparing it is to

pour liquid chloride of cyanogen into butylic alcohol. The reaction takes place quickly if aided by heat, more slowly at ordinary temperatures. It is generally indicated (in case the butylic alcohol contains water) by the formation of a mass of crystals within the liquid; it is complete when the odour of chloride of cyanogen has completely disappeared. The best mode of accelerating it, is to heat the mixture in a sealed tube immersed in a water-bath. After cooling, the crystals must be well pressed, then introduced into a retort and distilled, the receiver being changed as soon as $\frac{2}{3}$ of the liquid has passed over, and the portion which distils at 220° being collected apart. This product, the butylic urethane, is an oily liquid which solidifies on cooling, and partly collects in the retort in a shining, crystalline, unctuous mass. It must be carefully collected and pressed between folds of bibulous paper. It is finally purified by crystallization from boiling alcohol.

Beautiful nacreous crystals, having a strong lustre, unctuous to the touch, melting at a very gentle heat, and distilling without alteration. They are insoluble in water, but dissolve in alcohol and ether.

				Humann.
10 C 60 51.28	51.09
N 14 11.97		
11 H 11 9.40	9.18
4 O 32 27.35		
C ¹⁰ NH ¹¹ O ⁴				
	117 100.00		

May be regarded as a compound of carbonate of butyl with carbamide: C¹⁰NH¹¹O⁴ = C⁸H⁹O, CO² + CNH²O. (Humann.)

e. Nitrogen-nuclei.

a. Nitrogen-nucleus C⁸NH⁷.

Butyronitrile. C⁸NH⁷.

DUMAS, MALAGUTI & LEBLANC. (1847.) *Compt. rend.* 25, 442, and 658.

LAURENT & CHANCEL. *Compt. rend.* 25, 884.

Preparation. 1. By distilling butyrate of ammonia with anhydrous phosphoric acid. (Dumas, &c.)— 2. By passing vapour of butyramide over lime heated to dull redness. (Laurent & Chancel.) The second mode of preparation is not so good as the first. (A. W. Hofmann, *Ann. Pharm.* 65, 56.)

Properties. Transparent, colourless oil, of sp. gr. 0.795 at 12.5° ; boils at 118.5° . Has an agreeable aromatic odour, like that of bitter almond oil (Dumas, Malaguti & Leblanc.)

Calculation, according to Dumas, Mal. & Lebl.			
8 C 48 69.56	
N 14 20.29	
7 H 7 10.15	
C ⁸ NH ⁷			
	69 100.00	

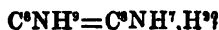
Decompositions. The compound dissolves in boiling potash with evolution of ammonia, and forms butyrate of potash:



With potassium, it forms cyanide of potassium and a mixture of hydrogen gas and a carburetted hydrogen which is denser than that which is evolved by potassium from acetonitrile (ix. 294). (Dumas, Malaguti & Leblanc.) [According to the equation: $C^6NH^7 + K = C^6NK + H + C^6H^6$, this gaseous hydrocarbon should be propylene.]

[Just as acetonitrile, C^4NH^3 , may be regarded as cyanide of methyl or hydrocyanate of methylene, C^2H^2, C^2N or C^2H^2, C^2NH , so also may butyronitrile, C^6NH^7 , be regarded as cyanide of propyl, C^3H^3, C^3N , or hydrocyanate of propylene, C^3H^6, C^3NH .]

Petinine.



ANDERSON. (1848.) *Phil. Mag.* 7, 33, 174; also *J. pr. Chem.* 45, 160; abstr. *Ann. Pharm.* 70, 32.

From *perceivés* volatile. Constitutes a very small portion of the empyreumatic oil obtained by the dry distillation of bones.

Preparation. Crude tarry bone-oil, to the amount of about 15 pounds, is distilled at a gradually increasing heat in a half-filled iron retort, till about $\frac{2}{3}$ has passed over; the resulting pale yellow oil separated from the watery distillate, then set aside, and frequently agitated for 8 to 14 days, with a mixture of 1 pt. oil of vitriol and 10 pts. water; the acid liquid diluted with a larger quantity of water and separated from the oil; and the oil again treated several times with dilute sulphuric acid to remove the volatile alkaloids completely. The dark brown or red-brown acid extracts thus obtained, which, besides a number of bases, contain also a neutral oil and pyrrol, are boiled, after addition of more sulphuric acid, in a porcelain or copper vessel; freed from the red resin which separates out and causes violent percussion; and continuously boiled, with renewal of the water, till a sample, subjected to distillation, no longer evolves pyrrol. The liquid is then filtered from fresh portions of resin which have separated out, neutralised with potash or ammonia, and distilled together with the oil smelling of ammonia and stinking sea-crabs, which rises to the surface, as long as the oil which passes over continues to dissolve in the watery portion of the distillate. If the distillation be further continued, and the receiver changed, a small portion of oil passes over, which sinks in the water; and in the retort there remains, above the watery liquid, an oily mixture of less volatile alkaloids. — On dissolving hydrate of potash in the watery distillate thus obtained, an oily mixture of ammonia, petinine, picoline, and two or three other alkaloids, rises to the surface, and may be removed by a siphon, whilst a portion of the petinine remains dissolved in the aqueous potash. — *a.* To obtain the petinine from the oily mixture, this mixture is dehydrated by adding hydrate of potash to it as long as that substance takes up water; and then repeatedly distilled in

a retort fitted with a thermometer, the oil which passes between 71° and 100°, and consists chiefly of petinine, being collected apart. — *b*. The petinine which remains dissolved in the aqueous potash is separated therefrom by a short distillation, and from the water which passes over with it by treatment with hydrate of potash. — Lastly, the two portions of petinine obtained by *a* and *b* are united, and completely purified by repeated fractional distillation, with a well cooled receiver, whereby a large quantity of ammonia is expelled, the process being continued till the boiling point of the distillate becomes constant. Complete dehydration is attained by leaving the product for several days in contact with caustic potash, then decanting and rectifying.

Properties. Transparent, colourless, strongly refracting liquid, lighter than water, boiling at about 70·5°. Has a very pungent odour, resembling that of ammonia, but not exactly the same; in the dilute state, it has the offensive odour of rotten apples; its taste is hot and very pungent. It blues reddened litmus, and forms white fumes with hydrochloric acid held over it.

	Calculation, according to <i>Gm.</i>		Anderson.
8 C	48	67·61	66·66
N	14	19·72	
9 H	9	12·67	13·97
<hr/>			
C ⁸ NH ⁷ ,H ³	71	100·00	

Anderson prefers the formula: C⁸NH¹⁰; Gerhardt (*N. J. Pharm.* 14, 378, and *Compt. Chim.* 1849, 12), the formula C⁸NH¹¹. According to this latter formula, petinine is identical or metameric with butylamine; also metameric with biethylamine and methylpropylamine.

Decompositions. 1. Bromine-water dropt into aqueous petinine precipitates an oil soluble in acids, whilst hydrobromate of petinine remains in solution. The oil is perhaps C⁸NBr²H⁷ [or C⁸NBr²H⁶]. — 2. Cold aqueous chloride of lime does not colour aqueous petinine, but causes it immediately to emit an extremely pungent odour. — A solution of petinine in excess of concentrated nitric acid may be boiled for a long time without perceptible decomposition. — ¶ Petinine is decomposed by nitrous acid, with evolution of nitrogen and formation of small oily globules, probably consisting of nitrite of butyl. (A. W. Hofmann, *Chem. Soc. Qu. J.* 3, 239.) The decomposition appears to be similar to that of ethylamine (ix, 58), supposing that petinine is identical with butylamine. ¶

Combinations. Petinine dissolves in *Water* in all proportions. It combines with the stronger acids, the combination being attended with evolution of heat. It precipitates ferric salts, and is the strongest of all the alkalis contained in bone-oil. The *Petinine-salts* crystallize readily, are very permanent, and do not become coloured by exposure to the air; those which contain volatile acids may be sublimed. — They are all soluble in water.

Sulphate of Petinine. — Dilute sulphuric acid neutralized with petinine gives off petinine when evaporated and leaves a syrup which solidifies to a laminated mass of a very acid and somewhat deliquescent salt, which dissolves very readily in water,

Hydrochlorate of Petinine. — Dry petinine dissolves in hydrochloric acid with great evolution of heat, and yields a salt which sublimes in fine needles, and is extremely soluble in water.

Petinine dissolves in dilute but not in concentrated solution of *potash*; it dissolves a small quantity of hydrate of potash.

It precipitates *cupric oxide* from its salts, but redissolves it when added in excess, and forms a solution of a fine blue colour.

An alcoholic solution of petinine forms with *protochloride of mercury*, a white precipitate which dissolves in a large quantity of hot water, more readily in hot alcohol, and crystallizes from the solution in silvery laminæ. It dissolves very readily in cold dilute hydrochloric acid. Its aqueous solution gives off petinine when boiled, and deposits a white powder.

With *terchloride of gold*, petinine forms a pale yellow precipitate which does not dissolve when the liquid is boiled.

With *bichloride of platinum*, in not too dilute solutions, petinine forms a yellow precipitate, which, by crystallization from hot water, is obtained in golden yellow tables resembling iodide of lead. These crystals dissolve with tolerable facility in cold, readily in hot water, also in alcohol, and are not decomposed by boiling the aqueous solution.

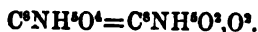
<i>Crystals.</i>		Anderson.			
8 C	48.0	...	17.32	16.93
N	14.0	...	5.05		
10 H	10.0	...	3.61	4.17
Pt	99.0	...	35.71	35.46
3 Cl	106.2	...	38.31		
$C^6NH^9, HCl + PtCl^2$	277.2	...	100.00		

According to Anderson, it is $C^6NH^{10}, HCl + PtCl^2$; according to Gerhardt, $C^6NH^{11}, HCl + PtCl^2$.

Petinine dissolves in all proportions in *alcohol, ether, and oils.* (Anderson.)

β . *Nitrogen-nucleus.* $C^6NH^4O^2$.

Bisuccinamide.



FEL. D'ARCET. (1835.) *Ann. Chim. Phys.* 58, 294; also *Pogg.* 36, 86.

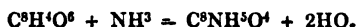
FEHLING. *Ann. Pharm.* 49, 198.

LAURENT & GERHARDT. *Compt. chim.* 1849, 108; also *J. pr. Chem.* 47, 71.

Succinamide (D'Arcet); *Succinimide*, (Laurent & Gerhardt.)

Formation and Preparation. When dry ammoniacal gas is passed over succinic anhydride, heat is evolved sufficient to melt and volatilize a portion of the bisuccinamide produced, and of the water, so that it is only

necessary to heat the vessel a little towards the end of the operation, till all the bisuccinamide is sublimed (D'Arcet.):



The same sublimate is also obtained on passing dry ammoniacal gas into succinic acid fused at 180°. (Fehling.)— 2. When neutral succinate of ammonia is heated, bisuccinamide sublimes, after previous evolution of water and ammonia. (Fehling.)— 3. When succinamide is heated for some time to 200°, till ammonia is no longer evolved, and the heat then increased, the residue sublimes as bisuccinamide. (Fehling.)

The sublimate must be purified by crystallization from water, and the crystals dehydrated at 100°. (Fehling.)

Properties. White, sublimable. (D'Arcet.) Reddens litmus. (Laurent & Gerhardt.)

			D'Arcet.		Fehling.	
8 C	48	48.49	48.78
N	14	14.14	15.29
5 H	5	5.05	5.55
4 O	32	32.32	30.38
<hr/>						
C ⁸ NH ⁴ O ⁴	99	100.00	100.00

Decompositions. 1. When heated with potash-ley, it gives off ammonia (D'Arcet), and forms succinate of potash. (Fehling.)— 2. Similarly, with the stronger acids, it yields an ammoniacal salt and free succinic acid. (Fehling.) On the other hand, a boiling aqueous solution of bisuccinamide forms with bichloride of platinum a clear mixture, which, when evaporated to a syrup, and again taken up with alcohol, leaves but traces of chloroplatinate of ammonium. (Fehling.) From a solution in hot concentrated potash, it separates out unaltered. (Laurent & Gerhardt.)

Combinations. Bisuccinamide dissolves abundantly in *Water*, and when the solution is left to evaporate, separates in beautiful rhombohedrons (D'Arcet), which give off their 15.94 p. c. (2 At.) water at a temperature considerably below 100°. (Fehling.) Rhombic octohedrons converted by truncation of their summits into rhombic tables (*Fig.* 42), $p : a = 125^\circ$; acute angle of the rhombohedron = 67° nearly. The crystals, when exposed to the air, gradually give off their water. (Laurent & Gerhardt.)

		<i>Hydrated Crystals.</i>		D'Arcet.	
8 C	48	41.03	42.62
N	14	11.96	12.74
7 H	7	5.98	6.04
6 O	48	41.03	38.60
<hr/>					
C ⁸ NH ⁴ O ⁴ + 2Aq.	117	100.00	100.00
<hr/>					
		Or :		Fehling.	
C ⁸ NH ⁴ O ⁴	99	84.61	84.06
2 HO	18	15.39	15.94
<hr/>					
C ⁸ NH ⁴ O ⁴ + 2Aq.	117	100.00	100.00

From a mixture of *Baryta-water* and bisuccinamide, carbonic acid throws down only part of the baryta. But aqueous bisuccinamide boiled with carbonate of baryta, dissolves but a very small quantity of it. (Fehling.)

Aqueous bisuccinamide dissolves, even at a gentle heat, but more quickly on boiling, a large quantity of *Lead-oxide*, without giving off a trace of ammonia, unless the boiling be continued unnecessarily long. The solution evaporated in vacuo, leaves a very viscid, amorphous mass, which dries up slowly but completely, and fuses to a clear liquid below 100° without further loss of weight. It contains 57.65 p. c. PbO , 18.63 C, 5.23 N, 2.56 H, and 15.93 O, and is therefore = $4PbO, 3C^6NH^4O^4 + 3HO$. When too strongly heated, it gives off ammonia, and afterwards forms a turbid solution with water. It quickly becomes moist when exposed to the air, and forms with water a clear solution, from which alcohol throws down a concentrated aqueous solution of the lead-compound in the form of a viscid transparent mass. If carbonic acid be passed through the aqueous solution as long as lead-oxide is precipitated thereby, and the filtrate evaporated in vacuo, a white opaque mass is left, which melts below 100° ; it contains 40.15 p. c. PbO , and is therefore = $2PbO, 3C^6NH^4O^4$. The solution obtained by heating carbonate of lead for some time with aqueous bisuccinamide in the water-bath, probably contains the same compound. (Fehling.)

¶ *Mercury-compound.* $C^6NH^4HgO^4$. — Bisuccinamide dissolves mercuric oxide with great facility, this compound being formed, with elimination of 1 At. water:



The solution somewhat concentrated, and filtered while hot, becomes filled on cooling with delicate silky needles which, after washing and drying in vacuo, are found to contain 50.48 p. c. mercury. The above formula requiring 50.50. (Dessaignes, *Ann. Pharm.* 82, 234.) ¶

Silver-compound. — Obtained by adding a few drops of ammonia to a boiling concentrated alcoholic solution of bisuccinamide, then nitrate of silver, and leaving the solution to crystallize by cooling. If the bisuccinamide is mixed with succinic acid, the liquid, after addition of the nitrate of silver, must be filtered hot from the precipitated succinate of silver. — Beautiful four-sided prisms with pyramidal summits. (Laurent & Gerhardt.)

<i>Crystals.</i>		Laurent & Gerhardt.	
8 C	48	23.30	23.0
N	14	6.80	
4 H	4	1.94	2.1
Ag	108	52.43	52.3
4 O	32	15.53	
<hr/>		<hr/>	
$C^6NH^4HgO^4$	206	100.00	

The crystals, when suddenly heated, detonate like oxalate of silver; when gradually heated, they emit a peculiar sharp odour, and give off an oil which crystallizes on cooling. They give off ammonia only when treated with hot solution of potash. With dilute hydrochloric acid, they are resolved into chloride of silver and reproduced bisuccinamide. They dissolve very readily in ammonia, sparingly in cold, and pretty readily in hot water or alcohol.

When this compound is boiled for a short time with water containing a few drops of ammonia, the solution yields on evaporation, small, shining, right rhombic prisms, with acute lateral edges of 75° , which, when

suddenly heated, are decomposed without detonation, and leave a residue of silver containing charcoal; they dissolve in water much more readily than the preceding compound, but behave in the same manner with hydrochloric acid. According to the following analysis, they are either bihydrated silver-bisuccinamide, or — which is more probable — succinamate of silver = $C^6NH^4AgO^6$. (Laurent & Gerhardt.)

Crystals.		Laurent & Gerhardt.	
8 C	48	21.43	21.7
N	14	6.25	
6 H	6	2.68	2.7
Ag	108	48.21	48.3
6 O	48	21.43	
224		100.00	

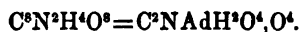
Ammoniacal Silver-compound. — The solution of silver-bisuccinamide in a small quantity of ammonia, leaves by spontaneous evaporation an alkaline syrup which gradually solidifies in a hard crystalline mass composed of square or rectangular prisms. This substance gives off ammonia when treated with potash-solution, even at ordinary temperatures. In contact with concentrated hydrochloric acid, it becomes very strongly heated, and gives off fumes of sal-ammoniac. After the ammonia has been precipitated from the solution of the compound in hydrochloric acid by excess of bichloride of platinum, the filtrate, if boiled with strong hydrochloric acid and evaporated to dryness, yields another quantity of chloroplatinate of ammonium about equal to the former. (Laurent & Gerhardt.)

Crystals.		Laurent & Gerhardt.	
8 C	48	21.52	
N	14	6.28	6.0
4 H	4	1.80	
Ag	108	48.43	48.2
4 O	32	14.35	
NH ³	17	7.62	7.0
NH ³ , C ⁶ NH ⁴ AgO ⁴		223	
		100.00	

Bisuccinamide dissolves pretty readily in *alcohol*, sparingly in *ether*. (D'Arcet.)

γ. *Nitrogen-nucleus.* $C^6NAdH^3O^4$.

Dialuric Acid.



LIEBIG & WÖHLER. (1838.) *Ann. Pharm.* 26, 276.

GREGORY. *Phil. Mag. J.* 24, 187; also *J. pr. Chem.* 32, 277.

Formation. When sulphuretted hydrogen is passed through a boiling aqueous solution of alloxan as long as any action takes place, the liquid no longer deposits alloxantin on cooling; gives with baryta-water out of

contact of air, not a blue but a white precipitate; and produces with carbonate of ammonia a large quantity of crystals of dialurate of ammonia:



Zinc and hydrochloric acid also reduce aqueous alloxan partly to alloxantin, partly to dialuric acid. (Liebig & Wöhler.)

Preparation of Dialurate of Ammonia. 1. A boiling aqueous solution of alloxan is completely decomposed by a stream of sulphuretted hydrogen, and the acid liquid, after filtration from the sulphur, is neutralized with carbonate of ammonia, which produces, with effervescence, a white crystalline precipitate of dialurate of ammonia. — 2. A solution of uric acid in dilute nitric acid is mixed with a quantity of hydrosulphate of ammonia, sufficient to nearly neutralize its acid reaction, so that it still reddens litmus slightly; the resulting pasty precipitate washed with cold water; dissolved in boiling water; and the filtrate mixed with carbonate of ammonia, whereupon it solidifies on cooling to a crystalline mass of dialurate of ammonia. — 3. An aqueous solution of alloxan is treated with zinc and hydrochloric acid, and the liquid decanted from the precipitated alloxantin is mixed with carbonate of ammonia till the oxide of zinc at first precipitated is redissolved; it then, after a while, yields crystals of dialurate of ammonia. (Liebig & Wöhler.) — 4. Ammonia is added at ordinary temperatures to the mother-liquid obtained in the preparation of alloxan or alloxantin, till the liquid reddens litmus but slightly; sulphuretted hydrogen is then passed through it, till the sulphur at first precipitated is redissolved; the liquid heated till the dialurate of ammonia which thickens the liquid is dissolved; a small quantity of hydrosulphate of ammonia added, if necessary, to dissolve any sulphur that may have remained undissolved; the clear liquid left to cool; the crystallized dialurate of ammonia collected on a filter; washed, first with dilute hydrosulphate of ammonia, then with alcohol till the wash-liquid runs through pure and colourless; pressed quickly in the filter between bibulous paper; and dried in vacuo over oil of vitriol. (Gregory.) If it should still be not quite pure, it must be once more dissolved in warm water containing hydrosulphate of ammonia, and the crystals washed and dried as above. (Gregory.)

Preparation of Dialuric acid. From a solution of dialurate of ammonia in warm hydrochloric acid, the dialuric acid separates on cooling in crystals, which must be quickly separated from the mother-liquor and dried. (Gregory.) — This experiment had been previously made by Liebig & Wöhler, who, however, from their analysis of the crystals thus obtained, regarded them as alloxantin, which, on account of the peculiar crystalline form, they regarded as dimorphous. Gregory suggests that the crystals of dialuric acid first produced may have been converted into alloxantin by the oxygen of the air, without changing their form.

Properties. Colourless crystals, which resemble those of alloxantin, and redden litmus strongly. (Gregory.)

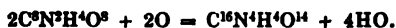
Crystallized Acid, according to Gregory.

8 C	48	...	33.33
2 N	28	...	19.45
4 H	4	...	2.78
8 O	64	...	44.44

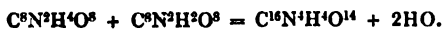
$C^6N^2H^4O^8$ 144 100.00

Liebig & Wöhler had previously determined the constitution of the acid from their analysis of the ammonia-salt.

Decompositions. 1. Aqueous dialuric acid (and likewise the crystallized acid when immersed in the aqueous mother-liquor) is partially converted, doubtless with absorption of oxygen from the air, into alloxantin, so that it no longer forms a white precipitate with baryta-water, but flesh-coloured, purple, or violet, according to the quantity of the alloxantin produced (Gregory):



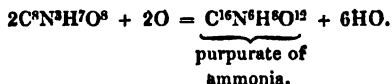
When dilute sulphuric acid is poured upon crystallized dialurate of ammonia, an indistinctly crystalline residue [of dialuric acid] is obtained, which dissolves in a large quantity of water. This solution deposits alloxantin in a few hours [on exposure to the air?]; and the filtrate, when freed from sulphuric acid by boiling with carbonate of baryta, and then filtered and evaporated, solidifies with formation of transparent prisms [of dialuric acid?] resembling oxalic acid; no urea is produced in this reaction. On the other hand, a solution of dialurate of ammonia in warm hydrochloric acid yields on cooling, crystals of dimorphous alloxantin [dialuric acid converted into alloxantin by the action of the air], and urea is found in the mother-liquor. (Liebig & Wöhler.)—2. When an aqueous solution of dialuric acid is boiled, oxalic acid and other products of decomposition are formed.—The boiling aqueous solution of alloxan, completely converted into dialuric acid by the action of sulphuretted hydrogen, then filtered from sulphur, and concentrated in a retort out of contact of air, deposits on cooling: (1.) a thick white, warty crust of dialuric acid more or less altered, which turns red on drying; reddens litmus strongly; dissolves with difficulty in cold water and then reduces silver; forms a violet precipitate with baryta-water; and, on addition of carbonate of ammonia, deposits after a while a small quantity of dialurate of ammonia;—and (2.) a mother-liquor containing ammonia, oxalic acid and a body which crystallizes in hard yellow opaque crystals. (Liebig & Wöhler.)—3. Aqueous dialuric acid mixed with aqueous alloxan deposits crystals of alloxantin. (Liebig & Wöhler.)



Combinations. The acid does not appear to dissolve very abundantly in water.

It neutralizes alkalis completely. The *Dialurates* in the dry state are quite permanent in the air. (Gregory.)

Dialurate of Ammonia.—Preparation (p. 156). Soft white crystalline powder, or delicate white silky needles, which become rose-coloured when dried at ordinary temperatures, and blood-red at 100°, but without giving off ammonia (Liebig & Wöhler):



Small needles which, when dried in the air, unite into a mass having a silky lustre. (Gregory.) The salt dissolves sparingly in cold, readily in hot water, from which it separates almost completely on cooling, especially on addition of carbonate of ammonia. The aqueous solution instantly reduces silver-salts. (Liebig & Wöhler.) A solution of dialu-

rate of ammonia, which probably also contained alloxantin, acquired by the action of hydrosulphate of ammonia a beautiful but transient sky-blue colour. (Gregory, *Ann. Pharm.* 33, 336.)

	<i>Crystallized.</i>		Liebig & Wöhler.	
8 C	48	29·81	29·84	
3 N	42	26·09	25·91	
7 H	7	4·35	4·54	
8 O	64	39·75	39·71	
$C^6N^2H^8(NH^4)O^3$	161	100·00	100·00	

Dialurate of Potash. — Deposited, on mixing a potash-salt with aqueous dialuric acid, in hard crystals which are sparingly soluble in water. (Gregory.) The ammonia-salt dissolves in potash-ley with evolution of ammonia, forming a liquid in which acids do not form any precipitate. (Liebig & Wöhler.)

Dialurate of Baryta. — The ammonia-salt forms with baryta-salts a white precipitate containing 36 p. c. baryta. (Liebig & Wöhler.) Dialuric acid throws down from dissolved baryta-salts a white powder scarcely soluble in water. (Gregory.)

The ammonia-salt added to neutral acetate of lead, throws down yellow flakes which turn violet on exposure to the air. (Liebig & Wöhler.)

Appendix.

Hydurilic Acid.

SCHLIEPER. (1845.) *Ann Pharm.* 56, 9.

Produced occasionally, together with alloxan, alloxantin, dialuric acid, &c., by the action of 2 pts. of cold nitric acid of sp. gr. 1·25 on 1 pt. of uric acid. If the mother-liquor, after cooling, be filtered from the crude alloxan, concentrated below 50°, and the crystalline magma which forms over night, thrown upon a filter and washed with water, acid hydurate of ammonia, [or perhaps the free acid?] remains, in the form of a yellow crystalline powder which, by solution in boiling water, digestion with animal charcoal, and crystallization, may be obtained in loose, snow-white, very slender needles. As this salt is not decomposed by acids (even boiling concentrated hydrochloric acid does not abstract ammonia from it), it must be decomposed by boiling with potash and the hydurilic acid separated from the liquid by hydrochloric acid. From the hot solution, the hydurilic acid separates after some time only, in a form similar to that of acid hydurate of ammonia; from the cold solution, it separates immediately in the form of a white powder. [It is not stated by what characters hydurilic acid is distinguished from the so-called acid hydurate of ammonia.] In subsequent treatments of uric acid by nitric acid, as above described, no hydurilic acid was obtained.

Dried hydurilic acid is a white loose powder composed of fine needles.

Hydurilic acid is converted by nitric acid into nitrohydrilic acid (*vid. inf.*). It dissolves in oil of vitriol with blackening, and only a small portion of it is precipitated from the solution by water.

It is nearly insoluble in cold water, and dissolves but sparingly and slowly in boiling water.

It decomposes the alkaline carbonates with the aid of heat. [Schlieper assumes the existence of neutral and acid dialurates, but has not demonstrated the existence of any one of the latter.]

Ammonia-salt. — Obtained by evaporating the ammoniacal solution of hydrilic acid, or of the [so-called] acid hydrilate of ammonia, in the water-bath, with frequent addition of ammonia, and cooling. Delicate, white, flattened needles, with almost a silvery lustre. It dissolves pretty readily in pure water, very easily in water containing ammonia; acids added to the solution throw down the [so-called] acid salt, in delicate white needles.

Potash-salt. — The solution of the acid in caustic potash, crystallizes only after complete drying, in small nodules, which are insoluble in alcohol.

Soda-salt. — When carbonate of soda is added to the acid diffused in water, as long as effervescence is produced, the acid dissolves, but immediately afterwards the soda-salt is precipitated in the form of a crystalline powder, which increases in quantity as the liquid cools, and on addition of alcohol, after drying, it forms a white heavy crystalline meal, which gives off water even below 100°, and crumbles to a reddish white powder.

The aqueous solution of the neutral ammonia-salt forms with *baryta*-salts a white precipitate; with *lead*-salts, a white precipitate soluble in nitric, but insoluble in boiling acetic acid; and with *silver*-salts a white precipitate, which turns grey at 100°.

Hydurilic acid is insoluble in alcohol (Schlieper).

Here follow Schlieper's analyses, together with the very improbable formulæ which he deduces therefrom.

<i>Hydurilic acid</i> at 100°.	<i>Neutral</i> <i>Ammonia-salt.</i>	<i>Soda-salt</i> at 100°.	<i>Silver-salt</i> at 100°.
$C^{12}N^3H^6O^{11}$	$2NH^3, C^{12}N^3H^3O^9, 3Aq.$	$2NaO, C^{12}N^3H^3O^9, 5Aq.$	$2AgO, C^{12}N^3H^3O^9$
12 C.... 34.58	12 C..... 28.97	2 NaO.... 28.77	2 AgO.... 54.56
3 N.... 20.79	5 N..... 28.48	12 C..... 24.74	12 C.... 17.75
5 H.... 2.33	12 H..... 5.14	3 N..... 2.59	3 N.... 1.03
11 O.... 42.30	12 O..... 37.41	14 O.....	9 O.....
100.00	100.00		

Laurent (*Compt. rend.* 31, 353) assigns to hydrilic acid the formula $C^{12}N^3H^6O^{10}$.

Nitrohydrilic Acid.

SCHLIEPER. *Ann. Pharm.* 56, 16.

Hydurilic acid is suspended in water so as to form a magma; the whole mixed with half its volume of nitric acid, and gently and continuously

heated till the evolution of nitrous acid and a little carbonic acid, which is violent at first, entirely ceases as the liquid cools; the liquid, which is clouded by a white powder, diluted with cold water; then filtered (the filtrate contains alloxan); the white powder washed in cold water, and purified by solution in cold oil of vitriol, and precipitation by water, washing, and drying.

In this manner, nitrohydrilic acid is obtained, in the form of a white powder, which reddens litmus.

Deflagrates like gunpowder when heated.

It is insoluble in cold, sparingly soluble in hot water. Dissolves in concentrated sulphuric or nitric acid, whence it is precipitated by water.

It is insoluble in ammonia, but dissolves pretty readily in potash, and is precipitated from the solution by acids.

<i>Nitrohydrilic acid, dried at 100°.</i>			Schlieper.
8 C	48	23·53	23·12
3 N	42	20·59	20·46
2 H	2	0·98	1·22
14 O	112	54·90	55·20
$C^8N^2H^2O^{14}$	204	100·00	100·00

Laurent (*Compt. rend.* 31, 353, assigns to this acid the formula $C^8N^2H^2(NO^4)O^{10} = C^8N^2H^2O^{14}$, representing it in fact as nitroalloxanic acid.

Alloxanic Acid.



LIEBIG & WÖHLER (1838). *Ann. Pharm.* 26, 292.

SCHLIEPER. *Ann. Pharm.* 55, 263; 56, 1.

Formation. By bringing alloxan in contact with aqueous fixed alkalis. (Liebig & Wöhler):



Preparation. A warm aqueous solution of alloxan is mixed with baryta-water not in excess, the precipitated alloxanate of baryta collected, and decomposed with an equivalent quantity of dilute sulphuric acid; and the filtrate evaporated to a syrup, which solidifies in a few days in a crystalline form. (Liebig & Wöhler.)

To hit the exact proportion of sulphuric acid, the alloxanate of baryta, stirred up with water, must be treated with a quantity of the acid less than sufficient to decompose it; the liquid set aside for a few hours in a warm place, so that the undecomposed alloxanate of baryta may dissolve in the aqueous acid; and the remaining portion of baryta carefully precipitated from the filtrate by sulphuric acid. The liquid is then again filtered and evaporated to a syrup below 40°. (The syrup obtained by evaporation between 50° and 60°, forms a viscid mass, which does not crystallize even after a long time.) (Schlieper.)

Properties. Hard white needles, arranged in radiated groups, and permanent in the air. (Liebig and Wöhler.) Sometimes small needles grouped in warty masses. Very sour with sweetish after taste. (Schlieper.)

Crystallized acid. Calculation according to Liebig & Wöhler.

8 C	48	30.0
2 N	28	17.5
4 H	4	2.5
10 O	80	50.0
<hr/>			
C ⁸ N ² H ⁴ O ¹⁰	160	100.0

Decompositions. 1. The acid when heated melts with violent intumescence, and becomes carbonized, with evolution of cyanic acid vapours. (Schlieper.)—2. The aqueous solution, heated to between 60° and 100°, is resolved, with abundant evolution of carbonic acid, into leucoturic acid (ix. 444.) which falls down as a white powder, on adding water to the solution after evaporation, — diffuan (ix. 448.) which remains in solution, but may be precipitated by alcohol, — and a very small quantity of a substance which dissolves in water and alcohol, crystallizes in crusts, and appears to be C⁸N²H⁴O⁴, (Schlieper, *Ann. Pharm.* 56, 1.) The diffuan forms the largest portion of the product; if, however, the aqueous alloxanic acid be evaporated in a platinum capsule over the water-bath, till the residual syrup flows quietly without frothing, a much larger quantity of leucoturic acid is obtained, viz. about 20 to 30 per cent. (Schlieper.)—3. Alloxanic acid heated with nitric acid, is converted into parabanic acid (ix. 442). (Schlieper.) [Probably thus :



4. When alloxanate of baryta is boiled with water, (Liebig & Wöhler,) or when aqueous alloxanic acid is mixed with excess of baryta-water, or with a mixture of chloride of barium and a large quantity of ammonia or potash (Schlieper), a gelatinous or pasty, strongly alkaline precipitate is formed, which rapidly absorbs carbonic acid from the air, is tolerably soluble in water, and contains mesoxalate of baryta (ix. 425.) with perhaps basic alloxanate of baryta, while urea remains in the filtrate :



5. The solution of alloxan in caustic potash, forms an indigo-blue precipitate with ferrous salts. (Brugnatelli.)— Alloxanic acid is not decomposed by sulphuretted hydrogen (Liebig & Wöhler), or by boiling with bichromate of potash or bichloride of platinum. (Schlieper.)

Combinations. The acid dissolves readily in water. (Schlieper.)

It decomposes carbonates and acetates, (Liebig & Wöhler.) The *neutral* or *bibasic alloxanates* are = C⁸NAdM²O⁴O⁶; the *acid* or *monobasic alloxanates* = C⁸NAdHMO⁴O⁶. The aqueous solution of bibasic alloxanate of baryta, strontia, or lime, deposits mesoxalate and carbonate of baryta, &c. when boiled, while mesoxalic acid and urea remain in the solution. (Liebig.)

Alloxanate of Ammonia.—*a. Bibasic.*—The solution of the salt *b* in ammonia deposits, on addition of alcohol, a portion of the salt in the form of a thick solution, which, on standing, is converted into a white crystalline mass; the remaining portion crystallizes after a while from the alcoholic mixture. The crystals continually give off ammonia, even when dried over lime, and their aqueous solution yields crystals of the salt *b* by spontaneous evaporation. (Schlieper.)

b. Monobasic. The acid saturated with aqueous ammonia yields, by spontaneous evaporation, shining, somewhat yellowish, hard crystals belonging to the oblique prismatic system, which redden litmus strongly. They yield by dry distillation a small quantity of water, then carbonate and hydrocyanate of ammonia, then oxamide, which sublimes as a white powder, and urea, which sublimes in long needles. They dissolve in 3 or 4 pts. of water, but are insoluble in alcohol, which precipitates them from water. (Schlieper.)

<i>Crystals dried at 100°.</i>				Schlieper.
8 C.....	48	27.12	26.75
3 N.....	42	23.73	23.66
7 H.....	7	3.95	4.24
10 O.....	80	45.20	45.35
$C^6N^2H^6(NH^2)O^{10}$				177
				100.00
				100.00

Alloxanate of Potash. — a. Bibasic. A concentrated aqueous solution of alloxan is mixed with an equal volume of strong potash-ley; strong alcohol carefully added to the mixture, which has generally a yellowish colour, till the turbidity, which at first disappears as fast as it is produced, begins to become permanent; a drop of water then added, which removes the turbidity; and the mixture set aside for a few days to crystallize, with frequent addition of alcohol, whereby the quantity of crystals is increased. If too much potash be added, the alcohol throws down a concentrated solution, which solidifies in the crystalline form; if the quantity of potash be too small, alcohol throws down the acid potash-salt, which, from its insolubility in alcohol, can no longer be converted into the neutral salt by adding potash to the mixture. The solution of alloxan in potash-ley likewise yields large crystals by spontaneous evaporation; but when evaporated in the water-bath, it leaves a glutinous mass, which, however, may be converted into crystals by resolution in water and spontaneous evaporation. — Transparent, colourless, shining crystals, belonging to the double oblique prismatic system; bitter; neutral. They give off 15.61 p. c. (5 At.) water at 100°, but retain the sixth atom obstinately, even at 150°, at which temperature they begin to turn yellow. They dissolve readily in water, but are insoluble in alcohol and ether. (Schlieper.) — The very sweet solution of alloxan in potash-ley soon decomposes and turns sour, assumes a yellow colour when evaporated, and finally leaves a red mass, which forms a red solution in water. (Brugnatelli.)

<i>Air-dried Crystals.</i>				Schlieper.
2 KO.....	94.4	32.16	32.00
8 C.....	48.0	16.53	16.48
2 N.....	28.0	9.64	
8 H.....	8.0	2.76	2.86
14 O.....	112.0	38.91	
$C^6N^2H^2K^2O^{10}, 6Aq$				290.4
				100.00

b. Monobasic. — 3 vol. of saturated alloxan solution are mixed with 1 vol. concentrated potash-ley, and the resulting salt precipitated in the form of a crystalline meal, by the addition of a large quantity of alcohol. When potash-ley is dropt into an alcoholic solution of alloxan, the salt is precipitated in the form of a viscid mass, which passes but slowly into the crystalline state. — White granular powder, which has a strong acid

cially in drying. It dissolves with some difficulty in water, and when the solution is evaporated, remains in the form of a thick gum, which takes a long time to crystallize. It dissolves sparingly in hydrated alcohol, and is, therefore, precipitated, but imperfectly, by alcohol from its aqueous solution. (Schlieper.)

	Dried at 100°.		Schlieper.	
KO	47·2	23·81 23·27
8 C	48·0	24·22	
2 N	28·0	14·13	
3 H	3·0	1·51	
9 O	72·0	36·33	
<hr/>				
C ⁸ N ² H ³ KO ¹⁰	198·2	100·00	

Alloxanate of Soda. — Bibasic. — From a concentrated mixture of aqueous alloxan and solution of caustic soda, alcohol throws down a concentrated solution of the salt, which, on account of its great tendency to deliquesce, does not crystallize even when left to stand over oil of vitriol or when treated with absolute alcohol; if the mixture just mentioned be evaporated at 100°, it leaves a deliquescent gummy mass; if it be evaporated in vacuo over oil of vitriol, small crystalline nodules are produced in the syrup. (Schlieper.)

Alloxanate of Baryta. — a. Neutral. — 1. An aqueous solution of alloxan saturated in the cold is heated to 60°, and baryta-water dropt into it till a precipitate begins to form; this precipitate then dissolved by the addition of a small quantity of alloxan; the liquid left to crystallize by cooling, and the mother-liquor again treated in the same manner with baryta-water. (Liebig.)— 2. Three vol. of cold-saturated aqueous alloxan are mixed with 2 vol. of cold saturated aqueous chloride of barium; the mixture heated to 60° or 70°; and potash-ley added with brisk agitation, till the precipitate which redissolves at first begins to become permanent. At this moment, the liquid becomes suddenly filled with precipitated alloxanate of baryta, which quickly falls down in the form of a heavy granular powder, and may be freed from chloride of potassium by washing with cold water. (Schlieper.) If the proper quantity of potash be added, the filtrate contains but little alloxan; if it is not sufficient, a little more must be added, in order to obtain more baryta-salt; if too much potash has been added, a thick curdy precipitate of basic alloxanate of baryta is produced mixed with mesoxalate. This precipitate must therefore be quickly redissolved by a further addition of the alloxan-solution, which is easily done. (Schlieper.)

Short, transparent, colourless prisms or white nacreous scales. They give off 20·2 p. c. water between 100° and 120°, and 22·2 p. c. (8 At.) in all, at 150°, and become milk-white. When ignited, they leave carbonate of baryta and cyanide of barium. They dissolve very sparingly in cold, more readily in hot water, very readily in acids. (Liebig & Wöhler.)— The precipitate formed by alloxan in baryta-water dissolves in excess of alloxan; when exposed to the air, it is converted into carbonate of baryta. Similarly with lime-water. (Brugnatalli.)

<i>Dried at 120°.</i>		<i>Liebig & Wöhler.</i>	
2 BaO	153·2	50·36	49·35
8 C	48·0	15·78	16·01
2 N	28·0	9·20	9·21
3 H	3·0	0·99	1·17
9 O	72·0	23·67	24·26
$C^6N^2H^2Ba^2O^{10} + Aq.$		304·2	100·00

b. Monobasic. — 1. The salt *a* is partially decomposed by digestion with dilute sulphuric acid, the filtrate evaporated, and left for some days in a cool place, whereupon it deposits crusts consisting of small nodules. —

2 The acid ammonia-salt is mixed with chloride of barium, evaporated and set aside. The salt crystallizes when its aqueous solution is evaporated at 30°, in beautiful silky nodules. It reddens litmus; dissolves in water more readily than the neutral salt, still more readily in aqueous alloxanic acid, and sparingly in alcohol, which does not precipitate it from the aqueous solution. (Schlieper.)

<i>Air-dried crystals.</i>		<i>Schlieper.</i>	
BaO	76·6	31·19	31·83
8 C	48·0	19·54	19·15
2 N	28·0	11·40	
5 H	5·0	2·04	2·22
11 O	88·0	35·83	
$C^6N^2H^2BaO^{10} + 2Aq.$		245·6	100·00

Alloxanate of Strontia. — *Bibasic.* — Prepared like the baryta-salt (1). Small transparent needles, which completely give off their 22·5 p. c. (8 At.) water at 120°. (Liebig & Wöhler.)

<i>Air-dried crystals.</i>		<i>Liebig & Wöhler.</i>	
2 SrO	104	32·70	32·60
8 C	48	15·10	15·14
2 N	28	8·80	8·76
2 H	2	0·63	0·90
8 O	64	20·13	20·10
8 HO	72	22·64	22·50
$C^6N^2H^2Sr^2O^{10} + 8Aq.$		318	100·00

Alloxanate of Lime. — *a. Bibasic.* — 1. Aqueous alloxan forms with chloride of calcium on addition of ammonia a thick gelatinous precipitate, which on standing is converted into transparent crystalline grains and short prisms, which give off their water at 120°, and dissolve readily in acetic acid. (Liebig & Wöhler.) — 2. A mixture of aqueous alloxan and chloride of calcium is precipitated by potash not in too great quantity. (Schlieper.) — 3. A mixture of neutral alloxanate of potash and chloride of calcium, if concentrated, immediately deposits a white granular crystalline meal; if dilute, it yields by evaporation small prisms having a strong lustre. Dissolves in water more readily than the baryta-salt, but is insoluble in alcohol, which precipitates the aqueous solution. (Schlieper.)

<i>Air-dried.</i>		<i>Schlieper.</i>	
2 CaO	56	19·44	19·47
8 C	48	16·67	15·65
2 N	28	9·72	
12 H	12	4·17	4·21
18 O	144	50·00	
$C^6N^2H^2Ca^2O^{10} + 10Aq.$		288	100·00

with chloride of calcium immediately deposits a crystalline meal; a dilute solution yields in a few days, transparent, shining prisms, which have a harsh and bitter taste, effloresce quickly, give off 20.17 p. c. (5 At.) water of crystallization over oil of vitriol or at 100°, dissolve in 20 pts. of water, and are not precipitated from the aqueous solution by alcohol. (Schlieper.)

<i>Dried at 100°.</i>		Schlieper.
CaO	28	15.64
C ⁸ N ² H ² O ⁹	151	84.36
C ⁸ N ² H ² CaO ¹⁰	179	100.00

Alloxanate of Magnesia. — Alloxanate of potash and chloride of magnesia mixed in the state of concentrated solution yield, after a while, crystalline crusts consisting of silky nodules, and an additional quantity may be obtained by evaporating the mother-liquor. They dissolve with tolerable facility in water, but sparingly in alcohol, which precipitates the aqueous solution. (Schlieper.)

<i>Air-dried crystals.</i>		Schlieper.
2 MgO	40	14.71
8 C	48	17.65
2 N	28	10.29
12 H	12	4.41
18 O	144	52.94
C ⁸ N ² H ² Mg ² O ¹⁰ + 10Aq.	272	100.00

Alloxanate of Manganese. — The solution of carbonate of manganese in aqueous alloxanic acid yields crystalline grains by evaporation. — When sulphate or acetate of manganese is precipitated by alloxanate of potash (if too small a quantity of the potash salt is used, the precipitate redissolves on agitation); the copious white flakes thus produced, washed out of contact of air, with weak alcohol, as they are somewhat soluble in water; and dried quickly at 90° to 100° in a stream of hydrogen, a white amorphous powder is obtained, which remains permanent in the air even when moistened; whereas the recent and still moist precipitate deliquesces to a brown mass when exposed to the air. But even the dried powder, which does not alter in the air, is not alloxanate of manganese, but perhaps mesoxalate of manganese with alloxanate of potash, inasmuch as it contains potash, and when burnt with oxide of copper, yields a mixture of 6 vol. carbonic acid gas and 1 vol. nitrogen. (Schlieper.)

Alloxanate of Zinc. — *a. Tribasic.* — When alloxanic acid in slight excess is poured upon recently precipitated carbonate of zinc, the carbonic acid is completely expelled, and a soluble monobasic salt is obtained, together with an undissolved tribasic salt, provided the acid is not in too great excess. — 2. When bibasic alloxanate of potash is mixed with sulphate or acetate of zinc, a thick precipitate of tribasic alloxanate of zinc is obtained, which increases on addition of a small quantity of alcohol, while monobasic alloxanate of potash and sulphate or acetate of zinc remain in solution. — [In this reaction, 2 At. bibasic alloxanate of potash, with 3 At. sulphate of zinc produce 3 At. sulphate of potash, 1 At. monobasic alloxanate of potash, and 1 At. tribasic alloxanate of

zinc; Schlieper's calculation, according to which 5 At. bibasic alloxanate of potash and 5 At. sulphate of zinc, produce 6 At. sulphate of potash, 4 At. monobasic alloxanate of potash, and 2 At. tribasic sulphate of zinc, appears to be founded on a mistake.] — The precipitate obtained by (1) or (2) exhibits, after washing and drying in vacuo, the appearance of a horny, translucent, fissured mass, which may be rubbed to a snow-white powder, gives off 21·39 p. c. (8 At.) water at 110°, dissolves slowly in water, especially when dry, but readily in aqueous alloxanic acid, in the form of monobasic salt. (Schlieper.) — Warm aqueous alloxan forms with oxide of zinc a colourless solution, which becomes turbid on cooling, and forms with potash a white precipitate which dissolves with rose-red colour in a larger quantity of potash. (Brugnatelli.)

		<i>Dried in vacuo.</i>		Schlieper.		
3	ZnO	120·6	36·04	35·72
8	C	48·0	14·34	13·80
2	N	28·0	8·37	
10	H	10·0	2·99	3 08
16	O	128·0	38·26	
<hr/>						
ZnO, C ⁸ N ² H ² Zn ² O ¹⁰ + 8Aq.		334·6	100·00		

b. Monobasic. — Zinc dissolves in the aqueous acid with evolution of hydrogen. (Liebig & Wöhler.) The solution of carbonate of zinc or of the salt *a* in excess of acid yields by spontaneous evaporation a gummy mass in which crusts made up of nodules, soon form and may be freed from the viscid mother-liquor by rinsing. The crystals have a pure sweet taste, without the metallic after-taste of zinc: they dissolve with tolerable facility in water, and are precipitated therefrom by alcohol. (Schlieper.)

		<i>Dried over oil of vitriol.</i>		Schlieper.		
	ZnO	40·2	17·69	17·78
8	C	48·0	21·13	20·64
2	N	28·0	12·33	
7	H	7·0	3·08	3·56
13	O	104·0	45·77	
<hr/>						
C ⁸ N ² H ² ZnO ¹⁰ + 4Aq.		227·2	100·00		

Alloxanate of Cadmium. — Cadmium dissolves in the aqueous acid with evolution of hydrogen, and forms an acid salt. When a cadmium-salt is precipitated by bibasic alloxanate of potash, a white precipitate is formed containing potash. (Schlieper.)

Alloxanate of Lead. — *a. Tribasic.* — The aqueous acid forms with subacetate of lead a thick white precipitate, which dries up in vacuo to a snow-white nacreous powder, which is insoluble in water, but soluble in aqueous alloxanic acid. (Schlieper.)

		<i>Dried at 100°.</i>		Schlieper.		
3	PbO	336	70·29	70·58
8	C	48	10 04	
2	N	28	5·86	
2	H	2	0·42	
8	O	64	13·39	
<hr/>						
PbO, C ⁸ N ² H ² Pb ² O ¹⁰		478	100·00		

3 PbO	336	...	68.99	69.11
8 C	48	...	9.86	9.78
2 N	28	...	5.75	
3 H	3	...	0.61	0.96
9 O	72	...	14.79	

PbO, C⁸N²H²Pb²O¹⁰ + Aq. 487 100.00

b. Bibasic. — Water extracts the monobasic salt *c*, and leaves the bibasic salt in the form of a loose white powder. (Schlieper.)

		Dried at 100°.		Schlieper.	
2 PbO	224	...	58.33	58.44
8 C	48	...	12.50	12.76
2 N	28	...	7.30	
4 H	4	...	1.04	1.28
10 O	80	...	20.83	

C⁸N²H²Pb²O¹⁰ + 2Aq. 384 100.00

Sesquibasic? — By precipitating aqueous monobasic alloxanate of lead with absolute alcohol, a white curdy precipitate is obtained, which, so long as it remains moist, deliquesces to a transparent syrup on exposure to the air, but dries up in vacuo to a white powder, which is resolved by water into the salts *b* and *d*. It contains 48.41 p. c. oxide of lead, but gives off 7.87 p. c. water at 100°, and then contains 52.36 p. c. oxide of lead. (Schlieper.)

d. Monobasic. — The solution of recently precipitated carbonate of lead in the aqueous acid leaves by spontaneous evaporation a viscid syrup, which, after a while yields nodules consisting of silky needles. These crystals very slowly give off 6.36 p. c. (2 At.) water at 100°, are resolved by alcohol into free acid and the salt *c*, and dissolve with tolerable facility in water. (Schlieper.)

		Air-dried.		Schlieper.	
PbO	112	...	39.86	39.74
8 C	48	...	17.08	17.16
2 N	28	...	9.96	
5 H	5	...	1.78	1.86
11 O	88	...	31.32	

C⁸N²H²PbO¹⁰ + 2Aq. 281 100.00

The fresh solution of alloxan in ammonia or potash forms a deep blue precipitate with iron-salts. (Brugnatelli.)

Alloxanate of Cobalt. — The red solution of carbonate of cobalt in the acid dries up in vacuo to a viscid mass, which changes in a few weeks into small crystalline nodules. These crystals, after being rinsed with water and dried, present the appearance of a rose-coloured crystalline meal, which turns violet at 100°, dissolves but partially in water, is insoluble in alcohol, and contains 20.56 p. c. CoO, 22.24 C, and 1.98 H, and is therefore a mixture of bibasic and monobasic salt. (Schlieper.)

Alloxanate of Nickel. — *Bibasic.* — The very acid solution of carbonate of nickel in the acid leaves in vacuo a viscid non-crystallizing mass; on the other hand, alcohol throws down the greater part of it in green flakes. These, when washed with water and exposed to the air while

still moist, decompose quickly and dry up to a green mass; but when washed with alcohol and dried in vacuo, they leave a whitish green powder, which is permanent in the air, and dissolves, for the most part, in water, apparently in the form of tribasic salt, since, when dried at 100° , it contains 41.86 p. c. oxide of nickel. (Schlieper.)

	Dried at 100° .		Schlieper.
2 NiO	75	29.64	29.15
8 C	48	18.97	19.67
2 N	28	11.07	
6 H	6	2.37	2.71
12 O	96	37.95	
$C^8N^2H^2Ni^2O^{10} + 4Aq.$	253	100.00	

Alloxanate of Copper. — a. Tribasic. — The aqueous acid forms with an excess of recently precipitated carbonate of copper a dark green acid solution, which, when filtered from the excess of carbonate of copper, deposits, after a while, the tribasic salt in the form of a powder, which has a bluish green colour, even after drying, and is insoluble in water.

b. Bibasic. — 1. On evaporating the liquid filtered from *a*, there is obtained a blackish green gum, and but seldom crystals. — 2. If on the other hand, the solution filtered from the excess of carbonate of copper be mixed immediately with alloxanic acid, till the dark green colour has changed to light blue, and till a few drops evaporated on a glass for a sample, yield crystals, the mixture, when left to evaporate freely, crystallizes to the last drop in blue, shining, crystalline nodules, which become green and opaque at 100° , without giving off their water of crystallization. They dissolve in 5 or 6 pts. of water, forming a blue liquid which becomes green when heated, and is precipitated by alcohol in green flocks, but not by alkalis. (Schlieper.) The solution of cupric oxide in aqueous alloxan yields a green salt which crystallizes in plumose tufts, and is turned blue by ammonia or potash without any precipitation. (Brugnatelli.)

	Salt <i>a</i> dried at 100° .		Schlieper.
3 CuO	120	44.28	44.04
8 C	48	17.71	
2 N	28	10.33	
3 H	3	1.11	
9 O	72	26.57	
$CuO, C^8N^2H^2Cu^2O^{10} + Aq.$	271	100.00	

	Salt <i>b</i> dried at 100° .		Schlieper.
2 CuO	80	27.21	27.21
8 C	48	16.33	16.61
2 N	28	9.52	
10 H	10	3.40	3.17
16 O	128	43.54	
$C^8N^2H^2Cu^2O^{10} + 8Aq.$	294	100.00	

Mercuric Alloxanate. — The solution of mercuric carbonate in alloxanic acid (which decomposes very readily when heated, with precipitation of a scaly powder consisting of mercurous salt), yields with absolute alcohol a powder which is white and loosely coherent when dry, gives off 12.55 p. c. (6 At.) water at 100° , and is insoluble in water. (Schlieper.)

2 HgO	200	58.48	59.68
8 C	48	14.04	13.10
2 N	28	8.19	
2 H	2	0.58	
8 O	64	18.71	

$C^8N^2H^2Hg^2O^{10}$ 342 100.00

Alloxanate of Silver. — *a. Bibasic.* — Bibasic alloxanate of ammonia forms with silver-salts a white precipitate which becomes grey when dry. — The precipitate, when heated in the liquid, also turns, first yellow, then black by reduction of silver, and gives off carbonic acid, if it contains free ammonia, which first decomposes alloxanic acid into urea and mesoxalic acid, whereupon the mesoxalate of silver is resolved by heat into silver and carbonic acid. Alloxanic acid precipitates nitrate of silver only on addition of ammonia. The white precipitate, when boiled with the liquid, merely turns yellow without further decomposition. — The dried precipitate exhibits, considerably below a red heat, a decomposition which spreads through the entire mass, and is attended with slight detonation, — and leaves a residue which when further heated, gives off a large quantity of cyanic acid, and leaves a residue of silver. (Liebig & Wöhler.)

					Liebig & Wöhler.
2 AgO	232	62.03	61.43
8 C	48	12.85	13.07
2 N	28	7.48	7.57
2 H	2	0.53	0.66
8 O	64	17.11	17.27

$C^8N^2H^2Ag^2O^{10}$ 374 100.00 100.00

b. Monobasic? — A solution of silver-oxide in aqueous alloxanic acid dries up to a gum when evaporated. (Liebig & Wöhler.)

Alloxanic acid dissolves in 5 to 6 pts. of *alcohol*; the solution in absolute alcohol may be boiled and evaporated without decomposition. — In *ether* it is less soluble than in alcohol. (Schlieper.)

It has not been found possible to prepare *Alloxanic ether* by any process whatever. (Schlieper.)

Appendix to Alloxanic Acid.

The following acid must, from the mode of its preparation and many statements respecting its properties, be regarded as impure alloxanic acid; but on account of the many diversities which it likewise exhibits, it is best treated separately, at least till these discrepancies are cleared up.

Oxuric Acid.

VAUQUELIN. *Mém. du Mus.* 7, 253.

Acide purpurique blanc. Ac. urique suroxygéné.

Preparation. 1 pt. of uric acid is dissolved in a cold mixture of 2 pts. (or rather more) nitric acid of 34° Bm. and 2 pts. water (the vessel, according to Quesneville, being surrounded with ice); the solution saturated with milk of lime; the basic oxurate of lime, which separates from

the red mixture in white shining crystals, dissolved in a sufficient quantity of dilute acetic acid to neutralize the alkaline reaction; and the liquid left to cool till the neutral lime-salt crystallizes. The crystals of the lime-salt are dissolved in 24 times their quantity of water; the lime precipitated therefrom by 30 per cent. of crystallized oxalic acid; the filtrate evaporated to dryness; and the acid dissolved out with alcohol, filtered to separate a small quantity of oxalate of lime which had remained dissolved through the medium of the oxuric acid, and evaporated. — (Quesneville, (*J. Chim. méd.* 4, 225; also *Pogg.* 12, 629), precipitates the above solution with subacetate of lead, after neutralization with ammonia; washes the fine red precipitate with a large quantity of cold water; suspends it in water; and decomposes it with excess of sulphuretted hydrogen — because, if too small a quantity be used, the purpuric acid likewise present remains undecomposed; — then filters and evaporates.)

Properties. White crystals having a very acid taste like that of oxalic acid; they melt at a gentle heat, and solidify in a brittle gummy mass on cooling.

The lead-salt of this acid contains 75 p. c. lead-oxide and 25 p. c. hyp. anhydrous acid; the latter containing 37·34 p. c. C, 16·04 N, 17·22 [?] H, and 29·34 O.

Decompositions. Yields by dry distillation, hydrocyanate and carbonate of ammonia, empyreumatic oil and charcoal. Does not leave any red residue when dissolved in nitric acid and evaporated.

Combinations. The acid dissolves very readily in water.

The *Alkaline Oxurates* are colourless, perfectly neutral, form white precipitates with stannous and with lead-salts, and do not precipitate nitrate of silver.

Oxurate of Ammonia. — The acid neutralized with aqueous ammonia, yields by evaporation in sunshine, crystals which have an acid reaction in consequence of the partial volatilization of the ammonia.

Oxurate of Lime. — *a. Basic.* — Precipitated in the preparation of oxuric acid (*vid. sup.*). Tastes sweet and slightly alkaline. Contains 27·5 p. c. lime and 31 water; becomes yellowish when dry, and then effervesces slightly with acids. Dissolves sparingly in cold, much more freely in hot water; but the solution, if saturated at a gentle heat, deposits part of the lime at 100°. — *b. Neutral* — Formed by dissolving the salt *a* in hot dilute nitric acid, till the alkaline reaction is removed, and cooling. Neutral colourless crystals permanent in the air, having a slightly sweet taste, and containing 12·6 p. c. lime, and 25·5 water. By dry distillation, they first yield water, then carbonate of ammonia which condenses in needles, and a liquid containing hydrocyanate with a small quantity of carbonate of ammonia, and leave a residue of carbonate of lime mixed with charcoal. Dissolves in more than 40 pts. of cold water, and in a smaller quantity of boiling water, without decomposition, and crystallizes out on cooling.

Oxurate of Lead. — Free oxuric acid does not precipitate neutral acetate of lead, but oxurate of lime forms a white precipitate with that salt; a large portion of the oxurate of lead, however, remains dis-

rating it nearly to dryness, after which the salt may be washed with water. It contains 75 lead oxide and 25 acid.

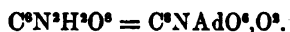
Mercurous Oxurate. — Oxuric acid forms a white precipitate with mercurous nitrate.

Oxurate of Silver. — The free acid and its lime-salt do not precipitate nitrate of silver if diluted to a certain point. White needles which taste like nitrate of silver, and turn red on exposure to light.

Oxuric acid dissolves readily in alcohol.

δ. *Nitrogen nucleus.* C^8NAdO^6 .

Alloxan.



GASPARD BRUGNATELLI. *Brugn. Giorn.* 11, 38 and 117; also *Ann.*

Chim. Phys. 8, 201; also *Schw.* 24, 308; also *N. Tr.* 3, 1, 88.

PROUT. *Ann. Phil.* 14, 363.

LIEBIG & WÖHLER. *Ann. Pharm.* 26, 256.

FRITZSCHE. *J. pr. Chem.* 14, 237.

SCHLIEFER. *Ann. Pharm.* 55, 253.

Discovered in 1817 by Brugnatelli, who named it *Acido ossieritrico*, *erythric acid*; more completely examined by Wöhler & Liebig in 1838.

Formation. In the decomposition of uric acid by nitric acid (Brugnatelli, Liebig & Wöhler), or by chlorine or iodine. (Brugnatelli.)

Preparation. 1. Two pts. of a mixture of ordinary and of the strongest fuming nitric acid, exhibiting a density of 1.48 to 1.50, are placed in a flat basin, and 1 pt. of uric acid added in small portions and with constant stirring, each portion being added after the effervescence caused by the former portion has subsided and the mixture has become cool. The solution, which is now solidified to a white crystalline magma, is left to cool completely, and then placed on a brick or on blotting paper several times folded; the white powder which remains after 24 hours, dissolved in an equal weight of warm water, and the bihydrated alloxan left to crystallize from the filtered solution in a warm place. (Liebig & Wöhler.) — In a cool place, it would yield octohydrated crystals by which the purification would be rendered more difficult. If weaker nitric acid is used, other products are formed together with the alloxan, and completely prevent the separation of the latter. (Liebig & Wöhler.) The alloxan-crystals are often contaminated with a little alloxantin, from which they must be freed by solution in a small quantity of cold water and filtration. (Liebig.)

2. Twelve hundred grains of uric acid are added in successive portions, and with constant stirring, to 1700 grains of nitric acid of sp. gr. 1.412 contained in a flat dish (during which process the liquid may be allowed to become slightly warm, but too much heat, which would decompose the alloxan, must be prevented by cooling the dish in water).

The whole is then left to cool over night; the crystalline magma thrown into a funnel plugged with asbestos [or better with coarsely pounded glass]; the last portions of the mother-liquor carefully displaced by ice-cold water till the liquid which runs through exhibits but a faint acid reaction; the crystals dissolved in the smallest possible quantity of water of 50° to 60°; the solution filtered and cooled till it crystallizes; and a few more crystals obtained by evaporating the mother-liquor at 50°. The heat must not be allowed to exceed that limit, as in that case, the nitric acid still adhering to the crystals would convert a portion of the alloxan into alloxantin, and perhaps also into acid oxalate of ammonia. — The mother-liquor which remains after the separation of these crystals, together with that which has run from the draining funnel, mixed with a threefold quantity of water, is treated with sulphuretted hydrogen gas, which produces alloxantin and a small quantity of dialuric acid; and then exposed for some days to evaporation in the air, as long as alloxantin separates out (which may be purified by solution in boiling water, filtering from sulphur and crystallization), while the mother-liquor still yields a small quantity of parabanic acid, less however as the process has been more successful. In this manner, 100 parts of uric acid yield 90 pts. of crystals of octo-hydrated alloxan, and a quantity of alloxantin corresponding to 10 pts. of hydrated alloxan. Sometimes 100 pts. of uric acid yield altogether 106 to 107 pts. of octo-hydrated alloxan. Calculation (C¹⁰N⁴H⁴O⁶ : C⁶N²H²O⁶, 8 Aq = 168 : 214 = 100 : 127.4) gives as the maximum 127.4 pts. of octo-hydrated alloxan from 100 pts. of uric acid. (Gregory, *Ann. Pharm.* 33, 335; *Phil. Mag. J.* 28, 550; also *J. pr. Chem.* 39, 218.)

Gregory formerly used nitric acid of sp. gr. of 1.30 to 1.35, but this was afterwards declared both by Schlieper and by Gregory himself to be less advantageous. Gregory also added uric acid to the nitric acid only till crystals of alloxan began to appear in the warm liquid; placed the crystalline magma which formed on cooling on a funnel stopped with asbestos, washed it with a very small quantity of ice-cold water; dissolved fresh quantities of uric acid in the mother-liquor which ran off; placed the cooled mass in a fresh funnel; and proceeded in the same manner several times with the mother-liquor which ran away, till it no longer acted upon uric acid even when gently heated.

Of similar nature is the following method proposed by Schlieper: 4 oz. of nitric acid of sp. gr. 1.40 to 1.42 are placed in a beaker-glass surrounded with cold water; and uric acid added with constant stirring and in successive quantities, as much as can be laid on the point of a knife, each portion being allowed to dissolve before the next is added, and care being taken that the heat evolved, which up to a certain point favours the regular decomposition, does not rise above 30° or 35°, as it is likely to do, if the portions of uric acid are added too quickly one after the other, or if too much is added at once, in which case the alloxan is decomposed with evolution of red fumes. As often as crystals of alloxan form in the mixture, they are collected on a funnel plugged with asbestos, to withdraw them from the further action of the nitric acid, whilst the liquid which runs off is again mixed with uric acid, which may be added in larger quantities and with less cooling of the vessel, as the violence of the action diminishes. In this manner crystals of alloxan are repeatedly collected in the funnel, and a thickish mother-liquor runs away, which when exposed to a low temperature for 24 hours, yields a fresh quantity of alloxan-crystals to be collected in a funnel. The

with half its weight of warm water, heated to 60° or 80°, and filtered; the undissolved portion is treated in the same manner. The mixed filtrates yield on cooling large crystals of octohydrated alloxan. The mother-liquor yields by evaporation at 30°, impure, yellowish alloxan, and from the mother-liquor then remaining, parabanic acid may be prepared by boiling with a little nitric acid. To obtain in the form of alloxantin the alloxan still contained in the thinner mother-liquor run off from the asbestos-funnels, this liquid is nearly neutralized with chalk or carbonate of soda; $\frac{1}{2}$ of it saturated with sulphuretted hydrogen gas, whereby sulphur and alloxantin are precipitated, and at the same time a certain quantity of dialuric acid is produced by the further action of that gas; and the remaining $\frac{1}{2}$ of the mother-liquid added, the alloxan of which acts upon the dialuric acid in such a manner as to form alloxantin; the alloxantin, which is completely precipitated in the course of 24 hours, is then collected on a filter, washed with cold water, dissolved in boiling water, filtered from the sulphur, and left to crystallize. — By this treatment, 100 pts. of uric acid yield 41·7 pts. of pure, 11·7 pts. of yellowish octohydrated alloxan, 5·0 pts. of parabanic acid, and 11·7 pts. of alloxantin. (Schlieper.)

¶ Delffs (*J. pr. Chem.* 58, 438) adds uric acid in small portions to twice its weight of nitric acid of sp. gr. 1·42, in a capacious platinum crucible standing in cold water; the anhydrous [bihydrated] alloxan thus obtained amounts to 83 or 85 p. c. of the uric acid consumed. ¶

3. Into a basin containing 4 oz. of uric acid and 8 oz. of moderately strong hydrochloric acid, 6 drams of pure pulverized chlorate of potash are added, in the course of half an hour, by successive portions, and with constant stirring, whereby a liquid containing alloxantin and urea is produced, and, provided the process be carefully conducted, without any evolution of carbonic acid or chlorine: the action is attended with rise of temperature, which however must not exceed a certain limit. The resulting liquid is diluted with twice its bulk of cold water; decanted after three hours from the undissolved uric acid; this residue heated to 50° with a small quantity of strong hydrochloric acid, and another 2 drams, or less, of chlorate of potash gradually added till the uric acid has disappeared. The alloxan contained in the mixture of the two solutions is then converted by sulphuretted hydrogen into alloxantin, which is collected on the filter together with the sulphur (while a solution containing urea runs off); separated from the sulphur by solution in boiling water and filtration; and then left to crystallize. To convert the 2 oz. 7 dr. 20 gr. of alloxantin thus obtained into alloxan, half of it is boiled with a double quantity of water, nitric acid being dropt in at the same time till an effervescence of nitric oxide becomes perceptible; the liquid kept hot on the water-bath till the effervescence is ended; a portion of the second half of the alloxantin then added till a fresh portion produces no effervescence; then again a small quantity of nitric acid, and so on, till only a small quantity of alloxantin remains in excess, and the nitric acid is completely decomposed; the liquid filtered hot; and 3 or 4 drops of nitric acid added, to convert the alloxantin completely into alloxan, whereupon the liquid yields on cooling beautiful crystals of alloxan. (Schlieper.)

Brugnatelli added nitric acid to uric acid as long as effervescence ensued; decanted the liquid from the yellow flakes which were deposited; left these flakes to drain upon bibulous paper; dissolved them in water; and left the filtrate to crystallize by evaporation.

To obtain anhydrous alloxan from the bihydrated or octohydrated compound, the latter must be very carefully heated to 100°, in order to convert it into the bihydrated compound, and this, or the pulverized crystals of the same hydrate, must be heated for some time to 150°—160° in a stream of dry hydrogen gas. (Gm.)

Properties. Alloxan in the pure state is doubtless white; but a product formed by the action of heat imparts to it a pale brown-red colour. (Gm.)

The aqueous solution tastes pungent at first, but afterwards sweetish. (Brugnatelli.) Its taste is slightly astringent; it reddens litmus; colours the skin purple after a while, and imparts to it a peculiar and disgusting odour. (Liebig & Wöhler.)

Calculation according to Liebig & Wöhler's analyses of bihydrated alloxan.

8 C	48	33·80
2 N	28	19·72
2 H	2	1·41
8 O	64	45·07
C ⁸ N ² H ² O ⁸			
	142	100·00

Liebig & Wöhler regarded bihydrated alloxan (C⁸N²H⁴O¹⁰) as the anhydrous compound.

Decompositions. 1. The aqueous solution of alloxan exposed to the action of a voltaic current, gives off oxygen gas at the positive pole and deposits crystalline crusts of alloxantin at the negative pole. (Liebig & Wöhler.) It yields oxygen gas at the positive pole, and scarcely any hydrogen at the negative pole, but acquires at that part a dark red colour. (Brugnatelli.) — 2. Bihydrated alloxan yields by dry distillation a peculiar crystalline product. (Liebig & Wöhler.) — It acquires a slight reddish tinge even at 100° (Liebig & Wöhler); and even by exposure to the heat of the sun. (Brugnatelli.) This reddish tinge, which inclines to brown, increases somewhat at 150°, at which temperature there is likewise formed a trace of a white, mealy sublimate red at the bottom. The pale red solution of this strongly heated alloxan soon becomes spontaneously decolorized, and like the colourless solution of alloxan, yields alloxantin with sulphuretted hydrogen. (Gm.)

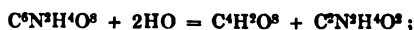
3. Hot dilute nitric acid converts alloxan into parabanic acid, with evolution of carbonic acid (Liebig & Wöhler);



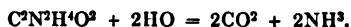
The parabanic acid, when heated for a longer time with nitric acid, is converted into carbonic acid and nitrate of urea. Alloxan cannot therefore be recovered from its solution in weak nitric acid by evaporation. But bihydrated alloxan is scarcely decomposed by heating with strong nitric acid. (Schlieper.) Alloxan does not give off nitrous vapours when heated with copper and oil of vitriol. (Liebig and Wöhler.)

4. Alloxan dissolves in warm concentrated hydrochloric or in dilute sulphuric acid, with continuous effervescence, and with formation of alloxantin. The solution when heated for some time, becomes turbid, and on cooling deposits shining crystals of alloxantin, while the mother-liquor yields by evaporation acid oxalate of ammonia. The first products of the reaction are alloxantin, oxalic and oxaluric acid:

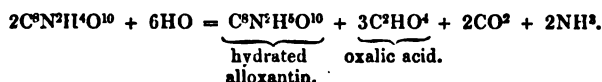
the oxaluric acid is converted by further action of hydrochloric acid into oxalic acid and urea:



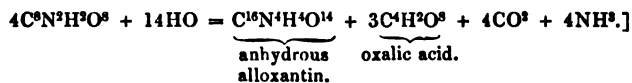
and the urea is finally resolved into carbonic acid and ammonia, which remains combined with the oxalic acid. (Liebig & Wöhler):



Liebig (*Chim. org.* 1, 229) gives the equation:



[The equation might be however:



The solution rendered turbid by heating for a short time frequently does not deposit any crystals of alloxantin on cooling, but only on dilution with water and standing for some time.

The hydrochloric acid solution, after being heated for a short time, forms with baryta-water a white precipitate (alloxan), but after longer heating, continually darker violet precipitates (alloxantin), the colour however continually diminishing by longer boiling, a proof that the alloxantin is decomposed. The solution then deposits, on cooling, instead of alloxantin, a yellow powder which dissolves slowly in water but readily in ammonia, whence it is slowly precipitated by acetic acid; its composition is $C^6N^2H^4O^8$, and it forms yellow crystalline grains with ammonia, but when heated with excess of ammonia, is converted into a yellowish gelatinous powder, which dissolves slowly in water but readily in ammonia, and resembles mycomelate of ammonia (Liebig & Wöhler.)

5. The solution, after boiling for a short time with excess of aqueous sulphurous acid, forms a white precipitate with baryta-water, and after longer boiling, a violet precipitate, the colour of which however diminishes continually when the boiling is continued still longer. (Liebig & Wöhler.)— But when aqueous alloxan is saturated with sulphurous acid and evaporated at a gentle heat, the liquid yields on cooling large transparent efflorescent tables of a substance, which, when treated with ammonia, does not form crystals of thionurate of ammonia, but solidifies with it to a reddish transparent paste. (Liebig & Wöhler.) These crystals appear to be a compound of 1 At. alloxan with 2 At. sulphurous acid; for on adding potash to a mixture of aqueous alloxan, and excess of sulphurous acid till a slight alkaline reaction is produced, hard shining crystals of a potash-salt are obtained, whose acid is composed of 1 At. alloxan and 2 At. sulphurous acid. (Gregory, *Phil. Mag. J.* 24, 189; also *J. pr. Chem.* 32, 280.)

6. When aqueous sulphurous acid is added to a cold-saturated solution of alloxan till its excess becomes perceptible by the odour, then

ammonia added, and the mixture boiled for a short time, a solution of thionurate of ammonia is formed, which on cooling crystallizes in shining laminae. (Liebig & Wöhler):

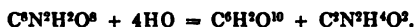


7. Aqueous alloxan heated with peroxide of lead forms carbonate of lead and urea (Liebig & Wöhler):



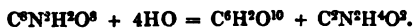
The urea amounts to 38.41 of the bihydrated alloxan. [Calculation gives 37.5 p. c. (160 : 60 = 100 : 37.5).] Oxalic acid and a white powder insoluble in water but soluble in ammonia, which are also formed in small quantity, must be regarded as unessential. (Liebig & Wöhler.)

8. Aqueous alloxan gradually dropt into a boiling solution of neutral acetate of lead, forms a precipitate of mesoxalate of lead (ix. 426), which is flocculent at first, but afterwards aggregates in the form of a crystalline meal, while urea remains dissolved in the liquid:



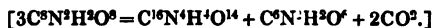
But when the acetate of lead is poured into the solution of alloxan, a scanty rose-coloured precipitate is obtained, which is greatly increased by addition of alcohol, and contains alloxantin and oxalic acid. (Liebig & Wöhler.)

9. Aqueous alloxan forms with baryta or lime-water, after a while only if the alkali is in insufficient quantity, but immediately if it is in excess, a shining crystalline precipitate of alloxanate of baryta or lime. A similar action is produced by strontia-water, and by mixtures of chloride of barium, strontium or calcium, or of nitrate of silver, with ammonia. (Liebig & Wöhler, pp. 158 and 160). When the alkali is in excess, urea is found in the filtrate, and the precipitated alloxanate of baryta is mixed with mesoxalate. (Schlieper.)—Alloxan boiled with aqueous alkalis is resolved into mesoxalic acid and urea (Liebig & Wöhler):



10. The solution of alloxan in ammonia, which has a scarcely perceptible reddish tint, turns yellow when gently heated, and solidifies on cooling or evaporation, to a yellowish jelly of mycomelate of ammonia. (Liebig & Wöhler; see page 181.) The liquid retains in solution alloxanate and mesoxalate of ammonia, together with urea. (Liebig.)—The ammoniacal solution, which is yellow at first, reddens and becomes turbid on standing, and deposits yellow flakes which dissolve with red colour in water. (Brugnattelli.)—Ammoniacal gas passed at 100° over bihydrated alloxan forms a light brown-red mass, which dissolves in water, forming a carmine-coloured solution. (Gm.)

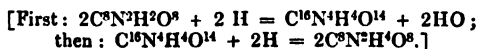
11. The saturated aqueous solution of alloxan gives off carbonic acid when boiled, the evolution of gas continuing for a considerable time, and the alloxan being resolved into alloxantin and parabanic acid:



In consequence of the formation of alloxantin, the boiled liquid forms a blue precipitate with baryta-water, purpurate of ammonia when treated with carbonate of ammonia, and yields a large quantity of alloxantin-

the alloxan-solution is boiled down, a red substance remains together with the alloxan; this substance forms with water a bright red solution, which in course of time becomes decolorized and deposits white flakes; it is also decolorized by boiling, and gives off red vapours [?]. (Brugnatelli.)

12. Protochloride of tin, or aqueous hydrochloric acid with zinc or sulphuretted hydrogen, converts aqueous alloxan into alloxantin, and the two latter reagents then convert the alloxantin into dialuric acid. (Liebig & Wöhler):



The chloride of tin immediately throws down crystals of alloxantin. When hydrochloric acid is used with zinc, dialuric acid is found in the liquid; and if the hydrochloric acid is hot or concentrated, the precipitated alloxantin is converted into the yellow shining crystalline powder mentioned on page 175. With sulphuretted hydrogen, the liquid first deposits sulphur, then crystals of alloxantin, which, especially at a boiling heat, is converted by the further action of the sulphuretted hydrogen, into dialuric acid. Aqueous cyanide of potassium likewise precipitates dialurate of potash from aqueous alloxan after a few hours. (Liebig & Wöhler, *Ann. Pharm.* 41, 291.)

13. Aqueous alloxan colours ferrous salts deep indigo-blue, at first without precipitation; but on addition of alkali, a precipitate is immediately formed. (Brugnatelli, Liebig & Wöhler.)—Aqueous alloxan dissolves iron with yellow, red, and blue colour; in either case the solution turns blue on addition of an alkali. Protoxide of iron forms a yellow solution which turns blue on exposure to the sun and by the action of alkalis, but recovers its yellow colour after a while. Sesquioxide of iron forms a yellow solution which yields a grey precipitate with a small quantity of alkali, but redissolves in a larger quantity, forming a blue solution. These iron-solutions when decomposed by the galvanic current, deposit a blue crust at the negative pole. (Brugnatelli.)

14. Bihydrated alloxan struck on the anvil in contact with potassium detonates slightly and with a faint light. (Gm.)

Combinations. With *water.*—*a. Bihydrated Alloxan.*—Crystallizes on evaporating a warm aqueous solution of alloxan, in oblique rhombic prisms belonging to the oblique prismatic (monoclinometric) system, and having the appearance of rhomboïdal octohedrons truncated at the summits (Hausmann). They are large, transparent, and colourless, have a glassy lustre, and are permanent in the air. (Liebig & Wöhler.)

				Liebig & Wöhler.	
8 C.....	48	30.0	30.41
2 N.....	28	17.5	17.96
4 H.....	4	2.5	2.56
10 O.....	80	50.0	49.07
<hr/>					
C ⁸ N ² H ⁴ O ¹⁰	160	100.0	100.00
Or:					
C ⁸ N ² H ² O ⁸	142	88.75	88.65
2 HO.....	18	11.25	11.35
<hr/>					
C ⁸ N ² H ² O ⁸ + 2Aq.	160	100.00	100.00

The bihydrated alloxan was heated for two hours to 150°—160° in a stream of dry hydrogen gas. Gm.

b. Octohydrated Alloxan.— An aqueous solution of alloxan saturated while warm yields on cooling, large, transparent, colourless crystals belonging to the right prismatic system, and having a nacreous [vitreous] lustre. They effloresce rapidly in warm air, and give off 26 to 27 p. c. water, either in a warm or a cold vacuum, or when heated to 100° in the air. (Liebig & Wöhler.)

	Liebig & Wöhler.		Gm.
$C^8N^2H^4O^{10}$	160	74·77	74·72
6 HO	54	25·23	25·28
$C^8N^2H^2O^8 + 8 Aq.$	214	100·00	100·00

c. Nonohydrated Alloxan.— A solution of alloxan containing a trace of nitric acid, deposited large masses having a rhombedral form and scaliform on the sides. They were found by analysis [the details of which are not given] to contain $C^8N^2H^4O^{10} + 7Aq.$ [or $C^8N^2H^2O^8 + 9Aq.$]. After being kept in a bottle for 2 or 3 years, they were found in summer, to be partly converted into a liquid and a quantity of crystals. The alloxan was then completely decomposed, the products of the decomposition being: (1), alloxantin; (2), a beautiful, easily crystallizing body, different from alloxan and alloxantin, and giving no colour with baryta-water; (3), a large quantity of a substance still more soluble and having a strong acid reaction. (Gregory, *Ann. Pharm.* 87, 126.) ¶

d. Alloxan dissolves readily and without colour in water. (Brugnatelli, Liebig & Wöhler.)

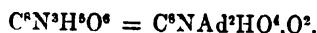
It is insoluble in strong nitric acid, and may be precipitated by that acid from its solution in water. (Schlieper.)

Aqueous alloxan does not decompose carbonate of baryta or carbonate of lime; neither does it act upon oxide of lead, even at a boiling heat.

Alloxan dissolves readily and without colour in *alcohol*. (Brugnatelli.)

c. Nitrogen-nucleus. $C^8NAd^2HO^4$.

Uramil.



LIEBIG & WÖHLER. (1838.) *Ann. Pharm.* 23, 274; 313 and 323.

Formation. 1. By boiling an aqueous solution of thionuric acid or of thionurate of ammonia supersaturated with dilute sulphuric or with hydrochloric acid, for a short time, till it becomes turbid, and then leaving it to cool. Even when the solution is moderately dilute, it solidifies to a crystalline magma while yet warm.—2. By boiling an aqueous solution of alloxantin with hydrochlorate or oxalate of ammonia.

Preparation. A solution of thionurate of ammonia saturated in the cold is heated to the boiling point, hydrochloric acid then added, the boiling continued for a few seconds, the liquid left to cool, and the needles which slowly separate, washed and dried.

p. umose tuits and turning red on exposure to the air.

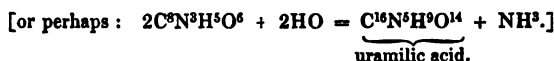
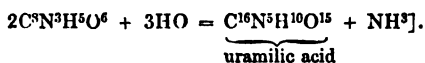
				Liebig & Wöhler.
8 C	48	33·56 33·29
3 N	42	29·38 28·91
5 H	5	3·50 3·77
6 O	48	33·56 34·03
C ⁸ N ³ H ⁵ O ⁶				143 100·00 100·00

[Uramil (C⁸N³H⁵O⁶) is to dialuric acid (C⁶N²H⁴O⁸) as oxamide (C⁴N²H⁴O⁴) to oxamic acid (C⁴NH³O⁶); and similarly, the unknown C⁸NH³O¹⁰ would correspond to oxalic acid (C²H²O⁴).]

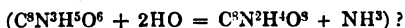
Decompositions. 1. Uramil treated with nitric acid gives off nitric oxide gas free from carbonic acid, and forms a solution which is coloured purple-red by ammonia, and when evaporated and cooled, solidifies to a crystalline magma of alloxan, while nitrate of ammonia remains in the mother-liquor. [Perhaps in this manner:



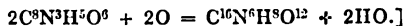
2. Uramil dissolves quietly in cold oil of vitriol, whence it is precipitated by water as a white powder, while only traces of ammonia remain in the liquid. But if the solution in oil of vitriol be diluted with water merely till it begins to show turbidity, and the mixture then boiled, with renewal of the water, till it is no longer precipitated by a large quantity of water, it yields by evaporation crystals of uramic acid, sulphate of ammonia being formed at the same time:



When too much sulphuric acid is added, no uramic acid is obtained; but the liquid, after exposure to the air for some time, yields crystals of dimorphous alloxantin (or dialuric acid?)



3. When mercuric oxide or oxide of silver is added by small portions and not in excess, to uramil suspended in boiling water, the metal is reduced, but without evolution of gas, and a purple liquid is obtained, which on cooling deposits crystals of purpurate of ammonia, while either alloxan or alloxantin remains in the mother-liquor. [Admitting that these latter products proceed from oxidation carried too far, and are therefore unessential, the equation will be:

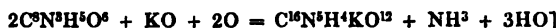


The slightest excess of metallic oxide decolorizes the purple liquid, which then contains alloxanate of ammonia. [Perhaps in this manner:



Purpurate of ammonia is more advantageously obtained by adding ammonia in small quantities, together with the metallic oxide to the uramil while boiling in water. [Perhaps the ammonia prevents the oxidation from going too far.]

4. When a hot dilute solution of potash is saturated with uramil, a small quantity of ammonia is evolved, and a pale yellow solution obtained which rapidly absorbs oxygen from the air, acquires a continually deeper purple or almost violet colour, and when exposed to the air over night deposits a large quantity of shining gold-green prisms containing potash [purpurate of potash]. The supernatant mother-liquor is neutral, and contains either alloxanate or mesoxalate of potash. — [If purpurate of potash be regarded as $C^{16}N^6H^4KO^{12}$, and the alloxanic or mesoxalic acid as a secondary product, the equation will be:

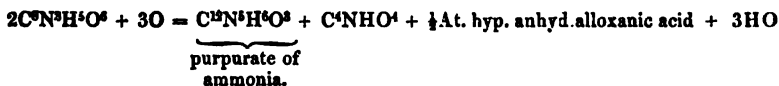


When a solution of uramil in potash is boiled for some time, a large quantity of ammonia is evolved; the quantity of undecomposed uramil which can be precipitated from the filtrate by hydrochloric acid continually decreases; and the hydrochloric acid filtrate supersaturated with ammonia, forms with chloride of calcium a white precipitate, which dissolves in a large quantity of water, and resembles uramilate, oxalurate or mesoxalate, — or, if the boiling with potash has been long enough continued, — oxalate of lime. According to Liebig, (*Chim. org.* 1, 225,) uramillic acid is produced in this reaction.

5. A solution of uramil in ammonia, boiled and evaporated in an open vessel, acquires a deep purple-red colour, and yields on cooling crystals of purpurate of ammonia:



According to this equation, the ammonia must be regarded merely as a solvent of the uramil]. — Liebig & Wöhler, on the other hand, give the equation:



A solution of uramil in ammonia mixed with an aqueous solution of alloxan, also yields a large quantity of purpurate of ammonia:



Gerhardt (*Ann. Chim. Phys.* 72, 184), who, with Liebig & Wöhler, regards purpurate of ammonia as $C^{12}N^6H^6O^8$, or rather as $C^{24}N^{10}H^{12}O^{14}$ gives the equation:



Combinations. Uramil is insoluble in cold, sparingly soluble in hot water, from which it crystallizes on cooling.

It dissolves in cold oil of vitriol, whence it is precipitated without alteration by water.

It dissolves without decomposition in cold aqueous ammonia or potash, from which it is precipitated by acids. (Liebig & Wöhler.)

Dilituric Acid.



SCHLIEPER. (1845.) *Ann. Pharm.* 56, 23.

When a hot aqueous solution of alloxantin is quickly boiled with hydrochloric acid; the mixture of allituric acid and alloxantin which precipitates on cooling, treated with nitric acid, to dissolve out the latter; the alloxan separated from the nitric acid solution in the form of alloxantin by sulphuretted hydrogen; and the filtrate mixed with nitric acid,—whereby the dialuric acid formed by the sulphuretted hydrogen is converted into parabanic acid,—and evaporated down to $\frac{1}{2}$ of its bulk: diliturate of ammonia separates in the form of a yellowish white powder, which may be purified by recrystallization from hot water, while scarcely anything but parabanic acid remains in the liquid.

Diliturate of ammonia [or the amide] crystallizes in yellow, brightly shining laminæ, the colour of which is not removable by animal charcoal, but appears to be essential.

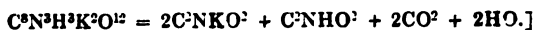
It dissolves in dilute potash (not in concentrated potash-solution, because the resulting potash-salt is insoluble in that liquid), with evolution of ammonia; and acids added to it, throw down the acid potash-salt, in the form of a yellowish white powder.

It is nearly insoluble in cold and but sparingly soluble in hot water; insoluble in ammonia; dissolves readily in oil of vitriol, whence it is precipitated by water undecomposed and with unaltered amount of nitrogen. It is neither dissolved nor decomposed by strong nitric acid.

<i>The so-called Ammonia-salt dried at 100°.</i>		Schlieper.	
8 C.....	48	25·26	25·57
4 N	56	29·47	30·16
6 H	6	3·16	3·30
10 O	80	42·11	40·97
$C^9N^4H^6O^{10}$	190	100·00	100 00

[If this compound is regarded, not as an ammonia-salt, but as an amide = $C^9NAd^2XH^3O^2, O^4$, a view which accords with all its chemical relations, the acid contained in it must be $C^9N^3H^3O^{12} = C^9NAdXH^3O^2, O^6$. — ($C^9N^4H^6O^{10} + 2HO - NH^3 = C^9N^3H^3O^{12}$). The analyses of the following salts are calculated according to this hypothesis. Schlieper on the contrary, regards the acid, which he likewise supposes to be bibasic, as $C^9N^3H^3O^{12}$, or in the hyp. anhydrous state, $C^9N^3HO^{11}$. — Laurent, *Compt. rend.* 31, 353), gives for the hydrated acid the formula $C^9N^3H^3O^{12} = C^9N^3XH^3O^8$.]

Potash-salt. — *a. Neutral.* — Obtained by boiling the ammonia-salt with dilute potash, till ammonia is no longer evolved, adding alcohol to the hot solution till the precipitate begins to become permanent, and leaving it to crystallize by cooling. Lemon-yellow, shining, loosely aggregated needles. They do not give off water at 100°, but at a higher temperature they deflagrate suddenly, with evolution of carbonic and cyanic acids, and are converted into cyanate of potash free from charcoal. [Probably thus:



They dissolve pretty readily in water, but are insoluble in alcohol.

Needles dried at 100°.			Schlieper.
2 KO	94.4	35.30	34.35
8 C	48.0	17.95	
3 N.....	42.0	15.71	
3 H.....	3.0	1.12	
10 O.....	80.0	29.92	
<hr/>			
$C^8N^4AdXHK^2O^2, O^6$	267.4	100.00	

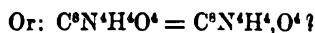
According to Schlieper, the formula is $2KO, C^8N^3HO^8 + Aq.$

b. Acid-salt. — Obtained by precipitating the aqueous solution of *a* with a stronger acid. Yellowish white powder, which behaves, when heated, like the salt *a*. It dissolves in oil of vitriol, and is precipitated therefrom by water without any alteration in the amount of potash. It dissolves sparingly in cold, more readily in hot water, whence it crystallizes out on cooling. Contains 21.78 p. c. potash, and is therefore $KO, C^8N^3HO^8, 2Aq.$ [The formula $C^8N^3H^4KO^{13}$ requires 20.6 p. c. potash.]

Silver-salt. — Nitrate of silver is not precipitated, either by the ammonia or by the acid potash-salt; but the neutral potash immediately throws down from it a powder of a bright lemon-colour. This salt detonates when heated almost like a fulminate, and in consequence of the scattering which takes place, leaves only 48.76 p. c. silver. (Schlieper.) [The formula $C^8N^3H^3Ag^2O^{12}$ would require 53.33 per cent.]

η. Nitrogen-nucleus. $C^8N^4H^4$.

Mycmelic Acid.



LIEBIG & WÖHLER. (1838.) *Ann. Pharm.* 26, 304.

Formation and Preparation. Aqueous alloxan assumes a yellow colour when gently heated with ammonia, and if the mixture is concentrated, deposits mycomelate of ammonia, immediately after the heat has been applied, as a heavy brownish yellow powder; but if the mixture is dilute, it deposits the salt after a while in the form of a yellowish transparent jelly. — [perhaps in this manner:



or, if perfectly dried mycomelic acid be not $C^8N^4H^5O^5$, but $C^8N^4H^4O^4$, the equation must be:



The acid may be precipitated by sulphuric acid, either from the hot aqueous solution of mycomelate of ammonia obtained as above, or immediately from the aqueous solution of alloxan heated with ammonia.

gelatinous substance; but after washing it dries up to a yellow, loosely coherent powder, which reddens litmus.

Dried at 100°.			Liebig & Wöhler.		Calculation.		b.	
8 C.....	48	32.22	33.13	8 C.....	48	34.29		
4 N.....	56	37.58	38.36	4 N.....	56	40.00		
5 H.....	5	3.36	3.57	4 H.....	4	2.85		
5 O.....	40	26.84	24.94	4 O.....	32	22.85		
<hr/>						<hr/>		
C ⁸ N ⁴ H ⁵ O ⁵	149	100.00	100.00	C ⁸ N ⁴ H ⁴ O ⁴	140	100.00		

Calculation *b* is founded on the supposition that the salt dried at 120° retains 1HO, which would escape at a higher temperature.

The acid dissolved in potash is decomposed on boiling, with evolution of ammonia. (Liebig, *Chim. org.*)

Combinations. Mycomelic acid dissolves slowly in cold, readily in hot water.

It decomposes the alkaline carbonates.

Mycomelate of Ammonia. — A solution of alloxan in warm concentrated ammonia, heated till it becomes decolorized, deposits this salt on cooling, in the form of a yellowish powder, sometimes flocculent, sometimes granular.

Mycomelate of Silver. — The ammonia-salt throws down from nitrate of silver, yellow gummy flakes, which may be heated in the liquid to the boiling point without decomposition, turn yellowish brown when washed, especially in the dark, and then dry up to hard grey lumps, which yield an olive-green powder. The salt when heated, yields a copious sublimate of cyanate of ammonia, which changes to urea when dissolved in water, and a crystalline substance, having a peculiar odour and reddened by the presence of another substance. It is insoluble in water. (Liebig & Wöhler.)

				Liebig & Wöhler.	
8 C.....	48	19.43			
4 N.....	56	22.67			
3 H.....	3	1.22			
Ag.....	108	43.73	44.39		
4 O.....	32	12.95			
<hr/>					
C ⁸ N ⁴ H ³ AgO ⁴	217	100.00			

Conjugated Compounds allied to the preceding.

Thionuric Acid.



LIEBIG & WÖHLER. (1838.) *Ann. Pharm.* 26, 268, 314, and 331.

Formation, p. 176, 6.

Preparation of Thionurate of Ammonia. 1. Sulphurous acid is added to a cold-saturated aqueous solution of alloxan till its odour is no longer

destroyed, the liquid then immediately supersaturated with ammonia, boiled for half an hour, and left to crystallize by cooling. — 2. Better : An aqueous solution of sulphite of ammonia is mixed with excess of carbonate of ammonia, then with aqueous alloxan, the mixture kept in a state of ebullition for half an hour, and then left to crystallize by cooling.

Preparation of Thionuric Acid. — A solution of thionurate of ammonia in hot water is precipitated by neutral acetate of lead, the precipitate washed, suspended in water, and decomposed by sulphuretted hydrogen, and the filtrate evaporate at a gentle heat.

Properties. White mass, consisting of needles; reddens litmus strongly; has a very sour taste; permanent in the air.

The acid mixed with ammonia reproduces the crystals of thionurate of ammonia.

Calculation of the free acid :

8 C	48	21.52
3 N	42	18.84
5 H	5	2.24
8 O	64	28.70
2 SO ²	64	28.70
C ⁸ N ³ H ⁵ O ⁸ ,2SO ²			
	223	100.00

Liebig & Wöhler assume, and probably with reason, according to the behaviour of the acid and its ammonia-salt in various reactions, that it contains, not sulphuric but sulphurous acid.

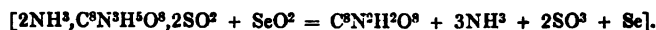
Decomposition. The aqueous acid becomes turbid when boiled, and solidifies during the ebullition, in consequence of the formation of silky needles of uramil, sulphuric acid being set free at the same time : — [Perhaps in this manner :



Combinations. The acid dissolves readily in water.

The neutral *thionurates* contain 2 At. base; they yield sulphite of potash by fusion with hydrate of potash, and evolve sulphurous acid when treated with oil of vitriol.

Thionurate of Ammonia. — For the preparation, *vid. sup.* — Colourless four-sided tables and laminae, having a mother-of-pearl lustre when dry. They assume a rose-colour at 100°, (giving off 6 p. c. or 2 At. water. [Liebig, *Chim. org.*]) They may be recrystallized without decomposition from water, in which they dissolve very sparingly at ordinary, but very readily at higher temperatures. When fused with hydrate of potash, they yield, not sulphate but sulphite of potash. The aqueous solution reduces selenium from selenious acid :



The solution reduces silver from the nitrate in the specular form. — At ordinary temperatures, it is not decomposed by an excess of sulphuric hydrochloric or nitric acid; but, at a boiling heat, the mixture becomes turbid, and solidifies to a magma, consisting of needles of uramil, (amounting to 47.05 p. c.), and the filtrate, which contains the liberated sulphuric acid, precipitates chloride of barium. — On evaporating the

phuric acid, at a gentle heat, a large quantity of fine white needles is obtained, consisting of acid thionurate of ammonia; with a large quantity of sulphuric acid, uramil is obtained, and changes to uramilic acid, and with a still larger quantity of sulphuric acid, the latter is converted into dimorphous alloxantin [or dialuric acid]. — (Acid thionurate of ammonia is obtained, when the aqueous solution of 1 At. of the neutral salt is evaporated at a gentle heat with 1 At. hydrochloric acid, in the form of white crusts composed of small crystals.) (Gregory, *Phil. Mag. J.* 24, 189.)

	<i>Crystallized.</i>	Liebig & Wöhler.	
8 C.....	48	17.45	18.02
5 N	70	25.45	26.10
13 H	13	4.73	4.88
8 O	64	23.27	22.47
2 SO ²	80	29.10	28.53
<hr/>			
2NH ³ ,C ⁸ N ⁵ H ¹³ O ⁸ ,2SO ² + 2Aq.	275	100.00	100.00

Thionurate of Baryta. — The ammoniacal salt throws down from chloride of barium, translucent, gelatinous flakes, which, after a while, become opaque and crystalline, dissolve readily in hydrochloric acid, and when boiled with nitric acid, yield sulphate of baryta, but no free sulphuric acid.

Thionurate of Lime. — A warm aqueous mixture of thionurate of ammonia and nitrate of lime deposits short silky needles, containing 19.5 p. c. (2 At.) lime.

Thionurate of Zinc. — An aqueous mixture of the ammonia-salt with a zinc-salt, soon deposits thionurate of zinc in small, lemon-yellow, sparingly soluble, crystalline nodules.

Thionurate of Lead. — The hot solution of thionurate of ammonia forms, with neutral acetate of lead, translucent gelatinous flakes, which on cooling change to white or rose-coloured slender needles, united in tufts. The salt yields by distillation, urea, and a peculiar product which crystallizes in large laminae. Its solution in hot nitric acid, the formation of which is attended with effervescence, deposits sulphate of lead, neither lead nor sulphuric remaining in the filtrate. It dissolves in dilute hydrochloric acid.

	Liebig & Wöhler.	
2 PbO	224	50.11
8 C	48	10.74
3 N	42	9.40
5 H	5	1.11
8 O	64	10.74
2 SO ²	64	17.90
<hr/>		
C ⁸ N ⁵ H ¹³ Pb ² O ⁸ ,2SO ² + 2 Aq.....	447	100.00

Thionurate of Copper. — The ammonia-salt forms, with sulphate of copper, a light brownish yellow precipitate, which is doubtless a cuprous salt. When heated, it dissolves with brownish yellow colour in the liquid, and separates again on cooling in the amorphous state. (Liebig & Wöhler.)

Alloxantin.



LIEBIG & WÖHLER. (1838.) *Ann. Pharm.* 26, 262 and 309.

FRITZSCHE. *Bull. scient. de l'Acad. de Petersb.* 4, 81; also *J. pr. Chem.* 14, 237.

Uroxin (Fritzsche), *Alloxantine*.

Formation. 1. By the action of warm dilute nitric acid upon uric acid. — 2. By heating alloxan for a short time with dilute sulphuric acid, or boiling it for a long time with water, or by treating the aqueous solution of alloxan with sulphuretted hydrogen, or with hydrochloric acid and zinc, or with protochloride of tin. — 3. By boiling uramil with dilute sulphuric or hydrochloric acid. — 4. By heating thionurate of ammonia with a larger quantity of dilute sulphuric acid. (Liebig & Wöhler.) — 5. Apparently also in the decomposition of caffeine by chlorine. (Rochleder, *vid. Caffein.*)

Preparation. 1. Dry uric acid is added to warm and very dilute nitric acid, till the resulting colourless or pale yellow liquid no longer acts upon it; the solution gently evaporated till it assumes an onion-red colour; then cooled; and the crystals purified by recrystallization from hot water. (Liebig & Wöhler.) — Or dilute nitric acid is gradually added to 1 pt. of uric acid in 32 pts. of water, till all the uric acid is dissolved; the solution then evaporated down to two-thirds; and the crystals which separate after a few days, purified by recrystallization. (Liebig.) A similar mode of preparation, which, however, yields a quantity of alloxantin amounting only to 10 p. c. of the uric acid, is described by Fritzsche.

2. Sulphuretted hydrogen is passed through an aqueous solution of alloxan; the resulting magma heated till the alloxantin dissolves; then filtered from the precipitated sulphur; and the filtrate left to crystallize. (Liebig & Wöhler.)

3. A solution of alloxan in dilute sulphuric acid is heated for a few minutes, whereby it becomes turbid, and yields crystals of alloxantin on cooling. (Liebig & Wöhler.)

4. Alloxantin is likewise obtained as a secondary product in the preparation of alloxan by Gregory's process (p. 171); also in Schlieper's method of preparing alloxan with nitric acid or chlorate of potash (p. 172.)

5. When dialurate of ammonia is evaporated at a gentle heat with a large excess of dilute sulphuric acid, and the solution left to stand for some time, *dimorphous alloxantin* crystallizes out, differing from ordinary alloxantin by its peculiar crystalline form, but exhibiting the same composition. (Liebig and Wöhler.) This product is crystallized dialuric acid converted into alloxantin by the action of the air. (Gregory.)

The crystals of alloxantin obtained by either of these processes are freed from their water of crystallization by heating them to 150°. (Liebig & Wöhler.)

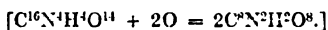
Of the properties of anhydrous alloxantin, nothing is known (*vid. Hydrated Alloxantin.*)

16 C	96	35.82
4 N	56	20.89
4 H	4	1.50
14 O	112	41.79
<hr/>		
C ¹⁶ N ⁴ H ⁴ O ¹⁴	268	100.00

[Alloxantin may be regarded as a conjugated compound of alloxan and dialuric acid:
 $C^8N^2H^2O^8 + C^8N^2H^2O^8 = C^{16}N^4H^4O^{14} + 2HO.$]

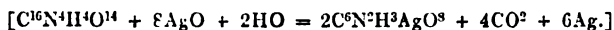
Decompositions. 1. Alloxantin yields by dry distillation a peculiar crystalline product. (Liebig & Wöhler.)

2. When heated in chlorine-water it is converted into alloxan. Also, with slight effervescence, when diffused in boiling water and mixed with a small quantity of nitric acid, the alloxan separating from the liquid after evaporation to a syrup. (Liebig and Wöhler.) The hot solution of alloxantin is likewise converted into alloxan by selenious acid, with precipitation of selenium (Liebig & Wöhler):



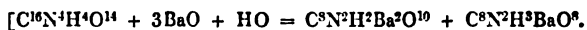
3. A solution of alloxantin in aqueous hydrochloric acid rapidly boiled down to a small quantity, deposits on cooling, a white powder of allituric acid (ix. 443), together with unaltered alloxantin. (Schlieper.) [With evolution of carbonic acid?]

4. Aqueous alloxantin reduces mercuric oxide with evolution of gas, and appears to form a solution of mercurous alloxanate. (Liebig & Wöhler; Liebig, *Chim. org.*) — When aqueous alloxantin is heated with oxide of silver, silver is reduced, with effervescence and formation of oxalurate of silver, which remains in solution (Liebig):



From a solution of nitrate of silver, aqueous alloxation immediately throws down black metallic silver, after which the filtrate yields a white precipitate with baryta-water. (Liebig & Wöhler.) — Alloxantin is decomposed by peroxide of lead, like alloxan. (Liebig & Wöhler.)

5. Aqueous alloxantin forms with baryta-water a thick violet precipitate, and when the mixture is heated, ultimately yields alloxanate and dialurate of baryta. (Liebig & Wöhler.)



[Does the violet colour which the precipitate at first exhibits arise from basic purpurate of baryta?] — The violet precipitate, when boiled, first turns white and then disappears. When baryta-water is gradually dropt into a solution of alloxantin in boiling water free from air, each drop produces a deep violet precipitate which redissolves without colour; as the quantity of baryta-water is further increased, the liquid suddenly becomes turbid and deposits dialurate of baryta in the form of a reddish-white powder; and after this powder has been completely precipitated by baryta-water, a still further quantity of that reagent produces a white precipitate of alloxanate of baryta, part of which remains in solution together with a small quantity of urea. (Liebig & Wöhler.)

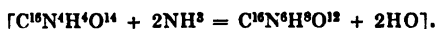
6. Aqueous solutions of alloxantin and sal-ammoniac thoroughly freed from air by boiling, immediately form a purple-red mixture which soon becomes paler in colour and deposits colourless or reddish shining

scales of uramil (p. 178), while alloxan and hydrochloric acid remain in solution (Liebig & Wöhler):



Other ammoniacal salts, as the oxalate and acetate, behave with alloxantin in the same manner as sal-ammoniac, excepting that the precipitate has a deeper red colour, and is thicker and less crystalline. (Liebig & Wöhler.)

7. When free ammonia comes in contact with alloxantin, 2 At. of it enter into combination, forming purpurate of ammonia (Gm.):



When dry ammoniacal gas is passed over finely pounded alloxantin, that substance turns red at the ordinary temperature, and at 100°, gives off water, and is completely converted into a deep brown-red powder of purpurate of ammonia. (Gm.).—To render the decomposition as complete as possible, the mass must be taken out a few times, finely triturated again, and the ammoniacal gas allowed to act upon it for several hours. (Gm)

[The conflicting results obtained by Liebig & Wöhler and by Fritzsche respecting purpurate of ammonia, alloxantin, and the allied compounds, induced me to attempt to bring them into accordance with one another and with the nucleus-theory, and to discover formulæ differing as little as possible from the analyses of those distinguished investigators, and affording at the same time a complete explanation of the remarkable decompositions of those compounds. But the formulæ which I found to be the most probable required that alloxantin should be completely converted by ammonia into purpurate of ammonia. It is true that those chemists had already observed the red tint of the ammoniacal solution of alloxantin, but they had by no means regarded it as the essential circumstance; on the other hand, it was stated by Liebig & Wöhler, as well as by Gregory, that to insure an abundant formation of purpurate of ammonia, a large quantity of alloxan must be present as well as alloxantin and aqueous ammonia. It must however be observed that an excess of aqueous ammonia quickly decolorizes purpurate of ammonia, and that the alloxan may serve to convert the uramil produced at the same time into purpurate of ammonia (p. 189, 8), and also to transform the excess of ammonia into alloxanate of ammonia, and thereby weaken its decomposing influence. The above-described experiment with pulverized alloxantin and ammoniacal gas, appears therefore to be decisive. The laws of the nucleus-theory, which guided me in these investigations, led me also to suspect that alloxan, previously supposed to be $C^8N^2H^4O^{10}$, really contained 2HO more, an idea which was confirmed by experiment.—My best thanks are due to Dr. v. Weltzien for the very pure alloxan and alloxantin with which he supplied me for this research].

Alloxantin turns red on exposure to air containing ammonia. Its hot aqueous solution is coloured purple-red by ammonia, but becomes colourless again when further heated, or when left for some time in the cold. (Liebig & Wöhler.)

When moistened alloxantin is introduced into a tube containing air and standing over mercury, and a few drops of ammonia passed up, the alloxantin immediately acquires a deep purple colour from the action of the rising ammoniacal gas, and absorbs a larger quantity of oxygen, but its colour is immediately afterwards diminished by the excess of ammonia. (Fritzsche.) [This copious absorption of oxygen I did not observe; at all events the preceding observations show that it is not necessary to the formation of purpurate of ammonia.]

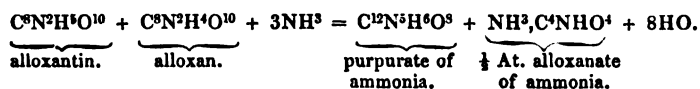
Aqueous alloxantin turns red when heated with acetate of ammonia, but not with nitrate; but when evaporated with the latter, it leaves a purple residue. (Gm.)

alloxantin, and samples of the liquid gently heated with ammonia, the ammonia produces, as the quantity of nitric acid, and consequently of alloxan, increases, a continually deeper purple colour; but when sufficient nitric acid has been added to convert the alloxantin completely into alloxan, the reddening with ammonia ceases. (Liebig & Wöhler.)— [This is perhaps explained by the preceding observations.]

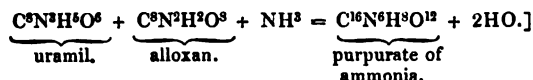
8. The solution of alloxantin in thoroughly boiled water, mixed with ammonia and boiled till the purple colour has completely disappeared, yields chamois-coloured crystalline crusts of uramil; the yellow mother-liquor becomes purple on exposure to the air, deposits crystals of purpurate of ammonia, and ultimately coagulates to a jelly of mycomelate of ammonia. (Liebig & Wöhler.)— In this reaction as in that with sal-ammoniac, uramil and alloxan are first produced, and these by their mutual action, with the aid of ammonia and the air, form purpurate of ammonia; moreover the alloxan with ammonia forms mycomelate of ammonia. (Liebig & Wöhler.)— [Or rather:



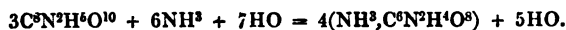
Part of the uramil which remains dissolved in the ammonia is at the same time converted by the oxygen of the air into purpurate of ammonia.]— When alloxantin dissolved in aqueous ammonia and boiled till it loses its colour is cooled to 70°, every drop of aqueous alloxan added to the liquid produces a deep purple colour, and the solution then deposits a few crystals of purpurate of ammonia, together with flakes of uramil (Liebig & Wöhler):



(Liebig & Wöhler.)— [Or perhaps, as uramil was found by Liebig & Wöhler to be present in the boiled ammoniacal solution of alloxantin:



9. When a solution of alloxantin in ammonia is repeatedly evaporated at a gentle heat in an open vessel, and each time redissolved in ammonia, it finally leaves pure oxalurate of ammonia (Liebig & Wöhler):



(Liebig & Wöhler.)— [Should not other products be formed at the same time?]

10. Alloxantin dissolved in water is decomposed by long keeping, even out of contact of air, and loses its characteristic properties. (Fritzsche.) It becomes in fact sour; forms with baryta water, no longer a violet but a white precipitate; and leaves when evaporated crystals having the appearance of alloxanic acid. (Gregory, *Phil. Mag. J.* 24, 190.)

11. Sulphuretted hydrogen passed through a solution of alloxantin in boiling water yields a precipitate of sulphur, and converts the alloxantin into dialuric acid (Liebig & Wöhler):



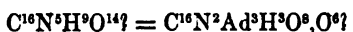
a. *Hydrated Alloxantin*. — Obtained by crystallization from water. Transparent, colourless or yellowish, oblique rhombic prisms, hard but very friable. The angle of the obtuse lateral edge is, in ordinary alloxantin = 105°; in dimorphous alloxantin = 121°. Alloxantin reddens litmus, even after being crystallized six times from water. It turns red by exposure to air containing ammonia. (Liebig & Wöhler.)

Crystals.		Liebig & Wöhler.		Fritzsche.	
16 C	96	29·81	30·52	30·06	
4 N	56	17·39	17·66	17·52	
10 H	10	3·11	3·15	3·04	
20 O	160	49·69	48·67	49·38	
<hr/>					
C ¹⁶ N ⁴ H ⁴ O ¹⁴ + 6Aq.	322	100·00	100·00	100·00	
<hr/>					
Or:		Liebig & Wöhler.			
C ¹⁶ N ⁴ H ⁴ O ¹⁴	268	83·23	84·6		
6 HO	54	16·77	15·4		
<hr/>					
C ¹⁶ N ⁴ H ⁴ O ¹⁴ + 6Aq.	322	100·00	100·00		

The crystals give off nothing at 100°, but at 300° (at 150° according to Liebig, *Chim. org.*) they give off 15·4 p. c. (Liebig & Wöhler.)

b. The crystals dissolve very sparingly in cold water, more abundantly, but still slowly in boiling water, from which solution the alloxantin separates almost completely on cooling. (Liebig & Wöhler.)

Uramilic Acid.



LIEBIG & WÖHLER. (1838.) *Ann. Pharm.* 26, 314.

Formation and Preparation. 1. Water is added to a solution of uramil in cold oil of vitriol, till it begins to become turbid; the liquid boiled with frequent renewal of the water, till it no longer forms a precipitate with water, and evaporated to the crystallizing point (p. 179, 2). — 2. A cold-saturated aqueous solution of thionurate of ammonia is evaporated at a gentle heat with a small quantity of sulphuric acid. The uramil which separates from the thionurate of ammonia is then gradually converted by the free sulphuric acid into uramilic acid; and this compound crystallizes after 24 hours from the evaporated liquid, which turns yellow during the evaporation.

If the quantity of sulphuric acid be too small, the mixture yields crystalline flakes of acid thionurate of ammonia instead of uramilic acid; but on dissolving these in water, and evaporating with fresh sulphuric acid, uramilic acid is obtained in the purest state. — If too much sulphuric acid be used, no uramilic acid is obtained, but after exposure to the air for some time, crystals of dimorphous alloxantin [or dialuric acid?] separate out. — The sulphuric acid liquid, when evaporated, sometimes yields, before the uramilic acid, sparingly soluble white grains whose solution forms a white precipitate with baryta-water. [Can this also be dialuric acid?]

strong vitreous lustre, and by rapid crystallization, needles having a silky lustre. They redden litmus slightly, and turn red at 100°, without diminishing in weight.

	<i>Crystals.</i>		Liebig & Wöhler.		<i>Anhydrous?</i>	
16 C.....	96	32·43	32·09	16 C..... 96 33·41
5 N.....	70	23·65	23·23	5 N..... 70 24·31
10 H.....	10	3·38	3·59	9 H..... 9 3·1
15 O.....	120	40·54	41·09	14 O..... 112 39·0
$C^{16}N^5H^{10}O^{15}$ 296		 100·00 100·00		$C^{16}N^5H^9O^{14}$ 287 100·0

[Liebig & Wöhler regarded the crystals as anhydrous uramilic acid and remark that they assume a rose-colour when dried by heat, but do not sustain any perceptible loss of weight. But as they do not state the temperature at which the crystals were dried it is possible that these crystals may still contain 1 At. water, and that uramilic acid dried at a higher temperature may be $C^{16}N^5H^9O^{14}$. The calculation headed *Anhydrous* in the preceding table is founded on this supposition.]

Decompositions. 1. Uramilic acid dissolves in cold nitric acid without evolution of gas; but when boiled with strong nitric acid, it gives off nitrous fumes, and yields by evaporation, a yellow liquid which on cooling, deposits a large quantity of white crystalline scales. These scales dissolve in hot water, from which they crystallize out on cooling, and in potash-solution with yellow colour, and are precipitated therefrom by acetic acid in the form of a white powder. — 2. Uramilic acid continuously boiled with hydrochloric or dilute sulphuric acid, forms a liquid which gives a violet precipitate (of alloxantin) with baryta-water, and on cooling deposits crystals of dimorphous alloxantin. [It appears certain from Gregory's experiments that dialuric acid is here produced, and is partially converted into alloxantin by the action of the air.]



Combinations. The acid dissolves in 6 or 8 pts. of cold and in 3 pts. of hot water.

It dissolves in oil of vitriol without blackening or evolution of gas.

With the more soluble alkalis, it forms crystallizable salts which are precipitated by acetic acid.

With baryta or lime salts it produces, on addition of ammonia, a thick white precipitate soluble in a large quantity of water.

With nitrate of silver it forms, on addition of ammonia, a thick white precipitate containing about 63·9 to 64·3 p. c. silver. (Liebig & Wöhler) [This is about 4 At. silver to 1 At. acid = $2AgO, C^{16}N^5H^7Ag^2O^{14}$.]

Purpuric Acid.



SCHÉELE. *Opusc.* 2, 74.

BERGMAN. *Opusc.* 4, 390.

PEARSON. *Scher. J.* 1, 48.

REINECKE. *Crell. Ann.* 1800, 2, 94.

W. HENRY. *Ann. Phil.* 2, 57.

VAUQUELIN. *J. Phys.* 88, 458. — *Mém. du Mus.* 7, 253.

PROUT. *Ann. Chim. Phys.* 11, 48. — *Ann. Phil.* 14, 363. — *Lond. Med. Gazette*, 1831, June; also *Froriep's Notizen*, 32, 23.

KODWEISS. *Pogg.* 19, 12.

LIEBIG & WÖHLER. *Ann. Pharm.* 26, 319.

FRITZSCHE. *J. pr. Chem.* 16, 380; 17, 42.

Purpursäure, Acide purpurique. — Scheele, in 1776, showed that the solution of uric acid in nitric acid reddens the skin, and leaves a deep red residue when evaporated. Prout, in 1818, obtained the colouring principle of this solution in the form of a crystalline substance, which he regarded as purpurate of ammonia, and from which he succeeded in preparing several other red purpurates by double decomposition. But he erred in regarding the colourless substance, murexan, separated from purpurate of ammonia by sulphuric acid, as pure purpuric acid, inasmuch as Liebig & Wöhler afterwards showed that further decomposition takes place in this process, and that murexan no longer forms red salts with bases. On the other hand, the view to which these chemists give the preference, that Prout's purpurate of ammonia is not a common ammoniacal salt, but an amide, to which they give the name *Murexid*, does not appear to be well founded; since this body gives off ammonia, even when treated with cold potash, and moreover the other purpurates exhibit equally conspicuous colours.

Purpuric acid is not known in the free state, but only in its salts, in the decomposition of which by stronger acids, the separated purpuric acid is resolved into other products, the principal of which is murexan.

Probable Calculation of Purpuric Acid.

16 C	96	35.96
5 N	70	26.22
5 H	5	1.87
12 O	96	35.95

$C^{16}N^5H^5O^{12}$ 267 100.00

The formula of the *normal purpurates* is $C^{14}N^6H^4MO^{13}$ (according to Fritzsche, $C^{16}N^6H^4MO^{11}$); these salts are distinguished by a splendid purple colour, and the light reflected from some of their crystalline faces exhibits the metallic yellowish green colour of the golden beetle. Some of the basic purpurates are indigo or violet coloured.

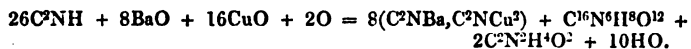
Purpurate of Ammonia. — Liebig & Wöhler's *Murexid*. — *Formation.* — By heating dialurate of ammonia (p. 157); by the action of the galvanic current upon aqueous alloxan (p. 174); by the oxidation of uramil by oxide of silver or mercuric oxide (p. 179); by the oxidation of uramil dissolved in ammonia on exposure to the air; by mixing uramil dissolved in aqueous ammonia with alloxan (p. 180); by the action of ammonia upon alloxantin (p. 189); by exposing an ammoniacal solution of murexan to the air (p. 204).

A solution of uric acid in dilute nitric acid, since it contains alloxan and alloxantin, likewise yields purpurate of ammonia on addition of ammonia (Liebig & Wöhler). [As this solution likewise contains nitrate of ammonia, and since a solution of alloxantin evaporated with this salt leaves a purple stain, we have an explanation of the purple residue which remains when the uric acid solution is evaporated in a capsule, and like-

inasmuch as the skin already contains ammoniacal salts. — The reddening of the skin produced by an aqueous solution of alloxan is perhaps due to a transformation of the alloxan into alloxantin by the hydrogenizing action of the skin.

Even when uric acid is decomposed by aqueous chlorine or iodine instead of nitric acid, the solution, probably because it likewise contains alloxantin, exhibits the purple colour on evaporation or on addition of ammonia.

In the preparation of cuprocyanide of barium from aqueous hydrocyanic acid, baryta, and carbonate of copper (viii. 7), the red solution, when left to evaporate, often yielded crystals having the colour of the wings of cantharides; the same liquid also gave with dilute hydrochloric acid, a dark violet precipitate of purpurate of copper, the formation of which was attended with evolution of hydrocyanic acid (Meillet, *N. J. Pharm.* 3, 445). [If murexid or any other compound of purpuric acid is really produced in this reaction, such a mode of formation may perhaps be explained by the following somewhat complicated equation, which however presupposes access of air and simultaneous formation of urea:



Preparation. A. From Uric acid and Nitric acid. — It is essential that the nitric acid solution contain in addition to alloxan an excess of alloxantin. (Liebig & Wöhler.) — 1. Uric acid is dissolved in dilute nitric acid, the liquid neutralized with ammonia, and slowly evaporated, whereupon it assumes a continually deeper red colour, and deposits dark red crystalline grains of purpurate of ammonia. (Prout.)

2. A perfectly saturated solution of uric acid in dilute nitric acid is evaporated; the large colourless crystals of alloxan [containing alloxantin?] which form on cooling, dissolved in boiling water; ammonia added to the boiling hot liquid, just to the point at which it produces a deep red colour (with too little or too much ammonia the process fails); and the purpurate of ammonia left to crystallize by cooling. (Prout.)

3. Nitric acid, diluted with half its quantity of water, is added to a mixture of 1 pt. uric acid and 10 pts. water contained in a capacious vessel, till only a small quantity of uric acid remains undissolved; the yellowish filtrate (which does not turn red on addition of ammonia, unless the boiling has been too long continued), evaporated down to 8 pts.; and ammonia then added; whereupon a dark red thickish liquid is obtained, which, on cooling, deposits crystals of purpurate of ammonia. (Kodweiss.)

4. One pt. of uric acid is boiled in a porcelain basin, with 32 pts. of water, and nitric acid of sp. gr. 1.425 diluted with a double quantity of water, added in small portions, waiting each time for the violent effervescence to subside, and continuing the additions till all the uric acid is dissolved; the liquid then boiled for a while with the residue; filtered; evaporated till it acquires the colour of onions (and till samples of it, mixed with ammonia, no longer produce turbidity and a red powder, but not till they form with ammonia a yellow gummy precipitate, in which case the liquid must be treated with sulphuretted hydrogen before the ammonia is added to it: *Liebig*); cooled exactly to 70°; dilute ammonia added till it appears by its odour to be in slight excess (if the liquid is

too hot, the purpurate of ammonia is decomposed by the excess of ammonia); and the purple mixture left to cool, whereupon it deposits crystals of purpurate of ammonia, generally mixed with red flakes of uramil, from which they may be freed by cold dilute ammonia. If the liquid was too cool when the ammonia was added, it must be diluted with an equal volume of boiling water: the crystals then separate more slowly, but with greater beauty. (Liebig & Wöhler.)

5. Uric acid is dissolved in strong, non-fuming nitric acid, as in Liebig & Wöhler's process for the preparation of alloxan; the great excess of acid partly neutralized during the heating, by addition of ammonia, till the liquid has assumed a slight purple-red colour; carbonate of ammonia then dropt in, when the temperature is near the boiling point, till the liquid, which then becomes dark red and turbid from admixture of the crystalline powder of purpurate of ammonia, smells faintly of ammonia; the vessel then quickly removed from the fire; the liquid after cooling decanted from the precipitate; and the precipitate washed with cold water, first by decantation and afterwards on the filter, till the wash-water exhibits a pure purple colour. So long as there is any mother-liquor still present, very little of the murexid dissolves in the water. (Fritzsche.)

B. From Alloxantin, Alloxan, Uramil. — 1. Carbonate of ammonia gradually added to a solution of pure alloxan concentrated at a temperature near the boiling point, causes it to assume a purple colour, continually deepening in intensity, and produces a precipitate of purpurate of ammonia; for the rest, the process is conducted as in A 5. (Fritzsche.) [Without alloxantin the liquid merely becomes slightly red.]

2. One pt. of alloxantin and 2·7 pts. of octo-hydrated alloxan are dissolved in boiling water, and the liquid, after cooling to 70°; neutralized with carbonate of ammonia, which must be added quickly, so that no red powder may be formed, and not in excess, because too much ammonia interferes with the formation of purpurate of ammonia. (Liebig, *Chem. org.* 1, 232.) — In this manner a deep purple mixture is obtained, which, on cooling, deposits a large quantity of crystals of purpurate of ammonia, whereas if the alloxan be left out, only a moderate reddening takes place; but instead of the alloxan, acid malate of ammonia may be used with an almost equally good result.

3. To a hot solution of 4 pts. of alloxantin and 7 pts. octohydrated alloxan in 240 pts. water, 80 pts. of a solution of carbonate of ammonia, saturated in the cold are added. A deep purple-red mixture is then obtained, which, on cooling, deposits gold-green crystals. (Gregory, *J. pr. Chem.* 22, 374; also *Ann. Pharm.* 33, 334.)

In one experiment, in which the mixture was stirred with a glass-rod, Gregory obtained instead of the crystals, a red powder which dissolved immediately with deep purple colour in dilute ammonia, and was therefore different from the ordinary salt.

4. One pt. of uramil and 1 pt. of mercuric oxide are dissolved in 30 to 40 pts. of water, a few drops of ammonia added; the liquid gradually heated to the boiling point, kept boiling for a few minutes, during which it acquires a deep purple colour and becomes thickish, and filtered boiling hot; (any uramil that may remain on the filter is treated as above with small quantities of fresh mercuric oxide and ammonia): the liquid on cooling yields crystals, the quantity of which may be increased by adding carbonate of ammonia when it is nearly cool. (Liebig & Wöhler.)

the ammonia and the alkaline reaction is nearly neutralized, after which the liquid is left to cool. (Liebig.)

6. Purpurate of ammonia may also be obtained when the mother-liquor obtained in the preparation of mycomelate of ammonia, and containing alloxanate of ammonia, is evaporated to expel the free ammonia, and an excess of alloxan then dissolved in it. (Liebig.)

7. Finely pounded alloxantin is heated in a flask over the water-bath, and dry ammoniacal gas made to stream upon it for a long time through a tube going deep into the flask, while a second tube passing through the cork carries off the excess of ammonia, together with the vapour of water; the brown-red mass, several times finely pulverized and ammoniacal gas again made to act upon it; all the free ammonia which, on addition of water, would exert a decomposing action, carefully removed by a current of air; the mass dissolved in the smallest possible quantity of hot water; the deep purple solution cooled to the crystallizing point; and an additional quantity of crystals obtained by rapidly evaporating and cooling the mother-liquor. (Gm.)

Properties. The salt dried at 100°; presents the appearance of a deep brown-red powder. (Kodweiss, Gm.) The crystallized salt (containing 2 At. water,) forms transparent, flat, four-sided prisms, according to Vauquelin, four-sided tables or four-sided prisms, either obliquely truncated with one face, or bevelled with two faces), which are garnet-coloured by transmitted light, but by reflected light exhibit, on the two broader-side-faces, a shining green colour, (gold-green, according to Kodweiss, like the wing-cases of the golden beetle, according to Liebig and Wöhler,) and on the narrow side-faces a red-brown, or in stronger light a greenish colour. (Prout.) The red powder of the crystals acquires, under the burnisher, a green colour and metallic lustre. (Liebig & Wöhler.) The salt is inodorous, and has a sweetish taste. (Prout.) [The statement of Kodweiss that the salt reddens litmus strongly, may perhaps be founded on an error arising from the red colour of the solution; it appears rather to redden turmeric.]

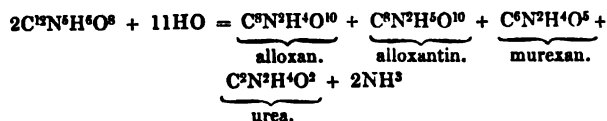
The crystals give off partially at 50°, and completely at 100°, or in vacuo over oil of vitriol, 6.54 p. c. (2 At.) water. (Fritzsche.)

				Kodweiss at 100°.	Liebig & Wöhler.	Liebig.	Fritzsche at 100°.
16 C	96	33.80	33.80	38.96	34.08	34.4	34.93
6 N	84	29.58	29.58	36.34	32.90	31.8	30.80
8 H	8	2.82	2.82	2.70	3.00	3.0	2.83
12 O	96	33.80	33.80	22.00	30.02	30.8	31.44
$C^{16}N^6H^8O^{12}$	284	100.00	100.00	100.00	100.00	100.0	100.00

Liebig & Wöhler observe that the air-dried crystals give off 3 or 4 p. c. when dried by heat; but they do not state in what condition of dryness the salt was analysed; neither does Liebig (*Chim. Org.* 1, 231). Liebig & Wöhler's formula is: $C^{16}N^6H^8O^8$; Fritzsche's: $C^{16}N^6H^8O^{11}$; Kodweiss's: $C^{10}N^4H^4O^8$.

Decompositions. 1. When two cups connected by asbestos are brought into the galvanic circuit, the positive cup containing water, and the negative cup an aqueous solution of purpurate of ammonia, this solution becomes alkaline, and of a brighter red colour, while the water in the positive cup remains colourless, and takes up a crystallizable acid, which forms a colourless salt with ammonia, and does not precipitate

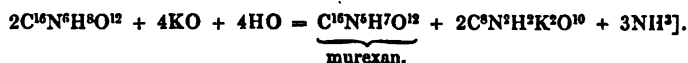
lead or silver-salts. (Lassaigne, *Ann. Chim. Phys.* 22, 332; also *Sci.* 39, 381.) The solution of the salt is instantly decolorized by chlorine. (Vauquelin.) — 3. The salt dissolves in gently heated oil of vitriol without evolution of gas, and forms a saffron-coloured liquid, from which water throws down a yellowish-white gelatinous mass, which dissolves with red colour in heated ammonia [with access of air?]. With boiling oil of vitriol, the salt forms, with evolution of carbonic and a small quantity of sulphurous acid, a brown solution which is not precipitated by water. (Kodweiss.) — 4. Dilute hydrochloric or sulphuric acid decomposes the salt, with separation of purpuric acid. (Prout.) — Not purpuric acid, but murexan. (Liebig & Wöhler.) — Gently heated sulphuric, hydrochloric, or nitric acid, converts the crystals of purpurate of ammonia into yellowish-white laminae, having a silky lustre. (Kodweiss.) The liquid above the precipitated murexan contains alloxan, alloxantin, urea, and ammonia. The quantity of murexan thus precipitated varies from 30 to 46 per cent. (Liebig & Wöhler):



(Liebig & Wöhler. [According to this equation, however, purpurate of ammonia could not yield so much as 46 per cent. of murexan. For this reason, the following equation is preferable:



This equation does not account for the presence of alloxantin and urea, which however might be formed by the action of the hot acid on the alloxan (p. 174).] — 5. The salt dissolves in potash, with evolution of ammonia, and forms a dark violet-coloured liquid (splendid indigo-blue, according to Liebig & Wöhler), from which, by long standing, if the potash is not in too great excess, small dark red crystals are deposited, containing potash and ammonia. The solution heated with excess of potash, becomes decolorised, and gives off a large quantity of ammonia, after which sulphuric acid throws down yellowish-white murexan, having a silky lustre. (Kodweiss.) The supernatant liquid contains alloxanic acid (Liebig & Wöhler). [With a small quantity of potash it is probable that a mixture of purpurate of ammonia and potash separates out; with excess of potash, the following equation is perhaps admissible:



6. The purple solution of the salt in pure water keeps for weeks in well-closed bottles perfectly filled with it; but if a little ammonia be added, it becomes decolorised, when left over night, with deposition of white flakes; and the supernatant liquid forms with chloride of calcium a precipitate (of alloxanate of lime?) soluble in acetic acid. At 80°, this decoloration by ammonia takes place even in a quarter of an hour. (Gm.) — 7. When the crystals are boiled for some time with a quantity of water not sufficient to dissolve them, they lose their colour, and the

When the aqueous solution is evaporated to dryness, the purpurate of ammonia is found to be for the most part unaltered, but mixed with a reddish-yellow substance which remains behind on digesting the residue in water. The aqueous solution, when exposed to the air, does not lose its colour for several weeks at ordinary temperatures, but is decolorised in a few days when heated; it does not absorb oxygen from the air, or, at all events absorbs it very slowly. (Gm.) The saturated solution is decolorised very slowly by exposure to light, the dilute solution very quickly; the red colour is restored each time the solution is evaporated, but becomes continually weaker. (Vauquelin.)—8. The purple aqueous solution of the salt is gradually decolorised by sulphuretted hydrogen, with precipitation of sulphur, and on subsequently evaporating the liquid, a yellowish salt remains. (Vauquelin.) The solution decolorised by sulphuretted hydrogen, deposits white silky-lustrous laminæ, which when heated with ammonia [in contact with the air?] dissolve, and form a dark red solution which again yields crystals of purpurate of ammonia. But when the solution is heated for a longer time, light red gelatinous flakes are deposited, which after some time unite into light red crystalline nodules. (Kodweiss.)—The silky-lustrous laminæ mixed with sulphur, which are precipitated by sulphuretted hydrogen, consist of murexan, and the supernatant liquid contains alloxantin and dialuric acid, which were perhaps produced by the sulphuretted hydrogen from the alloxan formed at the beginning of the action. (Liebig & Wöhler.) Hydrosulphate of ammonia is not formed in this process. (Liebig, *Ann. Pharm.* 33, 120.) [This reaction may perhaps be represented by the equation :



the decolorised liquid does not however contain free ammonia, but on the contrary reddens litmus slightly. This reaction requires therefore further elucidation.]

Combinations. Purpurate of ammonia dissolves with splendid purple colour in 1500 pts. of water (3000 according to Vauquelin) at 15°, and in a much smaller quantity of hot water, whence it crystallizes on cooling (Prout.) The purple colour changes to violet on addition of potash. A solution containing only 1 pt. of the salt in 30,000 pts. of water has still a bright purple colour. (Vauquelin.) It is not perceptibly soluble in water saturated with carbonate of ammonia. (Liebig & Wöhler.) It dissolves readily and without decomposition in strong acetic acid. (Kodweiss.) [It is insoluble in glacial acetic acid, and the solution in concentrated acetic acid becomes decolorised in a few hours]. It is insoluble in alcohol and ether. (Prout, Kodweiss.)

Purpurate of Potash.—*a. Basic.*—The indigo-coloured solution of purpurate of ammonia in cold potash-ley deposits a thick blue liquid on addition of alcohol. (Fritzsche.)

b. Normal. 1. The aqueous solution of purpurate of ammonia, saturated at a boiling heat, and mixed with bicarbonate of potash, deposits, when quickly cooled, a dark brown-red powder, and by slow cooling, crystals which exhibit the red and green colour like the ammonia-salt, and dissolve in water much more readily than that salt. (Prout.)—2. The ammonia-salt mixed with excess of nitrate of potash, in concentrated solutions, yields a brown-red crystalline powder, which

may be freed by boiling with nitre from any ammonia-salt that may remain mixed with it, and obtained by recrystallization, in larger crystals resembling the ammonia-salt in lustre and colour, but darker. The crystals, after drying at 100°, give off 3.04 p. c. (1 At.) water at 300°, and when heated above 300°, yield a white sublimate, sparingly soluble in water. The crystals are but slightly soluble in water, still less in solutions of nitre and other salts. (Fritzsche.)—3. A saturated solution of uramil in cold potash-ley assumes a deep purple colour on exposure to the air, and deposits gold-green prisms containing potash, which are very much like purpurate of ammonia, but harder. (Liebig & Wöhler, p 179.)

	Dried at 300°.		Fritzsche.
KO.....	47.2	15.47	15.48
16 C.....	96.0	31.46	31.22
5 N.....	70.0	22.93	24.05
4 H.....	4.0	1.31	1.33
11 O.....	88.0	28.83	27.92
<hr/>			
C ¹⁶ N ⁵ H ⁴ KO ¹³	305.2	100.00	100.00

Purpurate of Soda.—Prepared like the potash-salt (1). Dark brick-red. Dissolves in 3000 pts. water at 15°. (Prout.)

Purpurate of Baryta.—Obtained by precipitating the ammonia-salt with acetate of baryta. Dark green powder, which dissolves very sparingly in water, forming a purple solution. (Prout, Kodweiss.) The black-green crystalline meal becomes dark purple-red when triturated. After drying in the air, it gives off 8.78 p. c. [somewhat more than 3 At.] water at 100°, but no more at 250°. By trituration with baryta-water it is converted into violet flakes, apparently consisting of the basic salt, and very much like the precipitate which baryta-water forms with aqueous alloxantin. (Fritzsche.)

	Dried at 100°.		Fritzsche.
BaO.....	76.6	22.89	21.96
16 C.....	96.0	28.69	27.98
5 N.....	70.0	20.92	
4 H.....	4.0	1.20	1.72
11 O.....	88.0	26.30	
<hr/>			
C ¹⁶ N ⁵ H ⁴ BaO ¹³	334.6	100.00	

The salt, after drying at 100°, probably retains a certain portion of water, but certainly not 2 At. as supposed by Fritzsche.

Purpurate of Strontia.—Obtained in like manner with nitrate of strontia. Dark red-brown powder with a slight greenish tinge. Sparingly soluble with purple colour in water. (Prout.)

Purpurate of Lime.—By precipitation of chloride of calcium.—Greenish-brown powder, less soluble than the baryta and strontia salts in cold water, somewhat more soluble, and with purple colour in hot water. (Prout.)

Purpurate of Magnesia.—Very soluble, with purple colour. (Prout.)
A mixture of aqueous purpurate of ammonia and alum gradually loses its colour and deposits a small quantity of a white substance. (Prout.)

precipitate, together with iridescent films on the surface of the mixture. (Prout.)

With *Protochloride of Tin* it forms a scarlet mixture which subsequently loses its colour, and after a few hours deposits pearl-white crystals of a tin-salt.

Purpurate of Lead. — The aqueous ammonia-salt forms a rose-coloured mixture with nitrate of lead. (Prout.) With neutral acetate of lead it yields immediately 120 p. c. and on evaporation 44 p. c. more (164 in all), of a red precipitate, which contains 60 per cent. of oxide of lead, and turns yellow on the surface when exposed to the sun. (Vauquelin.) — It forms with neutral acetate of lead a purple-red precipitate containing ammonia, and somewhat soluble in water. When filtered from these, it deposits, after long standing, a loosely coherent substance of light purple-red colour, while the mother-liquid filtered therefrom still remains coloured. — *a.* The light purple-red substance, which may be washed with cold water without great loss, contains, when dried at 100°, 48.00 p. c. PbO, 17.5 C, and 1.34 H, and may be regarded as a basic salt containing acetic acid. It abstracts carbonic acid from the air, and is converted, by trituration with a few drops of nitric acid, into a dark purple crystalline powder, which is probably the *neutral salt*. — *b.* The coloured mother-liquor forms with ammonia, thick violet-flakes, which contain more than 75.00 p. c. PbO, 8.46 C, and 0.42 H, likewise absorb carbonic acid from the air, and appear also to contain acetic acid. (Fritzsche.)

The aqueous ammonia-salt forms with *ferrous sulphate* a clear, yellowish-red mixture (brownish-yellow according to Vauquelin); with acetate of *cobalt* after a while, red crystalline grains; with nitrate of *nickel* a clear greenish mixture; with *cupric* nitrate or acetate, a clear yellowish-green mixture; with *mercurous* nitrate, a purple, and with *mercuric* chloride, after a while, a pale rose-coloured precipitate. (Prout.) The precipitate formed by mercuric chloride is not decolorised either by light or by acids. (Vauquelin.)

Purpurate of Silver. — *a. Basic.* — A solution of nitrate of silver mixed with ammonia forms with aqueous purpurate of ammonia, thick violet-flakes, which, after washing, dry up to a friable mass, exhibiting a shining fracture. This mass when heated to 200°, is suddenly decomposed through and through, yielding a white sublimate very sparingly soluble in water, and perhaps identical with the sublimate obtained from the potash-salt, — and leaving a tumefied mass resembling coke. (Fritzsche.) Vauquelin likewise obtained dark violet-flakes by precipitation from perfectly neutral [possibly alkaline?] liquids.

b. Normal. — Purpurate of ammonia dissolved in warm water forms with nitrate of silver a dark purple-red precipitate (Prout) containing ammonia and somewhat soluble in water. (Kodweiss.) If the solutions are too much concentrated, a small quantity of the ammonia-salt may be thrown down by the nitrate of silver, together with the purpurate of silver, in which case a fine powder of a light purple-red colour will be obtained. But if the solutions mixed are moderately dilute, and if the silver-solution is previously acidulated with a few drops of nitric acid, which prevents the precipitation of salt *a*, and not added in too great

excess, the mixture becomes turbid in a few minutes and deposits crystals which resemble the ammonia-salt, but do not exhibit so bright a green colour. The air-dried crystals give off 5.71 p. c. [rather more than 2 At.] water at 100°, and then nothing more at 250°. (Fritzsche.)—The silver-salt may also be obtained by nearly neutralizing with ammonia a solution of 1 pt. uric acid in 2 pts. nitric acid of 34° Bm. and 2 pts. of water, precipitating with nitrate of silver, and washing the purple-red precipitate by decantation with cold water, in which it is somewhat soluble. (Vauquelin.) The dark purple-red crystals are not decolorized by exposure to light. They detonate when slightly heated, with sharp noise and emission of fumes, but without light, giving off carbonic acid gas, cyanogen, and a small quantity of aqueous vapour, and leave spongy silver, with a small quantity of charcoal. Even after being warmed with solution of potash (which extracts no nitric acid), and then washed and dried, they still detonate when heated. (Vauquelin.)

	<i>Dried at 130°.</i>		<i>Fritzsche.</i>
16 C	96	25.67	25.75
5 N	70	18.72	19.03
4 H	4	1.07	1.31
Ag	108	28.87	28.61
12 O	96	25.67	25.30
$C^{16}N^5H^4AgO^{12}$	374	100.00	100.00

When purpurate of silver is decomposed by a quantity of dilute hydrochloric acid far from sufficient to decompose it completely, a red liquid is obtained, which, when carefully heated, yields white crystals free from silver, and a few red crystals of smaller size containing that metal. This mass, when dissolved in water, leaves a rose-coloured residue which detonates with red sparks when heated, and when exploded in a glass tube, yields silver and charcoal, together with a white, acid sublimate. — The aqueous solution again evaporated, yields whitish, non-deliquescent, very sour, four-sided prisms free from silver (which swell up in the fire, exhaling a strong odour of hydrocyanate of ammonia, dissolve readily in water, and form with ammonia, a colourless compound which produces with silver-solution, a white curdy precipitate soluble in nitric acid) and yellowish deliquescent crystals containing silver. (Vauquelin.)

Purpurate of ammonia forms a yellowish precipitate with terchloride of gold and scarlet with bichloride of platinum. (Prout.)

Appendix to Purpuric Acid.

1. Rosacic Acid.

PROUST. *Ann. Chim.* 49, 162; also *Scher. J.* 7, 11. — *A. Gehl.* 3, 332. — VAUQUELIN, *J. Phys.* 73, 157; *Bull. Pharm.* 3, 416. — A. VOGEL, *Schw.* 11, 401; PROUT, *Schw.* 28, 184. — FROMHERZ & GUGERT, *Schw.* 50, 199.

Rosige Säure, rosenfarbene Säure, Acide rosacique. — First distinguished by Prout as the red colouring principle in the *brick-red deposit* or *Sedimentum latericum*, often produced in the critical urine in hot and cold

purpurate of ammonia or potash; for since, as he found, the brick-red deposit likewise contains nitric acid, it is possible that purpuric acid may be formed by the action of this acid upon the uric acid. It is true that the solubility of rosacic acid in alcohol, and certain other of its properties, are unfavourable to this view; but as the acid has not yet been obtained in the pure state, it is scarcely possible to arrive at any definite conclusion respecting it. — A flannel waistcoat which had been worn for five months by a patient suffering from intermittent fever, exhibited a deep red colour under the armpits, and yielded its red principle, not to water but to boiling alcohol or to potash-solution; on evaporating the alcohol, this substance was left in the form of a brick-red powder, and on mixing the potash-solution with sulphuric acid, it was precipitated as a red powder. (Landerer, *Repert.* 55, 234.)

Preparation. The red crystalline *Sedimentum latericium* deposited from the critical fever-urine, and consisting of rosacic acid, uric acid, mucus, and phosphate of lime, is washed with cold water, and boiled either with alcohol or with water, which liquids dissolve scarcely anything but the rosacic acid. The liquids are evaporated, after the greater part of the uric acid dissolved in the aqueous decoction has been separated out by cooling. (Proust, Vogel.) As the *sediment* likewise contains urate of soda, which dissolves more readily in water, it is better to boil with alcohol than with water; but even in that case, a small quantity of urate of soda remains mixed with the preparation. (Fromherz & Gugert.)

Properties. Bright scarlet powder; inodorous, has a faint taste; reddens litmus.

Decompositions. Impure rosacic acid thrown on red-hot coals exhales a pungent odour, but without the peculiar empyreumatic character of animal substances. (Proust.) — In chlorine gas it immediately assumes a yellow colour. (A. Vogel.) — It is quickly decomposed by strong nitric acid, with intumescence and formation of nitrous gas, and is converted into a yellow mass, which leaves red scales when volatilized, like uric acid treated with nitric acid. (A. Vogel.) — It dissolves quietly in oil of vitriol, forming a liquid which is first rose-coloured, then dark red, and from which a small quantity of water or alcohol throws down uric acid in the form of a white powder, destroying at the same time the colour of the liquid. With oil of vitriol diluted with 3 pts. of water, rosacic acid first assumes a beautiful red colour, and, after a few days, deposits a white powder exhibiting the characters of uric acid. (Vogel.) — Hydrochloric acid imparts a slight yellowish tint to rosacic acid, but only after some time. Aqueous sulphurous acid colours it deep carmine-red. (A. Vogel.) — The acid dissolved in water, turns yellow on the addition of mineral acids, and deposits a small quantity of uric acid. (Fromherz & Gugert.) — The red powder immersed in sulphuretted hydrogen water, disappears in a few months, giving off a putrid ammoniacal odour. (A. Vogel.) — Strong solution of potash imparts a brownish-yellow colour to rosacic acid, with considerable evolution of ammonia; acids then separate it from the potash with yellowish colour. (A. Vogel.) — With aqueous ammonia it forms, after a few hours, a yellowish powder, which

dissolves in water somewhat more readily than the free acid, and is reprecipitated on addition of an acid. (A. Vogel.)—Ammonia, potash, or baryta imparts a yellow colour to the aqueous solution. (Fromherz & Gugert. The entire sediment dissolves in potash, forming a dark green solution with reddish iridescence, and acids reprecipitate the rose-coloured substance, decolorizing the liquid at the same time. (Vauquelin.)—Nitrate of silver changes the red colour of the powder to green in a few hours. (A. Vogel.)

Rosacic acid dissolves pretty easily in water. The solution forms a pale rose-coloured precipitate with neutral acetate of lead. (Prout.) It forms a rose-coloured precipitate with acetate of lead, reddish-yellow with mercurous nitrate, and flesh-coloured with nitrate of silver. (Fromherz & Gugert.)

With uric acid it forms a red compound, insoluble in cold water, and decomposable only by hot water or by alcohol.

It dissolves readily in alcohol.

2. Yellow Acid formed by the Decomposition of Purpuric Acid.

When a solution of 1 pt. uric acid in 2 pts. nitric acid of 34° Bm. and 2 pts. water is precipitated with milk of lime, and the red filtrate evaporated at a gentle heat to the consistence of honey, then freed from nitrate of lime by digestion in alcohol of 40° Bm. and the brown residue thoroughly boiled with water, one-third of it then remaining undissolved, a brown solution is obtained, containing the compound of lime with a peculiar acid; and the undissolved matter consists of the same compound with excess of lime. By decomposition with oxalic acid, and evaporation, a brown-red mass is obtained, of the consistence of honey, from which, in 20 days, a large number of needles separate, united in stellate groups, less coloured, having a very sour taste, and deliquescing in the air. This acid is freed by digestion with lead-oxide and water from admixed oxuric [alloxanic] acid, which forms a soluble salt with lead, whilst a yellow lead-salt of the peculiar acid remains undissolved. This salt, when decomposed by dilute sulphuric acid, yields the pure acid, also with less colour, and the acid is obtained in a still less coloured state by decomposing the lead-salt with sulphuretted hydrogen, the colouring matter then adhering to the sulphide of lead.

The acid crystallizes indistinctly, forms yellow precipitates with protochloride of tin and acetate of lead, brown with nitrate of silver, and greyish white with mercurous nitrate. The precipitate formed with acetate of lead, disappears on heating the liquid, the lead-salt then separating in square yellow needles as the liquid cools. The lead-salt heated in a glass tube first gives off a small quantity of water, then hydrocyanate of ammonia and sublimed carbonate of ammonia, and leaves a black mass having the shape of the crystals. (Vauquelin.)

Murexan.



PROUT, (1818.) *Ann. Chim. Phys.* 11, 48. — *Ann. Phil.* 14, 363.

KODWEISS. *Pogg.* 19, 12.

LIEBIG & WÖHLER. *Ann. Pharm.* 26, 327.

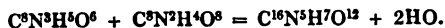
Prout's *Purpuric acid*. — Formed in the decomposition of purpurate of ammonia by the stronger acids, sulphuretted hydrogen or potash.

Preparation. 1. A solution of purpurate of ammonia in potash is boiled till it loses its colour and all the ammonia is volatilized, then gradually mixed with dilute hydrochloric or sulphuric acid, which throws down murexan in the form of a yellowish or grey powder. (Prout, Liebig, & Wöhler.) — 2. A solution of purpurate of ammonia in boiling water is mixed with sulphuric or hydrochloric acid. (Liebig & Wöhler.) When these acids are made to act directly on the crystals of murexid, the murexan obtained is more coloured. (Prout.) — The precipitated crystalline scales are purified by dissolving them in cold oil of vitriol, and gradually dropping the solution into cold water (Prout), or by dissolving in potash and precipitating with an acid. (Liebig & Wöhler.)

Properties. After precipitation from purpurate of ammonia: white, soft, nacreous, crystalline scales (Prout); often yellowish or reddish; after precipitation from oil of vitriol: snow-white powder (Prout); after precipitation from solution of potash: very loose, soft, yellowish-white powder, much heavier than water (Prout); with a silky lustre like uramil (Liebig & Wöhler). It is infusible, tasteless, and does not perceptibly redden litmus (Prout). It turns red in air, containing ammonia. (Prout, Liebig, & Wöhler.)

Calculation according to Gm.			
16 C	96	35.69
5 N	70	26.02
7 H	7	2.60
12 O	96	35.69
$\text{C}^{16}\text{N}^6\text{H}^7\text{O}^{12}$	269	100.00
Calculation according to Liebig & Wöhler.			
6 C	36	33.33
2 N	28	25.93
4 H	4	3.70
5 O	40	37.04
$\text{C}^6\text{N}^2\text{H}^4\text{O}^5$	108	100.00

Considering the great discrepancy of the two analyses, which appears to arise from the different states of purity and dryness of the murexan examined, I have assumed a formula containing C^{16} , which gives percentages intermediate between those of the two analyses, and leads to the simplest equations. If this formula be correct, murexan may be regarded as a conjugated compound of uramil and dialuric acid:



According to Kodweiss, who proposes the formula $\text{C}^{18}\text{N}^6\text{H}^6\text{O}^{12}$, murexan does not diminish in weight at 100°. According to Prout's earlier analyses, the formula should be $\text{C}^2\text{NH}^2\text{O}^2$.

Decomposition. 1. Murexan yields by dry distillation a large quantity of carbonate of ammonia, together with a little hydrocyanic acid, oily matter, and pulverulent charcoal. (Prout.) It yields cyanic acid, small quantities of hydrocyanic acid, and carbonate of ammonia, an oily substance which soon solidifies, and a small quantity of charcoal. (Kodweiss.)—2. When heated in contact with the air, it first reddens from formation of ammonia, without fusion or volatilization, and then burns without any peculiar odour. (Prout.)—It dissolves with decomposition in chlorine-water (Prout), without yielding cyanic acid. (Liebig, *Pogg.* 15, 569.)—4. It dissolves readily and with effervescence in strong nitric acid, and leaves purpurate of ammonia when evaporated. (Prout.) Strong nitric acid acts violently on murexan when heated, giving off nitrous and carbonic acid, and yielding by evaporation rhombohedrons of oxalate of murexan, surrounded by a yellow, deliquescent mass, which reddens when heated, and contains ammonia, nitric acid, oxalic acid, and murexan. (Kodweiss.)—5. Murexan, heated with oil of vitriol, gives off a large quantity of carbonic acid and a small quantity of nitrogen gas, and forms a brown solution, containing ammonia, and not precipitable by water. (Kodweiss.)—6. The colourless solution which murexan forms with aqueous ammonia, out of contact with the air, absorbs oxygen on exposure to the air, and assumes a deep purple-red colour, which gradually extends from above downwards, and when completely evaporated in the air, leaves nothing but crystals of purpurate of ammonia. (Kodweiss, Liebig, & Wöhler):



When the ammoniacal solution is left for some time in pure oxygen gas, the reddening is followed by a complete loss of colour, due to the formation of oxalurate of ammonia:



(Liebig & Wöhler.) [Should not other products be formed besides the oxaluric acid?]

Combinations. Murexan requires more than 10,000 pts. of water to dissolve it. The pale red liquid becomes slightly turbid when cool, but does not lose its colour. (Prout.)

It dissolves in cold oil of vitriol, and is precipitated therefrom without alteration by water (Prout, Kodweiss, Liebig, & Wöhler). It is not perceptibly soluble in dilute phosphoric, sulphuric, or hydrochloric acid. (Prout.)

It dissolves in warm dilute nitric acid without effervescence, and yields by slow evaporation, small rhombohedrons which appear to be *nitrate of murexan*. The crystals have a sour and astringent taste; they effloresce and turn red in the air, and become coloured when heated, giving off nitrous vapours. From their pale yellow solution in potash, sulphuric acid throws down unaltered murexan, while the filtrate yields by evaporation crystals of nitre, and leaves a deliquescent mass which turns yellow, and gives off ammonia when heated. The solution of the rhombohedrons in ammonia deposits, after a while, yellowish-white flakes, containing nitric acid, ammonia, and murexan. The crystals become dark red when heated with ammonia. Their aqueous solution forms with baryta and lime-salts, on addition of ammonia, a white gelatinous pre-

tion of ammonia, and often turns red when heated.

Murexan dissolves easily in aqueous solutions of ammonia and the fixed alkalis, without neutralizing them, and forms solutions which are colourless provided the air be excluded. (Liebig & Wöhler.)

Oxalate of Murexan? — 1. Aqueous oxalic acid containing a little nitric acid (without which no solution takes place), is saturated with murexan, and the solution crystallized by evaporation. — 2. Murexan, or its nitrate, is heated with excess of strong nitric acid, and the crystals obtained by evaporation, separated from the mother-liquor. — The first process yields six-sided prisms; the second, large rhombohedrons; the crystals are colourless. — When burnt with oxide of copper, they yield 4 vol. CO^2 to 1 vol. N. With hot oil of vitriol, they give off carbonic oxide gas. Heated and evaporated with a small quantity of potash-solution, they yield crystals of oxalate of potash, and a red deliquescent mass, which, when heated with a larger quantity of potash, gives off ammonia and turns yellow. Their solution in aqueous ammonia yields, by slow evaporation, long, slender, white needles containing oxalic acid, which turn red when heated. Their aqueous solution boiled with acetate of baryta forms a precipitate of oxalate of baryta, while the reddish filtrate contains purpurate of baryta. (Kodweiss.)

Murexan does not dissolve in alcohol or ether, or in aqueous acetic, tartaric, or citric acid. (Prout, Kodweiss.)

Primary Nucleus C^6H^{10} .

a. *Oxygen-nucleus* $\text{C}^6\text{H}^6\text{O}^4$.

Malic Acid.



SCHRELE. *Opusc.* 2, 196.

VAUQUELIN. *Ann. Chim.* 34, 127; also *Crell. Ann.* 1801, 1, 72. —

Further: *Scher. J.* 5, 291. — Further: *Ann. Chim. Phys.* 6, 237; also *Schw.* 24, 155; also *N. Tr.* 3, 1, 98.

BOUILLON LAGRANGE & A. VOGEL. *N. Gehl.* 3, 615; also *J. Pharm.* 3, 49.

DONOVAN. *Phil. Trans.* 1815, 231; also *Ann. Chim. Phys.* 1, 281.

BRACONNOT. *Ann. Chim. Phys.* 6, 239; also *Schw.* 24, 133; also *N.*

Tr. 3, 1, 111. — *Ann. Chim. Phys.* 8, 149; also *N. Tr.* 3, 1, 138; also *Repert.* 6, 207. — *Ann. Chim. Phys.* 51, 329.

DÖBEREINER. *Schw.* 26, 273; also *N. Tr.* 4, 1, 168.

A. VOGEL. *Güb.* 61, 230.

HOUTON-LABILLARDIERE. *Ann. Chim. Phys.* 8, 214; also *N. Tr.* 3, 2, 382.

TROMMSDORFF. *N. Tr.* 3, 1, 151.

LIEBIG. *Pogg.* 18, 357; also *N. Tr.* 20, 2, 146. — *Pogg.* 28, 195; also *Ann. Pharm.* 5, 141. — *Ann. Pharm.* 26, 166. — *Handwörterb.* 1, 97.

LISSAIGNE. *J. Chim. méd.* 4, 569.

PELOUZE. *Ann. Chim. Phys.* 56, 72; also *Ann. Pharm.* 11, 263; also *J. pr. Chem.* 3, 26.

RICHARDSON & MENZDORF. *Ann. Pharm.* 26, 135.

ROBERT HAGEN. *Ann. Pharm.* 38, 257.

E. LUCK. *Ann. Pharm.* 54, 112.

Aeyfelsäure, Vogelbeersäure, Spiersäure, Acide malique, Acide sorbique.

History. Malic acid was first obtained by Scheele in 1785, but not perfectly pure, and its properties were further examined by Vauquelin. Bouillon-Lagrange & Vogel showed that this acid under certain circumstances yielded acetic acid, and pronounced it to be a mixture of acetic acid and extractive matter. Donovan in 1818 obtained an acid, differing in some respects from Scheele's malic acid, which he regarded as a peculiar acid, and called *Sorbic acid* (*Vogelbeersäure*); but Braconnot in 1818 showed that this acid was nothing but malic acid in a state of greater purity. The first correct analysis of malic acid was given by Liebig.

Sources. Very widely diffused in the vegetable kingdom, together with acetic and oxalic acid. Found sometimes in the free state, sometimes combined with potash, lime, magnesia, or vegetable bases: In the root of *Althæa off.*, *Angelica Archangelica*, *Aristolochia Serpentaria*, *Arundo Donax*, *Asclepias Vincetoxicum*, *Asparagus off.*, *Berberis vulg.*, *Beta vulg.*, *Bryonia alba*, *Convolvulus Purga*, *arcensis* and *Batatas*, *Corydalis tuberosa*, *Cyperus esculentus*, *Daucus Carota*, *Glycyrrhiza glabra*, *Gypsophila Struthium*, *Helianthus tuberosus*, *Lathyrus tuberosus*, *Lobelia syphilitica*, *Nymphaea alba*, *Enanthe crocata*, *Paeonia off.*, *Polygala Senega*, *Polypodium Filix Mas*, *Primula Veris*, *Rheum*, *Rubia tinctorum*, *Rumex obtusifolius*, *Solanum tuberosum*, *Valeriana off.*; — in the wood of *Mesua ferrea*; — in the bark of *Clematis Flammula*, *Daphne Mezereum*, *Quassia Simaruba*, *Rhamnus Frangula*, *Viburnum Opulus*, *Monesia-bark*; — in the haulm (including stems) of *Achillea nobilis* and *Mullefolium*, *Agave americana*, *Aconitum Lycoctonum* and other species, *Actæa spicata*, *Artemisia vulg.*, and *Absinthium*, *Arum maculatum*, *Atropa Belladonna*, *Ballota lanata* and *nigra*, *Brassica oleracea*, *Bryonia alba*, *Calendula off.*, *Cannabis sativa*, *Cassia Senna* and *lanceolata*, *Chelidonium majus*, various species of *Cotyledon* and *Crassulæ*, *Centaurea benedicta*, *Charophyllum sylvestre*, *Convallaria majalis*, *Diosma crenata*, *Galeopsis grandiflora*, *Geranium zonale*, *Gratiola off.*, *Hyoscyamus niger*, *Hyssopus off.*, *Lactuca Sativa*, *Lychnis dioica*, *Lycopus europæus*, *Mamillaria pusilla*, various species of *Mesembryanthemum*, *Mercurialis annua*, *Morus alba*, *Papaver somniferum*, *Phormium tenax*, *Portulaca oleracea*, *Reseda luteola*, *Ricinus communis*, *Ruta graveolens*, *Saccharum officinarum*, *Salvia off.*, *Sambucus Elulus*, *Sedum acre* and *Telephium*, *Sempervivum tectorum*, *Spigelia anthelmia*, *Spinacia oleracea*, *Staphylæa pinnata*, *Syringa vulg.*, *Tanacetum vulgare*, *Thymus Serpyllum*, *Trifolium*, *Melilotus off.*, *Tropæolum majus* and *Valeriana off.*; — also, according to Garot (*N. J. Pharm.* 24, 308), in the leaves of the common ash; in the flowers of *Calendula off.*, *Matricaria Chamomilla* and *Parthenium*, *Sambucus nigra*, *Thymus serpyllum*, *Verbascum Thapsus* and *Viola odorata*; — in the pollen of *Cannabis sativa*, *Pinus Abies* and *sylvestris*, *Phœnix dactylifera*, *Typha latifolia*, and *Tulipa gesneriana*; — in the fruit of *Amygdalus persica*, *Annona triloba*, *Berberis vulgaris*, *Bromelia Ananas*, *Cornus sanguinea*, *Cucumis Melo* and *sativus*, *Cucurbita Pepo*, *Fragaria vesca*, *Musa paradisiaca*, *Prunus domestica*, and

typhinum and *copallinum*, *Ribes rubrum* and *Grossularia*, *Rosa canina*, *Rubus Idaeus* and *fruticosus*, *Sambucus nigra*, *Solanum Lycopersicum*, *mamosum*, *nigrum*, and other species, *Sorbus Aucuparia*, *Syringa vulgaris*, *Tamarandus indica*, *Vaccinium Myrtillus*, *Vitis vinifera*; — in the seed of *Anagyris foetida*, *Apium Petroselinum*, *Arachis hypogæa*, *Bariosma Tongo*, *Carum Carvi*, *Cocos nucifera*, *Cuminum Cyminum*, *Cytisus Laburnum*, *Datura Stramonium*; *Dephinsium Staphisagria*; *Illicium anisatum*, *Linum usitatissimum*, *Menispermum Cocculus*, *Myrtus Pimenta*, *Pimpinella Anisum*, *Piper nigrum* and *longum*, and in *Semen Cinæ*; — in lupulin; — in the milky juice of *Hura crepitans*; — in *asa foetida*, *opopanax*, *sagapenum*, *myrrh*, and *euphorbium*. Compare especially Scheele and Vauquelin; also Braconnot. (*Ann. Chim.* 65, 277; 70, 255.) ¶ It is also found in the decoction of *Tagetis erecta*, and in large quantity in *Ligusticum levisticum* (Dessaignes, *N. J. Pharm.* 25, 23), and in the ripe berries of *Hippophae rhamnoides* (O. L. Erdmann, *J. pr. Chem.* 55, 191): it likewise occurs abundantly, together with oxalic and saccharic acid, in the acid residue obtained in the distillation of *spirit. ætheris nitrosi* from nitric acid and alcohol.

Braconnot (*J. Phys.* 84, 276) likewise obtained from *Borago off.*, *Cochlearia off.*, *Momordica Elaterium* and *Saponaria off.*, acids which appeared to consist of impure malic acid.

The *Menispermic acid* obtained by Bonllay (*J. Pharm.* 5, 5; also *Repert.* 7, 79) from the berries of *Cocculus indicus*, appears, from his later investigations made in conjunction with Vauquelin (*J. Pharm.* 12, 108), to be malic acid.

Solanic acid, which, according to Peschier (*J. Chim. méd.* 3, 289; *N. Tr.* 14, 2, 270), occurs in all species of *Solanum*, but especially in the berries of *Solanum nigrum*, was recognized by John, Braconnot, Desfosses, Ilisch, and others, as malic acid.

Aceric acid (*Feldahornsäure*) obtained by J. A. v. Scherer from *Acer campestre*; *Stocklacksäure* by John (*Schw.* 15, 110) from stocklac, and by Esenbeck & Marquart (*Ann. Pharm.* 13, 393) from a spurious shellac; *tanacetie acid*, by Peschier (*N. Tr.* 14, 2, 175); *achilleic acid*, by Zanon (*Ann. Pharm.* 58, 31); the acid found by Braconnot (*Ann. Chim.* 62, 28), in the stems of *Phytolacca decandra*; *manihotic acid* obtained by O. Henry & Boutron-Charlard (*J. Pharm.* 20, 628; 22, 122); and *euphorbic acid*, by Riegel (*Jahrb. pr. Pharm.* 6, 165), from the flowering herb of *Euphorbia Cyparissias*. — all these acids are perhaps identical with malic acid. — ¶ According to Ritthausen (*J. pr. Chem.* 53, 413), the acid contained in *Lycopodium complanatum* is probably malic acid. — H. Schwartz (*Ann. Pharm.* 84, 83) found malic acid in unripe Silesian grapes. — Winckler (*Chem. Gaz.* 1853, 32) found in wine made from unripe grapes from the Bergstrasse, an acid possessing the physical properties of malic acid but the chemical relations of citric acid. Winckler regards this as a peculiar acid which he denominates *Paracitric acid*, Pasteur (*N. J. Pharm.* 24, 75), however, regards this acid as malic acid. Winckler, on the other hand (*N. Jahrb. Pharm.* 1, 75), persists in his opinion that it is a peculiar acid distinct from malic acid. ¶

A few other acids which have been more particularly examined, and perhaps belong to this head, will be given as an appendix to malic acid.

Formation. In the decomposition of asparagin or aspartic acid by cold nitrous acid. (Piria.) — ¶ The modification of aspartic acid, which

rotates the plane of polarisation of a ray of light, produces a malic acid possessing the same power and identical in all respects with ordinary malic acid; but the inactive modification of aspartic acid (*q. v.*) produces an inactive malic acid. (Pasteur, *N. Ann. Chim. Phys.* 34, 30.) ¶ Whether the acid which Lowitz obtained (*Crell. Ann.* 1792, 1, 222) by decomposing grape or gum-sugar with alkalis, is really malic acid, remains yet to be determined.

Preparation. I. *From the berries of the Mountain-ash.* — These likewise contain small quantities of tartaric and citric acid, especially while very unripe. (Liebig.)

1. The juice of mountain-ash berries not quite ripe, after being pressed, boiled up and filtered, is partly neutralized with carbonate of potash, leaving, however, a sufficient excess of acid to redden litmus pretty strongly; then precipitated by nitrate of lead (or with neutral acetate of lead, if carbonate of potash is not used); set aside for a few days, till the curdy precipitate is completely converted into small needles; these crystals freed from the admixed mucous or flocculent compound of lead-oxide and colouring matter (which is particularly abundant when acetate of lead is used) by careful elutriation with cold water; and lastly well washed with water. — *a.* The needles are either boiled with a quantity of dilute sulphuric acid not sufficient to decompose them, as long as any granular deposit continues to subside; the uniform pulpy mass mixed with aqueous sulphide of barium, till a filtered sample is found to contain baryta; the liquid filtered (the sulphide of lead then acting as a decolorising agent); the colourless filtrate boiled with excess of carbonate of baryta; the liquid again filtered (tartrate and citrate of baryta remaining in the filter); the baryta precipitated from the filtrate by careful addition of dilute sulphuric acid; and the filtrate, which should show no turbidity either with sulphuric acid or with chloride of barium, evaporated to the crystallizing point. If the filtrate should become turbid on addition of sulphuric acid, it must be evaporated down, the residue exhausted with alcohol; the liquid filtered from the remaining malate of baryta; and again evaporated. — *b.* Or these needles of impure malate of lead are boiled with a slight excess of dilute sulphuric acid, the filtrate divided into two equal portions; one portion exactly neutralized with ammonia; the other portion then added; and the reddish liquid evaporated and cooled; it then yields nearly colourless crystals of acid malate of ammonia, which may be rendered quite colourless by recrystallization. These crystals are then precipitated by acetate of lead, and the precipitate, after thorough washing, decomposed by sulphuretted hydrogen or sulphuric acid. (Liebig.)

2. The juice, after boiling and straining, is partially neutralized by ammonia; 72 pts. of it precipitated by 1 pt. of neutral acetate of lead; the liquid filtered after a few hours, to separate tartrate and citrate of lead and the compound of lead-oxide and colouring matter; the filtrate gradually mixed with small portions of a concentrated solution of nitrate of lead, stirring all the while, till a filtered sample is but slightly clouded by the nitrate of lead; the precipitate, which becomes crystalline, collected after a while on the filter, washed with cold water, suspended in water, and decomposed by sulphuretted hydrogen; the nearly colourless filtrate heated on the water-bath to expel sulphuretted hydrogen, neutralized with ammonia, and decolorised with bone-charcoal which has been purified by hydrochloric acid; the colourless filtrate precipitated by nitrate of lead; the precipitate well washed with cold water after it has

decomposed by sulphuretted hydrogen, the liquid being briskly agitated all the while; and the filtrate evaporated, first on the water-bath, and then at a gentle heat till it crystallizes. 22·7 pts. of mountain-ash berries yield 1 pt. of malate of lead. (Winckler, *Jahrb. pr. Pharm.* 1, 13.)

3. The filtered juice of ripe mountain-ash berries is precipitated with neutral acetate of lead, the precipitate thoroughly washed with cold water, and then treated on the filter with boiling water, as long as the wash-water continues to deposit malate of lead on cooling — The residue on the filter (which Donovan erroneously regards, not as neutral malate of lead closely aggregated and thereby rendered difficult of solution, but as basic malate), is decomposed with dilute sulphuric acid; the acid liquid precipitated with neutral acetate of lead; the precipitate again treated with boiling water, and this treatment once more repeated. — Lastly, all the crystals of the lead-salt, which, having separated from a colourless solution, are free from colouring matter, are decomposed by half an hour's boiling and constant stirring with 2·3 pts. of sulphuric acid of sp. gr. 1·09 (a quantity not sufficient to take up all the lead-oxide); the liquid filtered; the lead which is dissolved in the filtrate precipitated by sulphuretted hydrogen; and the liquid again filtered and evaporated. (Donovan.)

4. Vauquelin leaves the juice to ferment for 14 days, whereby it loses its viscosity; then precipitates it with neutral acetate of lead; boils the precipitate, consisting of malate of lead, a little phosphate, and a certain quantity of colouring matter, repeatedly with water; obtains the malate of lead in colourless crystals by repeated solution in hot water and cooling; and decomposes the crystals as in (3) by sulphuric acid and sulphuretted hydrogen.

5. Wöhler (*Pogg.* 10, 104) dilutes the juice of mountain-ash berries not quite ripe, with 3 or 4 pts. of water; filters; adds solution of acetate of lead to the liquid while in a state of ebullition as long as turbidity is thereby produced; and filters boiling hot. The filtrate immediately becomes turbid, and deposits dirty-coloured pulverulent malate of lead; the liquid decanted therefrom yields the pure salt in white needles as it cools.

6. Braconnot saturates the juice of mountain-ash berries not quite ripe with carbonate of lime, while boiling; evaporates the liquid to a syrupy consistence and skims it; separates the malate of lime which is deposited on cooling from the syrup; purifies it by washing with a small quantity of cold water and pressure between linen; boils for a quarter of an hour with an equal weight of crystallized carbonate of soda and with water; then filters the liquid containing malate of soda from the carbonate of lime, and frees it from the red colouring matter by boiling with a little milk of lime; and thus obtains a transparent and colourless filtrate, which he frees from lime by passing carbonic acid through it and precipitates with basic acetate of lead; after which he washes the malate of lead and decomposes it with sulphuric acid.

7. The juice of the unripe berries is boiled for some hours with a quantity of milk of lime not quite sufficient to neutralize it, as long as it continues to deposit malate of lime in the form of a sandy powder; this powder removed from the liquid and added, after washing with cold water, to a boiling mixture of 1 pt. nitric acid and 10 pts. water, as long as it dissolves; the hot filtrate left to cool; the nearly colourless crystals

or acid malate of lime which form, purified by recrystallization from boiling water; their hot solution precipitated by neutral acetate of lead; the precipitate, after washing with cold water, suspended in warm water and decomposed with sulphuretted hydrogen; and the filtrate evaporated, first on the open fire, then on the water-bath, to a syrup, which solidifies after some time to a crystalline mass. (Hagen.)

II. *From Houseleek.* The juice of this plant is rich in malate of lime.

1. The filtered juice of houseleek is evaporated nearly to a syrup, and gradually mixed with alcohol; the pasty mass which separates, repeatedly washed with fresh portions of weak alcohol, and dissolved in water, after being strongly pressed between linen; the brown solution mixed with a quantity of sulphuric acid sufficient only to precipitate half the lime; and the liquid separated from the gypsum by decantation and pressure. This liquid yields in 24 hours, crystals of acid malate of lime; and the supernatant mother-liquor evaporated to a syrup, yields an additional crop of crystals, first by 14 days standing in a cool place, and then by addition of alcohol, which however must be added with caution, as too large a quantity would likewise precipitate the brown colouring matter. The crystals are purified by dissolving them twice in hot water and recrystallizing; they are then again dissolved in water; the lime precipitated by sulphuric acid; the liquid filtered and digested with lead-oxide to remove the sulphuric acid; again filtered; the dissolved lead precipitated by sulphuretted hydrogen; the liquid filtered from this precipitate and evaporated to dryness; and the acid dissolved out by alcohol, which leaves small quantities of lime and lead-oxide undissolved. (Braconnot.)

2. Houton-Labillardière supersaturates houseleek juice with milk of lime; filters; evaporates down to three-fourths, whereupon a white pulverulent salt is deposited on cooling; decants the brown mother-liquor; washes the salt with alcohol of 12° to 15° Bm.; dissolves it in water; filters from the compound of lime and colouring matter; precipitates by nitrate of lead; washes the precipitate; suspends it in water; and decomposes it with sulphuretted hydrogen; then filters, and evaporates to a syrup, which yields crystals in a few days.

3. Donovan evaporates the syrup to two-thirds; mixes it, after filtration, with an equal quantity of alcohol; washes the precipitated malate of lime with alcohol; dissolves it in water; precipitates with neutral acetate of lead; and decomposes the washed precipitate as in I., 3.

When the malate of lime is precipitated by a lead salt, the resulting malate of lead contains lime, and yields malic acid, which also contains lime and therefore precipitates nitrate of lead or silver; it may be separated from the acid malate of lime (as in Braconnot's process) by evaporating to a syrup and extracting with strong alcohol. (Gay-Lussac, *Ann. Chim. Phys.* 6, 331; also *Schw.* 21, 216; also *N. Tr.* 3, 1, 95; *comp. Wackenroder, N. Br. Arch.* 25, 58.)

III. *From Cherries or Berberries.* — A. Vogel precipitates the juice with neutral acetate of lead; washes the blue precipitate with cold water; boils it repeatedly with water, the compound of lead-oxide and colouring matter then remaining undissolved; and obtains by cooling, as in Donovan's process, crystals of malate of lead, which he then decomposes by sulphuretted hydrogen.

malate of lime. After being separated from the stalks, they are repeatedly exhausted with boiling water; the red acid infusion partially evaporated; the liquid separated from the precipitate of oxidized extractive matter; the filtrate repeatedly evaporated and cooled, as long as it continues to yield brownish crystals of acid malate of lime; these crystals washed, and decolorized by recrystallization; their aqueous solution then precipitated by carbonate of potash; the filtrate precipitated by acetate of lead; the white crystalline malate of lead decomposed by sulphuretted hydrogen; and the crystallized acid obtained by evaporating the filtrate. (Trommsdorff, *Ann. Pharm.* 10, 328.)

The juice of the berries of *Rhus glabrum* or *typhinum* yields with acetate of lead a precipitate, which, when washed with cold water, recrystallized from hot water, and decomposed by sulphuretted hydrogen, immediately yields colourless crystals of the acid. (Lassaigne.)

V. *From the stems of various species of Rhubarb.* — The juice expressed from the stems and leaves of *Rheum palmatum* or *undulatum* is clarified by boiling with isinglass; then strained and evaporated to a thin syrup, which in a few days yields crystals of acid malate of potash, to be decolorized by pressure and recrystallization, and amounting to $3\frac{1}{2}$ per cent. of the stems and leaves. By precipitating this salt with acetate of lead, and decomposing the washed precipitate with sulphuretted hydrogen, very pure malic acid is obtained, which crystallizes well. (Winckler & Herberger, *Jahrb. pr. Pharm* 2, 201.) — Another mode of preparation was previously given by Th. Everitt. (*Phil. Mag. J.* 23, 327.)

VI. *From Apples.* — Apple-juice neutralized with carbonate of potash is precipitated with acetate of lead, and the washed precipitate decomposed with an equivalent quantity of dilute sulphuric acid. (Scheele.) — The acid thus obtained is a thick, brown, uncrystallizable syrup which dries up to a varnish when exposed in thin layers to a warm dry atmosphere. This inability to crystallize proceeds, according to Braconnot, from the presence of a brown substance which prevents the crystallization, not only of the acid, but also of its lead-salt. As this impure acid obtained by Scheele was formerly the only kind of malic acid known, the colourless and crystallizable acid which Donovan obtained from mountain-ash berries was regarded as a distinct acid.

The preparation of malic acid from *Artemisia Absinthium* is described by Luck.

Erdmann (*J. pr. Chem.* 55, 191) recommends the ripe berries of the sea-buckthorn (*Hippophae rhamnoides*) as a source for the preparation of malic acid.

Pure malic acid should be colourless and crystallizable; burn without residue (of potash, lime, oxide of lead, &c.); not become coloured with ammonia; and yield no precipitate with nitrate of lead or silver.

Properties. The aqueous acid evaporated to a syrup, and then left to evaporate further in a warm place, yields colourless needles or prisms united in feathery or spherical groups (Vauquelin, Braconnot, Liebig); according to A. Vogel, the crystals are six-sided; according to Winckler, four-sided. The crystals melt at 83° , but sustain a heat of 120° without diminishing in weight. (Pelouze.) They are inodorous and have a very sour taste. ¶ According to Pasteur, ordinary (optically active) malic

acid begins to melt at 100° and to decompose at 140° ; whereas optically inactive malic acid begins to melt at 133° , and to decompose at 150° . The latter crystallizes in the same manner as the ordinary acid, but more readily. (*N. Ann. Chim. Phys.* 34, 30.) ¶.

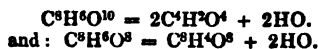
	Crystallized.		Pelouze.		Pasteur.
8 C.....	48	...	35.82	...	35.76
6 H.....	6	...	4.48	...	4.65
10 O.....	80	...	59.70	...	59.59
$C^8H^6O^4$	134	...	100.00	...	100.00

Pelouze obtained too much carbon, probably because malic acid, as Liebig has shown, gives off water at 130° .

Pasteur analysed the optically inactive malic acid obtained from inactive aspartic acid by the action of nitrous acid; the acid was crystallized and dried over sulphuric acid.

According to the radical-theory, the hyp. anhydrous acid = $C^8H^6O^4 = \bar{M}$, and the crystallized acid = $HO, C^8H^6O^4$. Prout found the hyp. anhydrous acid contained in the lead, lime or copper-salt, to consist of 40.68 p. c. C, 5.08 H and 54.24 O.

Decompositions. 1. The acid heated for some hours to between 175° and 180° in a retort placed in the oil-bath, is resolved, without any evolution of gas or carbonization, into water, maleic acid (viii. 151) which passes over in the liquid form with the water, and crystallizes soon afterwards, and about an equal quantity of fumaric acid (ix. 22), part of which distils over, while the rest remains in the retort, in the form of a crystalline mass. If the malic acid be suddenly heated to 200° , and kept for some time at that temperature, a comparatively large quantity of maleic acid is obtained; but at 150° , the malic acid is very slowly, but almost completely resolved into water and fumaric acid. The first product of the decomposition perhaps consists entirely of maleic acid, which, however, if the heat be not quickly raised to the point of volatilization, is converted into fumaric acid. (Pelouze.) Even by continued exposure to a heat of 120° to 130° , fused malic acid is converted, with turbidity and escape of water, into a pulpy mixture of fumaric acid laminæ, and undecomposed malic acid; the latter, when dissolved out by cold water, and heated as above after evaporation, again yields water and a similar mixture; and in this manner all the malic acid may be finally converted into water and fumaric acid. If the distillation be conducted as quickly as possible over a strong alcohol-flame, a large quantity of maleic acid passes over with the water, till the residue suddenly solidifies to crystalline fumaric acid. (Liebig.) — Equations for the formation of maleic and fumaric acid:



If a strong fire be made to act immediately on the malic acid, it swells up, turns brown, and yields, together with the maleic and fumaric acids, large quantities of carbonic oxide and carbonic acid gases, empyreumatic oil, and charcoal, which must be regarded as decomposition-products of the maleic and fumaric, not of the malic acid. (Lassaigne.) — 2. In the open fire, the acid burns with the odour of burnt sugar.

3. The acid in combination with potash is decomposed by bromine, with formation of bromoform. (Cahours, *N. Ann. Chim. Phys.* 19, 507.) — 4. Nitric acid easily converts it into oxalic acid, with evolution of carbonic acid. (Vauquelin) — It is not decomposed by aqueous iodic

carbonic oxide gas (Döbereiner), and at the same time forms acetic acid. (Liebig.) — 6. When heated with oil of vitriol and chromate of potash together, it gives off all its carbon in the form of carbonic acid. (Döbereiner.) — The aqueous acid does not act on peroxide of manganese. (Döbereiner.) — It is not converted into fumaric acid by boiling with strong hydrochloric acid. (Hagen.)

7. When cautiously heated with excess of potash-hydrate, it forms acetate and oxalate of potash [with evolution of hydrogen?]. (Riechter, *N. Br. Arch.* 39, 23.) — For the conversion into succinic acid, see *Malate of Lime*, pp. 216, 217.

Combinations. The crystallized acid deliquesces when exposed to the air; it dissolves in a small quantity of *water*, forming a colourless syrup; with a larger quantity, it forms a thin liquid. — The optically inactive modification is less soluble in water and less deliquescent than ordinary active malic acid. (Pasteur.)

The *Malates* are neutral = $C^6H^4M^2O^{10}$, and acid = $C^6H^2MO^{10}$. When subjected to dry distillation, they swell up, and, according to Unverdorben, give off two empyreumatic oils of different degrees of volatility. Between 250° and 300°, the malates of the fixed alkalis are converted, with loss of water, into fumarates. (Hagen.)



Nearly all malates are soluble in water. — The optically active and inactive modifications of malic acid yield respectively active and inactive malates. (Pasteur.)

MALATE OF AMMONIA. — *a. Neutral.* — Uncrystallizable, very soluble. (Braconnot.)

b. Acid. — Preparation (p. 208, 1, b). Large, transparent, colourless prisms belonging to the right prismatic system. *Fig. 75*, $y : y = 110^\circ 45'$; $y : m = 125^\circ 40'$; $m : u = 125^\circ$; $u' : u = 109^\circ 20'$; $n' : n = 138^\circ 54'$. (Nicklès; according to an epistolary communication, in which the numbers erroneously printed in the *Compt. rend.* are corrected; comp. also Kobell, *Reperit.* 71, 320.) The crystals have an agreeably acid saline taste (L. A. Buchner, *Reperit.* 71, 320); they are permanent in the air (Braconnot), and do not diminish in weight, even at 100° in a stream of dry air. (Buchner.) They dissolve very readily in water, but are insoluble in alcohol and ether (Braconnot, Buchner), and dissolve but very slowly in dilute alcohol. (Liebig.)

	<i>Crystals.</i>		<i>Buchner.</i>	
8 C	48	31.79	32.69
N	14	9.27	9.28
9 H	9	5.96	6.07
10 O	80	52.98	51.96
<hr/>				
$C^6H^4(NH^4)O^{10}$	151	100.00	100.00

Liebig also obtained by combustion of the crystals, 1 vol. nitrogen gas to 8 vol. carbonic acid.

T. According to Pasteur (*Ann. Pharm.* 82, 331), the acid ammonia-salt of ordinary (optically active) malic acid forms crystals belonging to the right prismatic system, often with hemihedral faces. Their specific

gravity compared with that of water at 12.5, is 1.5500. — Dissolves in 3.11 pts. of water at 15.7°. The solution rotates the plane of polarization of a ray of light. Heated in the oil-bath to 160°—200°, it is converted into a sparingly soluble substance, $C^8NH^4O^8 = C^8NH^7O^8 - 3HO =$ Aspartic acid *minus* water (p.).



Ammonia escapes, however, together with the water, and the residue contains fumaric and maleic acid, together with malic acid both active and inactive.

The acid ammonia-salt of inactive malic acid forms two kinds of crystals. (a) The solution when evaporated first yields crystals having the same composition as the active ammonia-salt, and the same form, with exception of the hemihedral faces, which are absent. — (b) The mother-liquor separated from these crystals deposits after a while, large, hard, transparent crystals containing 2 At. water more than the salt a, and belonging to the oblique prismatic (monoclinometric) system. They are decomposed by heat in the same manner as the active salt.

	<i>Crystallized.</i>		<i>Pasteur.</i>
8 C	48	28.40
N	14	8.28
11 H	11	6.51
12 O	96	56.81
$C^8H^8(NH^4)O^{10} + 2Aq.$	169	100.00

When the acid ammonia-salts of the two varieties of malic acid are heated in the same oil-bath, they exhibit, at temperatures differing but little from one another, the same alterations, viz loss of water and ammonia, and formation of the insoluble substance $C^8NH^4O^8$. (Pasteur.) ¶

MALATE OF POTASH. — *a. Neutral.* — Uncrystallizable, deliquescent, insoluble in strong alcohol. (Braconnot.) — *b. Acid.* — Crystals, permanent in the air, soluble in water, insoluble in alcohol (Donovan); containing in the dried state 24.3 per cent. of potash. (Döbereiner.)

MALATE OF SODA. — *a. Neutral.* — As with potash. — *b. Acid.* — Crystalline, permanent in the air, soluble in water, insoluble in alcohol. (Donovan.)

MALATE OF LITHIA. — In the neutral as well as in the acid state, it forms a syrupy uncrystallizable mass, which does not harden even in warm air. (C. G. Gmelin.)

MALATE OF BARYTA. — *a. Neutral.* — 1. The acid neutralized with baryta-water, leaves on evaporation a gummy mass, which is permanent in the air and soluble in water (Braconnot); when evaporated at a gentle heat, it yields crystalline scales, containing, after drying in the air, 2 At. water, one of which they give off at 30° and the other at 100°; they dissolve very readily in water; but on boiling the solution, the salt is deposited in the anhydrous state. (Hagen.)

2. The aqueous acid cannot be completely neutralized by boiling with excess of carbonate of baryta. (Liebig, Hagen.)

a. The acid saturated in the cold with carbonate of baryta yields by evaporation in vacuo (the quantity of acid in the mother-liquor increas-

water, and give on 10.6 p. c. water at 220 (at 100, they give on a smaller quantity and retain their solubility).

β . The saturated solution of these laminæ, and likewise malic acid saturated with carbonate of baryta, becomes turbid when boiled, and deposits a heavy crystalline meal consisting of insoluble anhydrous salt. (Richardson & Menzendorf.) The acid saturated while warm with carbonate of baryta, likewise deposits on evaporation, first, white amorphous crusts of the neutral anhydrous salt, and lastly films of a salt which has an acid reaction, and is soluble in water; the last deposited crusts of the neutral salt, on the contrary, do not dissolve either in cold or in boiling water, but readily on addition of a trace of nitric acid. (Liebig.)

			Hagen (1) at 100°.	Liebig 2, β .
2 BaO	153.2	56.91
C ⁶ H ⁴ O ⁸	116.0	43.09
<hr/>				
C ⁶ H ⁴ Ba ² O ¹⁰	269.2	100.00	
<hr/>				
Rich. & Menzendorf 2, α .				
2 BaO.....	153.2	50.19	
C ⁶ H ⁴ O ⁸	116.0	38.01	
4 HO	36.0	11.80
<hr/>				
C ⁶ H ⁴ Ba ² O ¹⁰ + 4Aq.	305.2	100.00	

The salt (1) dried at 30°, contains 54.44 p. c. baryta (therefore 1 At. water); and the air-dried salt contains 52.93 p. c. baryta (therefore 2 At. water). (Hagen.) [According to this, the salt should be different from 2, α .]

b. Acid. — Uncrystallizable, more translucent, and more soluble in water than *a*. (Braconnot.)

Braconnot formerly distinguished a *basic salt* which he stated to be deposited in white flakes on strongly supersaturating the acid with baryta-water; but, according to Lassaigne, an excess of baryta-water does not render the acid turbid; and according to Liebig, it does not produce turbidity in a solution of acid malate of ammonia; and Braconnot himself, in a later communication (*Ann. Chim. Phys.* 51, 331,) states that baryta-water does not produce turbidity in the acid.

MALATE OF STRONTIA. — *a. Neutral.* — 1. The acid is not rendered turbid by strontia-water (Lassaigne), and the mixture yields by rapid evaporation, a gum; by slow evaporation, a white translucent crystallo-granular mass; the salt is permanent in the air, and dissolves readily in water. (Braconnot.) — 2. The aqueous acid digested with carbonate of strontia, still retains the power of reddening litmus slightly, and after sufficient evaporation, deposits nodular masses. (Hagen.)

<i>Anhydrous.</i>				(2) dried at 100°.				Hagen.
2 SrO.....	104	47.27	2 SrO.....	104	43.70
C ⁶ H ⁴ O ⁸	116	52.73	C ⁶ H ⁴ O ⁸	116	48.74	
				2 HO.....	18	7.56	
<hr/>								
C ⁶ H ⁴ Sr ² O ¹⁰	220	100.00	+ 2Aq.....	238	100.00	

The air-dried salt (2) contains 41.17 p. c. strontia (Hagen).

b. Acid. — Deposited in the crystalline form on mixing the aqueous solution of the neutral salt with malic acid; does not melt in the fire; dissolves sparingly in cold, readily in hot water. (Braconnot.)

MALATE OF LIME. — *a. Neutral.* — 1. The acid does not become turbid on addition of excess of lime-water (Braconnot, *Ann. Chim. Phys.* 51, 331; Lassaigue); not even in concentrated solutions and on the application of heat, — a character by which malic is distinguished from citric acid. (H. Rose, *Pogg.* 31, 210; Winckler); according to Hagen, on the contrary, on heating the mixture [still more concentrated?] the anhydrous neutral salt is separated in the form of a granular powder. At all events there does not appear to be any *basic salt* precipitated, as was formerly supposed by Braconnot. — The acid neutralized with lime-water yields on evaporation in vacuo (an acid mother-liquor remaining) large, thin, shining laminæ, which dissolve readily in water, and after drying in vacuo at ordinary temperatures, give off all their water = 17 p. c. (4 At.) at 180°, and about half of it at 100°. Their aqueous solution, when left to evaporate in the air, again yields laminæ, but when heated to the boiling point, deposits a white, granular, nearly insoluble salt with 2 At. water. Hence the laminæ, in parting with half their water, likewise lose their solubility. (Richardson & Menzendorf, *Ann. Pharm.* 26, 135.)

2. Dilute malic acid agitated in the cold with excess of carbonate of lime, remains strongly acid; but the filtrate, when boiled, coagulates to a pulp composed of granules of the bihydrated neutral salt, which is nearly insoluble in water and in aqueous malic acid. (Richardson & Menzendorf.) Impure malic acid is not completely neutralized by digestion with excess of carbonate of lime, but with pure acid the neutralization is perfect. (Braconnot.) Even the pure acid is not completely neutralized. (Hagen.) From the solution thus obtained, the neutral salt separates in four-sided prisms, which grate between the teeth, dissolve in 83 pts. of cold and a somewhat smaller quantity of hot water (Lassaigue); or as a granular powder of anhydrous salt, which is nearly insoluble both in hot and in cold water. (Hagen.)

3. The same granular powder is thrown down from the aqueous solution of the acid salt by several hours' boiling. (Hagen.)

4. A mixture of aqueous chloride of calcium and neutral malate of soda deposits, after a while, the neutral malate of lime in transparent crystalline grains. This salt scarcely froths up in the fire; it is completely decomposed by the soluble alkaline carbonates. It dissolves in 147 pts. of cold water, forming a solution which tastes somewhat like nitre, and in at most 65 pts. of boiling water, from which it does not separate on cooling. (Braconnot.)

5. The solution of acid malate of lime, neutralized with a soluble alkaline carbonate, yields by evaporation at a gentle heat, hard shining crystals of the neutral salt, which contain 5 At. [or 6 At.] water, give off 1 [or 2] At. water at 100°, assuming the appearance of porcelain, and are completely dehydrated at 150°. (Hagen.)

6. The granular salt, left to itself in the moist state for two days, takes up water, and is converted, under circumstances not yet determined, into rough, translucent, globular crystals, which, after drying in the air, whereby they are rendered opaque, give off 22.49 p. c. (6 At.) water at 200°. (Dessaigues & Chautard, *N. J. Pharm.* 13, 243.)

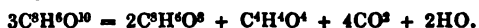
Neutral malate of lime; kept for some months under a shallow layer of water in a vessel covered with paper, is converted into succinate. (Dessaigues.) During the winter, crystallized hydrated carbonate of lime and a mucous organization are likewise produced; but in the summer months, the sole product consists of needles of succinate of lime,

quantity of gas is given off. (Dessaignes, *Compt. rend.* 28, 16.)

When a mixture of 4 pts. of malate of lime, 24 pts. of water, and 1 pt. of yeast, (or a smaller quantity of putrefying cheese or fibrin,) is set aside in a warm place, a tolerably brisk evolution of pure carbonic acid gas takes place; the muddy lime-salt begins in the course of 3 days, to become granular and heavy; and after the evolution of gas is terminated, appears under the microscope to consist of transparent needles united in stellate groups, and composed of succinate and carbonate of lime.

The supernatant liquid contains acetate of lime.

If too much yeast or cheese is used, or if the mixture becomes too hot, hydrogen gas is evolved as well as carbonic acid, and possibly in equal volume, and in that case there is obtained but little succinic and acetic, but a large quantity of butyric acid, and a colourless, volatile oil, smelling of apples, which may be obtained by distilling the liquid; this oil dissolves readily in water, and may be separated therefrom by chloride of calcium or carbonate of potash; it, however, dissolves a larger quantity of chloride of calcium in the dry state. For the fermentation in which succinic and acetic acid are produced, and pure carbonic acid is evolved, the equation is :



For the fermentation, when hydrogen is evolved :



or, if the evolution of hydrogen is subsequent to the formation of succinic acid :



[The formation of the volatile oil is not here taken into account.] — Part of the carbonic acid remains with the lime. (Liebig, *Ann. Pharm.* 70, 104, and 363.)

¶ According to E. J. Kohl (*Ann. Pharm.* 78, 252), malate of lime fermented with putrefying casein, gives off nothing but carbonic acid, and yields principally lactate of lime, with small quantities of succinate, acetate, and carbonate. W. Baer, (*Arch. Pharm.* [2], 69, 147,) obtained a similar result with the juice of mountain-ash berries, neutralized with carbonate of lime, mixed with beer-yeast, and left to stand at ordinary temperatures. — Winckler (*Jahrb. pr. Pharm.* 22, 300) found a large quantity of lactic acid in the acid residue of cider, and supposes it to have been formed by fermentation of the malate of lime contained in the juice of the apples. — Rebling (*Arch. Pharm.* [2], 67, 300) observed that, in the fermentation of malate of lime, valerianic acid is formed as well as succinic and butyric acid. ¶

		Rich. M.		Hagen	
		(1) at 200°.		(2).	
2 CaO	56	32·56	32·00	32·19	
C ⁸ H ⁶ O ⁸	116	67·44			
<hr/>					
C ⁸ H ⁴ Ca ² O ¹⁰	172	100·00			
		Rich. M.		Dess. Ch.	
		(1) at 100°.		(6) at 100°.	
2 CaO	56	29·48	31·03	30·96	
C ⁸ H ⁶ O ⁸	116	61·05			
2 HO	18	9·47			
<hr/>					
C ⁸ H ⁴ Ca ² O ¹⁰ + 2Aq.	190	100·00			

		Hagen		Rich. M.	
		(5) at 100°.		(1) air-dried.	
2 CaO	56	26·92	27·38		
$C^8H^6O^8$	116	55·77			
4 HO	36	17·31			17·00
<hr/>					
$C^8H^4Ca^2O^{10} + 4Aq.$	208	100·00			
		Hagen		Dess. Ch.	
		(5) air-dried.		(6) air-dried.	
2 CaO	56	24·78	26·11		24·56
$C^8H^6O^8$	116	51·33			
6 HO	54	23·89			22·49
<hr/>					
$C^8H^4Ca^2O + 6Aq.$	226	100·00			

The salt obtained by saturating the impure acid from apples with excess of carbonate of lime, reddens litmus slightly, dissolves readily in cold water, and is precipitated therefrom by alcohol, in the form of a greasy substance, which dries up to a varnish. (Scheele.)

¶ When a solution of inactive malic acid is neutralized with lime-water, no turbidity is produced; but on addition of alcohol, the neutral lime-salt is deposited in white amorphous flakes. On boiling the neutralized aqueous solution, a granulo-crystalline precipitate is formed, having the composition $C^8H^4Ca^2O^{10}$, and but sparingly soluble in water, either hot or cold. — When a solution of acid malate of ammonia containing the inactive acid, is mixed with a soluble lime-salt and excess of ammonia, no precipitate is formed at first, but after 24 hours, transparent crystals united in nodules are formed, containing $C^8H^4Ca^2O^{10} + 5Aq.$ (Pasteur.) ¶

b. Acid. — May be prepared from the stems of *Geranium sonale* (Braconnot). Also from the berries of *Rhus glabrum* or *copallinum*, by exhausting them with hot water, evaporating the infusion, decolorizing it with animal charcoal previously purified with hydrochloric acid, evaporating the filtrate further, setting it aside to crystallize, and purifying the resulting crystals, if necessary, by recrystallization. (Rogers, *Sill. Am.* p. 27, 294.) — The solution of the neutral salt in warm dilute nitric acid, deposits the acid salt in crystals on cooling. (Hagen.) — The clear, shining prisms and needles of this salt, which contain 8 At. water, belong to the right prismatic system. Fig. 68 without the *i*-face; $y : y = 122^\circ 18'$; $p : y = 152^\circ 13'$; $p : t = 90^\circ$; $y : u = 101^\circ 5'$; $t : u = 125^\circ 20'$; $u' : u = 129^\circ 25'$. (Nicklès, *epist. communication.*) Braconnot, Wackenroder and Rogers have given similar descriptions of the crystals, whereas Hagen obtained rhombic octohedrons. — ¶ According to Pasteur, the acid lime-salt, prepared with the optically octave (ordinary) acid often exhibits hemihedral faces; while the salt prepared with the inactive acid exhibits the same crystalline form, but without hemihedral faces. ¶ — The crystals have an agreeably acid taste (Rogers), stronger than that of cream of tartar (Braconnot). — At 100°, they give off 22·37 p. c. (nearly 6 At.) water, and at 180°, 31·06 p. c. (nearly 8 At.) in all. (Richardson & Menzendorf). When exposed for 8 days to a temperature of 100°, they give off only 19 or 20 per cent. of water, and leave a mass which draws out into threads when heated. At a somewhat higher temperature, they swell up, give off 22·53 p. c. water, and leave a transparent gum (Braconnot), which, when strongly heated, gives only pungently acid and tear-exciting vapours, becomes carbonized, with

tumefied, calcareous mass. (Rogers.) — The crystals dissolve in 50 pts. of cold water, more abundantly in hot water, and crystallize on cooling (Trommsdorff); they dissolve sparingly in water (Braconnot); abundantly (Rogers). By alcohol, which takes away the acid, they are converted into the neutral salt (Braconnot); they are insoluble in boiling 96 per cent. alcohol; boiling 70 per cent. alcohol dissolves them, leaving a white powder of salt *a*; and the solution, on cooling, yields crystals of salt *b*, while a super-acid lime-salt remains in solution. (Wackenroder.)

	Crystallized.		Braconnot.	Wackenr.	Rogers.	Hagen.
CaO	28	12.44	11.99
C ² H ² O ⁹	125	55.56	13.0
8 HO	72	32.00	12.5
<hr/>						
C ² H ² CaO ¹⁰ + 8Aq.....	225	100.00			

Hagen, from his own analysis, which however differs from all the rest, supposes the crystals to contain only 6 Aq.

Malate of Lime and Ammonia. — Obtained by combining a malate of lime containing a large excess of acid, with ammonia. Crystallizes in the form of acid malate of lime, although it contains but very little lime. (Braconnot.)

Malate of Lime and Potash. — When potash is added to a lukewarm solution of neutral malate of lime, two such compounds are formed, the one being precipitated, while the other remains in solution, and refuses to crystallize. (Braconnot.)

Malate of Lime and Soda. — Carbonate of soda scarcely produces any turbidity in a solution of acid malate of lime, even on application of heat. (Braconnot.)

MALATE OF MAGNESIA. — *a. Neutral.* — *a. Anhydrous.* — Obtained by precipitating a concentrated solution of the salt γ with absolute alcohol, washing with alcohol the thick flakes, which melt when heated into a mass that may be drawn out into threads, and drying them at 100°, (Hagen.)

	<i>a.</i>		Hagen.
2 MgO	40	25.64
C ² H ² O ⁸	116	74.36
<hr/>			
C ² H ² Mg ² O ¹⁰	156	100.00

β . With 2 At. Water. — Obtained by drying the crystals γ at 100°. (Liebig, Hagen.)

γ . With 10 At. Water. — The boiling dilute acid is saturated with magnesia, the neutral filtrate evaporated till it forms a crystalline film, and the solution left to crystallize by cooling. (Hagen.) The crystallization takes place with facility (Braconnot). The crystals are thick rhombic prisms, having a bitterish taste (Lassaigne). They are permanent in the air (Donovan); they effloresce in the air, and give off 29.5 to 30.0 p. c. (8 At.) water at 100°, but no more at higher temperatures, not even at the heat of a boiling solution of chloride of calcium. (Liebig.) They froth up in the fire; dissolve in 28 pts. of water. Donovan. — The salt of the impure acid deliquesces in the air (Scheele).

β		Liebig.	Hagen.
2 MgO	40	22·99	23·45
$C^2H^4O^3$	116	66·67	23·25
2 HO	18	10·34	

$C^2H^4Mg^2O^{10} + 2Aq.$ 174 100·00

γ		Hagen.
2 MgO	40	16·26
$C^2H^4O^3$	116	47·15
10 HO	90	36·59

$C^2H^4Mg^2O^{10} + 10Aq.$ 246 100·00

b. Acid. — Formed by half saturating the aqueous acid with carbonate of magnesia, and evaporating. — Flat prisms, which give off 2 At. water at 100° , and melt at a stronger heat. (Hagen.) Transparent gum, permanent in the air; its solution mixed with potash, yields a precipitate of *basic malate of magnesia and potash*. (Braconnot.)

<i>Dried at 100°.</i>		Hagen.
MgO	20	12·27
$C^2H^4O^3$	125	76·69
2 HO	18	11·04

$C^2H^4Mg^2O^{10} + 2Aq.$ 163 100·00

<i>Crystallized.</i>		Hagen.
MgO	20	11·05
$C^2H^4O^3$	125	69·06
4 HO	36	19·89

$C^2H^4Mg^2O^{10} + 4Aq.$ 181 100·00

MALATE OF YTTRIA. — 1. When an aqueous solution of malic acid is poured upon carbonate of yttria, part of the resulting salt dissolves, and is obtained by evaporation in small white nodules. — 2. Neutral alkaline malates throw down from yttria-salts — when the solutions of the two salts are concentrated and mixed in due proportion — a white, almost crystalline powder, which remains in white granules when its aqueous solution is evaporated. — The air-dried salt is $C^2H^4Y^2O^{10} + 2Aq.$ — It does not give off its water at 110° , and is but slowly decomposed at higher temperatures. It dissolves in 74 pts. of water; its solution in aqueous malic acid deposits the neutral salt unchanged, the excess of acid remaining in the mother-liquor. It dissolves abundantly in aqueous malate of soda, and does not crystallize out again on evaporation. (Berlin.)

MALATE OF ALUMINA. — *a. Basic.* — Sparingly soluble in water. (Braconnot.) — *b. Neutral.* — Transparent gum, which reddens litmus slightly, is permanent in the air, and dissolves readily in water, forming a solution which is not precipitated by potash or ammonia.

URANIC MALATE. — The impure salt has a pure yellow colour, and is sparingly soluble in water. (Richter.)

MANGANOUS MALATE. — *a. Neutral.* — Obtained by saturating the acid with carbonate of manganese. Uncrystallizable, gummy, very

to the solution of *a*; from solution in hot water, it separates in transparent, rose-coloured crystals. Does not melt in the fire, but decomposes with intumescence; dissolves in 41 pts. of cold water. (Braconnot.)

MALATE OF ZINC.—*a. Basic.*—Remains in the form of a whitish crystalline residue, on dissolving the neutral salt in water; contains 48.11 p. c. oxide. (Braconnot.) The solution obtained by continuous boiling of the aqueous acid with carbonate of zinc, solidifies on cooling to a tremulous jelly, which when diffused in water and boiled for a considerable time, is converted into a sandy powder. This powder is not decomposed by water at 100°, but at 200° it gives off water, and is partially converted into fumarate of zinc; for when the solution obtained by continuous boiling with water, and then is concentrated to a small bulk with addition of a little nitric acid, it deposits crystals of fumaric acid. (Hagen.)

<i>Dried at 200°.</i>				Hagen.
3 ZnO.....	120.6	50.97 49.03
8 C	48.0	20.29 21.86
4 H	4.0	1.69 1.84
8 O	64.0	27.05 27.27
<hr/>				
ZnO, C ⁸ H ⁴ Zn ² O ¹⁰	236.6	100.00 100.00
<i>Dried at 100°.</i>				Hagen.
3 ZnO.....	120.6	44.29 44.34
8 C	48.0	17.56 19.22
8 H	8.0	2.93 2.60
12 O	96.0	35.22 33.84
<hr/>				
ZnO, C ⁸ H ⁴ Zn ² O ¹⁰ + 4Aq.	72.6	100.00 100.00

Hagen prefers other formulæ which certainly agree better with the analyses: viz. for the salt dried at 200°: 3ZnO, C⁸H⁴O⁸ (basic malate of zinc) + ZnO, C⁴H²O⁴ (½ At. fumarate of zinc); and for the salt dried at 100°, the same formula + 4 At. water; he admits however that no fumaric acid can be obtained from the latter.

b. Neutral.—*a.* When the aqueous acid is saturated with carbonate of zinc at a temperature below 30°, the filtrate deposits, after a while, small shining crystals which gradually but completely give off their 6 At. water at 100°. (Hagen.)

β. When, on the other hand, the acid is saturated at a high temperature, and the solution filtered from the salt *a*, which separates on cooling, and further evaporated, crystals are deposited, containing indeed 6 At. water, but having a different form, and obstinately retaining about 1½ At. water at 100°. (Hagen.) They are short, hard, strongly lustrous four-sided prisms (square, according to Lassaigne), perpendicularly truncated, or bevelled with two faces; they redden litmus. (Braconnot.) They become opaque at 100°, giving off 10 per cent. of water, and at 120°, swell up and crumble to a white powder, giving off at the same time 10 p. c. more water. (Liebig.) They dissolve (leaving a small residue of salt *a*) in 55 pts. (67 pts. at 20°, according to Lassaigne) of cold, and 10 pts. of boiling water, from which the salt does not separate on cooling. (Braconnot.)

<i>α dried at 100°, or β above 100°.</i>				Hagen.	Lassaigne.
2 ZnO	80.4	40.93	40.74
C ⁸ H ⁴ O ⁸	116.0	59.07	
<hr/>					
C ⁸ H ⁴ Zn ² O ¹⁰	196.4	100.00	

222 PRIMARY NUCLEUS. C^8H^{10} : OXYGEN-NUCLEUS $C^8H^4O^4$.

β , dried at 100°.				Hagen.	Liebig.	Braconnot.
2 ZnO	80.4	37.50	38.32	37.75	35.50	
8 C	48.0	22.39	22.74			
6 H	6.0	2.80	2.51			
10 O	80.0	37.31	36.43			

$C^8H^4Zn^2O^{10} + 2Aq.$... 214.4 ... 100.00 ... 100.00

Hagen, in accordance with his own analysis, supposes this salt to contain only 1 or $1\frac{1}{2}$ Aq.

β . Air-dried crystals.				Braconnot.	Liebig.	Hagen.
2 ZnO	80.4	32.11	31.95	32.71	32.17	
$C^8H^4O^8$	116.0	46.33		46.73		
6 HO	54.0	21.56		20.56		

$C^8H^4Zn^2O^{10} + 6Aq.$... 250.4 ... 100.00 ... 100.00

c. Acid. — Obtained by supersaturating the salt *b* with the acid, and washing the resulting crystals with alcohol. Elongated square-based octohedrons, which swell up when heated, giving off 8.33 p. c. water, and are converted into a gum; they dissolve in 23 pts. of cold water. (Braconnot.)

Anhydrous.			
ZnO	40.2	24.33	
$C^8H^5O^9$	125.0	75.67	
$C^8H^5ZnO^{10}$	165.2	100.00	

Gum.				Braconnot.	Hagen.
ZnO	40.2	21.94	21.59	21.34	
$(C^8H^5O^9)$	125.0	68.23			
2 HO	18.0	9.83			

$C^8H^5ZnO^{10} + 2Aq.$ 183.2 ... 100.00

Crystals.				Braconnot.
ZnO	40.2	19.98	19.79	
$C^8H^5O^9$	125.0	62.13		
4 HO	36.0	17.89		
$C^8H^5ZnO^{10} + 4Aq.$	201.2	100.00		

Malate of Zinc and Ammonia. — Neutral malate of zinc is partially decomposed by ammonia, with formation of a double salt. (Braconnot.)

MALATE OF TIN. — Uncrystallizable; easily soluble; becomes somewhat moist on exposure to the air.

MALATE OF LEAD. — a. Basic. — Formed by digesting the neutral salt with ammonia. Flocculent powder which does not soften in boiling water. (Braconnot.) Dense and hard or granular mass, insoluble in water.

¶ When a solution of a salt of either active or inactive malic acid mixed with ammonia is precipitated with acetate of lead, the precipitate is in either case an anhydrous basic salt $4PbO, C^8H^4O^8$ [or $2PbO, C^8H^4Pb^2O^{10}$]; this formula requires 79.4 p. c. oxide of lead, while the salt prepared with the inactive acid gave 79.1, and that prepared with the active acid gave only 77.4, and in another case 74.5 p. c. (it was probably contaminated with acetate of lead). This basic salt does

water acidulated with acetic acid, it melts with considerable diminution of volume. (Pasteur.) ¶

b. *Neutral*. — The cold aqueous acid added to neutral acetate of lead, throws down bulky flakes which in a few hours aggregate in needles. (Braconnot, Vauquelin, Wöhler.) [The precipitate formed by inactive malic acid is amorphous at first, and takes a longer time to become crystalline than the active acid. (Pasteur.)] — Malic acid does not precipitate nitrate of lead unless it contains lime. (Gay-Lussac.) Neutral malate of potash throws down from acetate of lead a mixture of neutral and basic salt. (Braconnot.) According to Rieckher, on the contrary (*Ann. Pharm.* 39, 23), acid malate of ammonia added to tribasic acetate of lead, forms, with evolution of ammonia, a non-crystallizing, curdy precipitate, which however has the composition of the neutral salt; and Goupil found (*Compt. rend.* 23, 52) that the precipitated neutral salt forms needles after a few hours, only when the supernatant liquid contains a little free malic, acetic, or nitric acid, and therefore not when the acetate of lead has been precipitated by a neutral malate of one of the alkalis.

From a solution in hot water or in the hot aqueous acid, neutral malate of lead always separates in crystals, which are colourless, litmus-reddening, silky needles united in tufts, or four-sided, obliquely truncated prisms, or silvery micaceous laminae; when immersed in boiling water, they melt to a resinous mass which draws out into threads, and hardens into a brittle mass on cooling. (Braconnot.) [Inactive malate of lead melts under boiling water like the ordinary active salt, and separates from the solution, when left to cool quietly, in the form of an amorphous precipitate which slowly becomes crystalline. (Pasteur.)] — The crystals give off 14 p. c. (6 At.) water when heated; the recently precipitated salt, which has not yet become crystalline, contains the same quantity of water, and may therefore pass into the crystalline state without immersion in a watery liquid. (Pelouze.) The crystals melt and give off their water at 100°, and the remaining anhydrous salt, when further heated to 220°, is converted, with additional loss of 2 At. water, into fumarate of lead containing 69.33 p. c. PbO, 14.94 C, 1.16 H, and 14.57 O. (Rieckher.) At a still higher temperature, the residue burns with intumescence. (Braconnot.) The crystals dissolve very sparingly in cold water, somewhat better in hot water (less readily after passing into the resinous state), and separate out again on cooling. (Braconnot, Vauquelin.) Boiling aqueous acetic or malic acid does not exert a much more powerful solvent action on the salt than water, and on cooling deposits nearly the whole of it in the crystalline form. (Braconnot.) — The salt dissolves readily in nitric acid. With aqueous ammonia and with a hot aqueous solution of hydrochlorate, nitrate, or succinate of ammonia, it forms a clear solution; with a hot solution of sulphate of ammonia, first a clear and then a turbid solution, and with carbonate of ammonia, a permanently turbid solution. (Wittstein.) According to Rogers, it is insoluble in ammonia. — Donovan supposed that the salt does not dissolve in water as such, but in the form of an acid salt, while a basic salt remains behind. But, according to Lassaigne, the crystals dissolve completely when a sufficient quantity of water is present.

The compound of impure malic acid with oxide of lead is white, yellow, or brown, dissolves but very sparingly in boiling water, and is precipitated therefrom on cooling, not in crystals but in flakes: according to Vauquelin and Braconnot, it dissolves readily in vinegar.

2 PbO	224	65.88	65.35	65.39	65.70	65.1
8 C	48	14.12	14.38	14.36	14.27	11.4
4 H	4	1.18	1.26	1.26	1.22	1.0
8 O	64	18.82	19.01	18.99	18.81	22.5

$C^8H^4Pb^2O^{10}$	340	100.00	100.00	100.00	100.00	100.0
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In the salt, probably dried at a different temperature, Vauquelin found 67 p. c., Braconnot 61.15, and Lassaigne 57.39 p. c. oxide of lead.

<i>Air-dried crystals.</i>				<i>Piria.</i>			
2 PbO	224	56.85	56.66
8 C	48	12.18	12.20
10 H	10	2.54	2.49
14 O	112	28.43	28.65
<hr/>							
$C^8H^4Pb^2O^{10} + 6Aq.$	394	100.00	100.00
<hr/>							
<i>Or:</i>				<i>Pelouze.</i>			
$C^8H^4Pb^2O^{10}$	340	86.29	86
6 HO	54	13.71	14
<hr/>							
$C^8H^4Pb^2O^{10} + 6Aq.$	394	100.00	100

The crystals of the optically inactive salt have the same composition. (Pasteur.)

Malate of Lead and Ammonia. — Formed by decomposing neutral malate of lead with ammonia. Soluble, crystallizable. (Braconnot.)

Malate of Lead and Zinc. — Precipitated on mixing malate of lead with the neutral acetate. (Braconnot.)

FERRIC MALATE. — Both the neutral and the acid salt are brown, gummy, permanent in the air, readily soluble in water and alcohol. (Scheele, Braconnot.) Ferric salts mixed with malic acid are not precipitated by alkalis. (H. Rose.)

CUPRIC MALATE. — *a. Basic.* — *a. With 4 At. Water.* — Remains in the form of a green powder insoluble in the aqueous acid, when carbonate of copper is boiled with excess of malic acid. (Liebig.)

β. With 5 At. Water. — The solution of hydrated cupric oxide in cold concentrated malic acid deposits, on addition of alcohol, a blue-green salt, which redissolves in water and appears to contain 5 At. water. The latter solution has an acid reaction, and deposits the salt *a* when boiled, but the salt *γ* after standing for several days.

γ. With 6 At. Water. — When carbonate of copper is left to stand in the cold with the aqueous acid, a solution is obtained which deposits the salt *a* when boiled, but when evaporated in vacuo or below 40° (in which case a colourless mother-liquor remains, containing free acid), yields dark green crystals of the salt *γ*, which turn blue when dried in vacuo over oil of vitriol. (Liebig.)

<i>a. dried over oil of vitriol.</i>				<i>Liebig.</i>			
3CuO	120	44.12	43.83
8 C	48	17.65	17.90
8 H	8	2.94	3.06
12 O	96	35.29	35.21
<hr/>							
$CuO, C^8H^4Cu^2O^{10} + 4Aq.$	272	100.00	100.00

3 CuO	120	41.38	41.22
8 C	48	16.55	
10 H	10	3.45	
14 O	112	38.62	

CuO, C⁸H⁴Cu²O¹⁰ + 6Aq..... 290 100.00

b. Neutral. — When malic acid obtained from wormwood is heated with oxide of copper, and the filtrate evaporated, there remains a gummy mass, which, after the excess of acid has been removed by alcohol, forms a dark green amorphous residue, dissolving readily in water and producing a solution of a fine green colour. (Luck.) The neutral salt is a green varnish, permanent in the air. (Braconnot.)

2 CuO	80	37.38	37.18
8 C	48	22.44	22.64
6 H	6	2.80	2.67
10 O	80	37.38	37.51

C⁸H⁴Cu²O¹⁰ + 2Aq..... 214 100.00 100.00

c. Acid. — Cupric oxide obtained by precipitating blue vitriol with potash, and dried at a gentle heat, forms, when set aside for some time with the cold aqueous acid, a blue solution which, when evaporated under 40°, yields crystals of a splendid smalt-blue colour. They give off their 2 At. water at 100°. (Hagen.)

<i>Dried at 100°.</i>				<i>Hagen.</i>	
CuO	40	24.24	23.93
8 C	48	29.09	29.23
5 H	5	3.03	3.03
9 O	72	43.64	43.81

C⁸H⁶CuO¹⁰..... 165 100.00 100.00

<i>Crystallized.</i>				<i>Hagen.</i>	
CuO	40	21.86	21.52
C ⁸ H ⁶ O ⁹	125	68.31	
2 HO	18	9.83	9.99

C⁸H⁶CuO¹⁰ + 2Aq. 183 100.00

According to Braconnot, the acid salt is not crystallizable, and is but partially precipitated by potash, a double salt appearing to form. — According to Pfaff (*Schw.* 61, 357), the compound of cupric oxide and ammonia forms an olive-green mixture with aqueous malic acid.

‡. *Cupric Malate with Sulphate of Ammonia.* — When solutions of cupric sulphate and malate of ammonia are mixed, any excess of the former that may be present crystallizes out first, and afterwards the double salt, in beautiful grass-green, pointed crystals, which do not alter when exposed to the air. (H. Schulze, *Arch. Pharm.* [2], 57, 273.) ¶.

MERCUROUS MALATE. — Pure malic acid precipitates mercurous nitrate in white flakes (Lassaigne); according to Braconnot, however, no such precipitation takes place. — The impure acid throws down a white powder, easily soluble in malic acid and in the stronger acids. (Scheele, Braconnot.) The aqueous acid digested at 75° with mercurous oxide and filtered, deposits a crystalline powder. The same powder is precipitated

on mixing malate of potash with dilute mercurous nitrate. It tastes metallic after some time; assumes a grey colour when exposed in the moist state to the sun; contains, after drying at a gentle heat, 75.96 p. c. mercurous oxide, but no water; leaves charcoal when ignited; turns black by contact with alkalis; is resolved by continued boiling with water, into a basic and a soluble acid salt; dissolves in hot nitric acid, but is insoluble in water, alcohol, or ether. (Harff, *N. Br. Arch.* 5, 281.)

MERCURIC MALATE. — Obtained by dissolving mercuric oxide in the heated acid. Gummy, not crystallizable; resolved by water into a soluble acid and an insoluble basic salt. (Braconnot.) — When mercuric oxide is boiled with excess of concentrated malic acid, small crystals of an *acid salt* soluble in water separate from the filtrate; if, on the other hand, the oxide is in excess, the filtrate deposits, together with those crystals, a yellow powder consisting of a *basic salt*; this basic salt is likewise formed, when mercuric nitrate is precipitated by malate of potash, an acid salt then remaining in solution. The yellow powder has a faint metallic taste; leaves charcoal when ignited; yields a white powder with ammonia, and a yellow oxide with potash; dissolves in hydrochloric or nitric acid, and in 2000 pts. of water. (Harff.)

When mercurous malate is decomposed by ammonia, a black tasteless powder is formed, which contains 88.01 p. c. Hg^2O ; leaves charcoal when ignited; gives off ammonia with potash; dissolves in nitric acid, leaving only a white powder, and in strong acetic acid, leaving nothing but globules of mercury, which are likewise obtained by rubbing the moistened powder. — The white powder obtained by treating mercuric malate with ammonia gives off ammonia with potash, and dissolves almost completely in hydrochloric or nitric acid, whence potash then throws down a white powder. (Harff.)

MALATE OF SILVER. — *a. Basic?* — Aqueous malic acid heated with oxide of silver, acquires a brownish colour, produces carbonic and acetic acid, and is then decolorized, with deposition of brown-black flakes, consisting of a compound of silver-oxide with decomposed malic acid, while the filtrate yields by evaporation an amorphous gum. (Braconnot.) This salt was regarded by Braconnot as the neutral, and *b* as the acid salt, which however is not the case.

b. Neutral. — Only the impure acid forms a precipitate with nitrate of silver; the pure acid does not. (Scheele, Gay-Lussac, Braconnot.) — 1. From the solution of salt *a*, malic acid precipitates the salt *b* in granules. (Braconnot.) — 2. Alkaline malates added to nitrate of silver throw down the salt *b* in the form of a snow-white, granular, crystalline powder. When acid malate of ammonia is used for this purpose, only half the salt is precipitated, the other half not separating till the solution is mixed with ammonia. (Liebig.) — 3. With a warm dilute solution of malate of lime, nitrate of silver forms a precipitate containing lime, which however when dissolved, after washing, in very dilute nitric acid, and not completely precipitated by ammonia, so that the liquid remains acid, appears to be free from lime and from ammonia. (Liebig & Redtenbacher, *Ann. Pharm.* 38, 134.) — White, granular, crystalline powder, of sp. gr. 4.0016 at 15°. (Liebig & Redtenbacher.) — Blackens quickly when exposed to light. (Luck.) Turns yellow when dried at a strong heat (Liebig); and at a still higher temperature melts with slight

frothing (Braconnot, Liebig); gives off water, carbonic acid, carbonic oxide, and fumaric acid, with empyreumatic odour, and leaves 62·009 p. c. silver free from carbon, in the form of a porous cake. (Liebig & Redtenbacher.) It dissolves in boiling water, separating out with facility on cooling (Braconnot); it dissolves readily in boiling water, but does not yield crystals on cooling, merely depositing metallic silver, while the liquid turns black. (Liebig.) It dissolves slowly in boiling water, readily in acids, the portion which does not dissolve immediately becoming dark-coloured for a moment. (Luck.)

<i>Dried at 100°.</i>		Liebig.		Hisch.		Luck.	
8 C	48	13·79	13·88	13·47	13·84	13·84	13·84
4 H	4	1·15	1·17	1·36	1·18	1·18	1·18
2 Ag	216	62·07	62·01	60·93	61·70	61·70	61·70
10 O	80	22·99	22·94	24·24	23·28	23·28	23·28
$C^8H^4Ag^2O^{10}$	348	100·00	100·00	100·00	100·00	100·00	100·00

Hisch (*Ann. Pharm.* 51, 246), analysed the salt prepared with acid obtained from potatoes; Luck, that which was prepared with acid from wormwood.

Malic acid dissolves readily in *Alcohol*.

In attempting to prepare *Malic ether*, Hagen obtained fumaric ether (p. 31). — Thénard (*Mém. de la Soc. d'Arcueil*, 2, 12), by heating 15 pts. of malic acid with 18 pts. alcohol and 5 pts. oil of vitriol, till ether began to escape, and mixing the brown residue with water, obtained a yellowish, inodorous, non-volatile oil, which sank to the bottom of the liquid, was decomposed by potash with formation of malate of potash, dissolved sparingly in water and abundantly in alcohol, and was precipitated therefrom by water. [Deserves further investigation.]

¶ According to Demondesir (*Compt. rend.* 33, 227) the *malates of ethyl* and *methyl* are obtained by passing hydrochloric acid gas into a solution of malic acid in alcohol or wood-spirit, neutralizing with carbonate of soda, and agitating the liquid with common ether, which then takes up the compound ether and leaves it behind when distilled. The malate of ethyl or methyl thus obtained still contains water and alcohol or wood-spirit, which may be removed by evaporation in vacuo, or at a gentle heat in the air, and certain salts, from which it may be freed by dissolving it in very pure vinic ether. — The malates of ethyl and methyl are liquids, which are soluble in water, almost completely decomposed by distillation, and converted into malamide by ammonia. They rotate the plane of polarization of a ray of light.

Malomethylic and *Malovinic* acid are always formed by the above process simultaneously with the ethers. The lime-salts of these acids are soluble in alcohol. ¶

APPENDIX TO MALIC ACID.

Acids perhaps identical with Malic Acid.

1. Fungic Acid.

BRACONNOT. (1810.) *Ann. Chim.* 79, 293; 87, 242.

Pilzsäure, Acide fongique. — Occurs in *Peziza nigra*, *Hydnum hybridum* and *repandum*, *Boletus Juglandis* and *pseudoignarius*, *Phallus impudicus* and *Merulius Cantharellus* (Braconnot); in *Helvella Mitra*. (Schrader.)

the liquid evaporated to the consistence of an extract, coagulated albumin then separating; and the residue washed with alcohol. The portion insoluble in alcohol, which contains the fungate of potash, is dissolved in water and precipitated with neutral acetate of lead. By digesting the precipitate with dilute sulphuric acid, a brown liquid is obtained, containing fungic acid, phosphoric acid, animal matter, &c. This liquid mixed with ammonia, yields by evaporation crystals of fungate of ammonia, which, by repeated crystallization and pressure between blotting paper, may be obtained tolerably white. — The solution of the crystals thus purified is added to acetate of lead, and the pure fungate of lead thus precipitated is decomposed by dilute sulphuric acid.

Colourless, uncrystallizable, very acid liquid, which absorbs water from the air.

Fungate of Ammonia. — Rather acid, large, six-sided prisms, sometimes compressed, bevelled with 2-faces resting on the broad lateral faces (*Fig. 55*); they dissolve in 2 pts. of cold water.

Fungates of Potash and Soda. — Uncrystallizable salts easily soluble in water, insoluble in alcohol.

Fungate of Baryta. — Saline, amorphous crusts, which swell up in the fire, leaving a spongy mass of carbonate of baryta; the salt dissolves in 15 pts. of cold water.

Fungate of Lime. — Fungate of potash does not precipitate hydrochlorate of lime. When a solution of lime in the acid is evaporated, the salt is deposited in plates, composed of small crystals which appear to be four-sided prisms with dihedral summits. Tastes somewhat saline; is permanent in the air. Swells up in the fire, leaving a spongy mass of carbonate of lime. Requires at least 80 pts. of water to dissolve it.

Fungate of Magnesia. — Granular crystals, having a slight taste, swelling up slightly in the fire, and dissolving with tolerable facility in water.

Fungate of Alumina. — Uncrystallizable gum.

Manganous Fungate. — Uncrystallizable gum.

Fungate of Zinc. — Crystallizes readily in parallelopipeds; decomposes in the fire with intumescence; moderately soluble in water.

Fungate of Lead. — The free acid and fungate of potash precipitate acetate of lead in the form of hornsilver. The precipitate dissolves pretty readily in acetic acid.

Fungate of Silver. — Nitrate of silver is not precipitated by free fungic acid, but only by the alkaline fungates.

Ferrous and Cupric sulphates are not precipitated by fungic acid. (*Braconnot.*)

PELLETIER & CAVENTOU. (1819.) *Ann. Chim. Phys.* 10, 167; 26, 54.

Igasuräure, Acide igasurique.— In *Faba St. Ignatii, Nux vomica*, and *Lignum colubrinum*; probably also in the *Tiente-Upas*.

Preparation. Ignatius beans exhausted with ether are repeatedly boiled with alcohol, the alcoholic solution evaporated, the residue boiled with water and magnesia, and filtered. The mixture on the filter consisting of magnesia, igasurate of magnesia, and strychnine, is washed with cold water, then freed from strychnine with hot alcohol, and boiled with a large quantity of water. The water dissolves out the igasurate of magnesia; and the solution filtered, evaporated, and mixed with neutral acetate of lead, yields a precipitate of igasurate of lead, which is washed, suspended in water, and decomposed by sulphuretted hydrogen.

Properties. Brownish syrup, which when left at rest, deposits small hard granules; its taste is harsh and sour.

Combinations. Dissolves very readily in water and in alcohol.

With alkalis it forms salts which dissolve readily in water and alcohol. — Igasurate of baryta crystallizes with difficulty in little spongy masses, and dissolves readily in water. — Igasurate of ammonia does not precipitate or colour the salts of iron, mercury, or silver; in solutions of cupric salts, it forms a greenish white precipitate, very sparingly soluble in water.

Carriol (*J. Pharm.* 19, 155; abstr. *Ann. Pharm.* 8, 45), obtained from *Nux vomica*, an acid different from igasuric acid, the aqueous solution of which left a syrup when evaporated in vacuo, and when further heated above 100°, passed over apparently undecomposed, in the form of a crystalline sublimate or buttery mass. It dissolves readily in water, boiling alcohol, and ether, from which it crystallizes. Its salts are mostly crystallizable and easily soluble.

3. Nicotic Acid.

BARRAL. (1845.) *Compt. rend.* 21, 137.

Tabaksäure, Acide nicotique.— Dry tobacco-leaves are digested with water; the acid filtrate precipitated with acetate of lead; the precipitate washed, suspended in water, and decomposed by sulphuretted hydrogen; and the filtrate evaporated to a syrup, which, when further evaporated, either in vacuo or at a gentle heat in the air, yields the crystalline acid.

Micaceous laminae.

The acid is bibasic = 2HO , $\text{C}^6\text{H}^2\text{O}^6 = \text{C}^6\text{H}^4\text{O}^8 = \text{C}^6\text{H}^4\text{O}^3, \text{O}^6$; it stands to propionic acid in the same relation as oxalic to acetic acid. $\text{C}^6\text{H}^4\text{O}^8 : \text{C}^6\text{H}^2\text{O}^6 = \text{C}^4\text{H}^2\text{O}^8 : \text{C}^4\text{H}^4\text{O}^4$.

By dry distillation, and by treatment with oil of vitriol, the acid is resolved into acetic and carbonic acid. $\text{C}^6\text{H}^4\text{O}^8 = \text{C}^2\text{H}^4\text{O}^4 + 2\text{CO}^2$.

It dissolves readily in *Water*, and forms crystallizable salts with *Ammonia*, *Potash*, &c.—The *Lead-salt* is insoluble = $2PbO, C^8H^2O^8 = C^8H^2Pb^2O^8 = C^8H^2Pb^2O^8, O^4$. The *Silver-salt* has a similar composition. (Barral.)

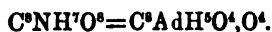
Barral's formulæ are not supported by analyses.

Vauquelin, Goupil (*Compt. rend.* 23, 51), and Reimann, (*Mag. Pharm.* 25, 2, 65), recognized the acid of tobacco as malic acid.

b. *Amidogen-nuclei.*

a. *Amidogen-nucleus* $C^8AdH^6O^4$.

Aspartic Acid.



PLISSON. *J. Pharm.* 13, 477; also *Ann. Chim. Phys.* 35, 175. *J. Pharm.* 15, 268; also *Ann. Chim. Phys.* 40, 303; also *Schw.* 56, 66; also *Br. Arch.* 31, 208; also *N. Tr.* 19, 1, 185.

PLISSON & O. HENRY. *Ann. Chim. Phys.* 45, 315.

BOUSTRON, CHARLARD & PELOUZE. *J. Pharm.* 19, 208; also *Ann. Chim. Phys.* 52, 90; also *Schw.* 67, 393; also *Ann. Pharm.* 6, 75.

LIEBIG. *Pogg.* 31, 222. — *Ann. Pharm.* 26, 125, and 161.

PIRIA. *Ann. Chim. Phys.* 22, 160; also *J. pr. Chem.* 44, 71.

DESSAIGNES. *Rev. scient.* [4], 1, 22; *Ann. Pharm.* 83, 83; abstr. *Jahresber.* 1852, 466.

PASTEUR. Active and inactive modifications of Aspartic acid. *N. Ann. Chim. Phys.* 34, 30; in full abstract: *Ann. Pharm.* 82, 324; in shorter abstract: *Compt. rend.* 33, 217; *Instit.* 1851, 273; *J. Phys. Ansl.* 3, 344; *J. pr. Chem.* 54, 50; *Ann. Pharm.* 80, 151; *Pharm. Centr.* 1851, 769; *Jahresber.* 1851, 176, 389.

Asparagsäure, Asparaginsäure. Acide aspartique, Acide asparamique. Discovered by Plisson, in 1827.

Formation. 1. By heating asparagine with acids or with the stronger solifiable bases and water. (Plisson.) — ¶ According to Dessaignes, asparagine heated alone to 200° , as long as any ammoniacal odour is evolved, leaves a brown, slightly soluble substance, which, when treated with hydrochloric acid, yields aspartic acid. — 2. By the fermentation of asparagine under the influence of casein. (Dessaignes.) — 3. By heating acid malate, maleate or fumarate of ammonia to about 200° , and treating the product with hydrochloric acid. (Dessaignes.) — The aspartic acid prepared in this manner is optically inactive, whereas that which is formed from asparagine rotates the plane of polarization of a luminous ray. (Pasteur.) ¶

Preparation. A. Of the Active acid. — 1. Asparagine is boiled with protoxide of lead, and with water which must be frequently renewed, as long as ammonia continues to escape; the residual lead-salt purified by

after diffusion in water; and the filtrate evaporated to the crystallizing point. (Plisson.)—2. Asparagine is boiled with baryta-water till the evolution of ammonia entirely ceases; the baryta precipitated from the still hot liquid by an exactly equivalent quantity of sulphuric acid; and the filtrate evaporated to the crystallizing point. (Boutron & Pelouze.)—3. Asparagine is boiled in a similar manner with potash; the liquid supersaturated with hydrochloric acid, and evaporated to dryness in the water-bath; and the chloride of potassium extracted by water, which then leaves the acid perfectly free from potash. (Liebig.)—¶ 4. Asparagine is boiled for three hours with excess of hydrochloric acid; the solution evaporated to dryness; and the residue, consisting of chloride of ammonium and hydrochlorate of aspartic acid, dissolved in a small quantity of water and half neutralized with ammonia. The liquid on cooling deposits abundance of aspartic acid, which is easily washed and purified. (Dessaignes.)

B. Of the Inactive acid.—When bimalate of ammonia is heated to 200°, and the reddish, resinous residue boiled for some hours with hydrochloric acid, a solution is obtained, which, by evaporation and cooling, yields a crystalline hydrochlorate of aspartic acid. This compound is dissolved in hot water, the solution divided into two equal parts, the one saturated with ammonia, and the other added to it. The mixture thus formed yields on cooling an abundant crystallization of inactive aspartic acid. (Dessaignes.) Or, the residue obtained by heating the bimalate of ammonia may be boiled with nitric acid, and from the crystalline nitrate of aspartic acid,—which is deposited from the cooled solution after the excess of nitric acid has been carefully expelled over the water-bath,—the aspartic acid may be obtained as above; or the solution of the nitrate may be neutralized with lime, the aspartate of lime precipitated by alcohol, and the solution of this salt carefully decomposed by oxalic acid. (J. Wolff, *Ann. Pharm.* 75, 293.) ¶

Properties. White shining crystalline powder, which, under the microscope, appears to consist of transparent, bevelled, four-sided prisms; sp. gr. = 1·873 at 8·5° (Plisson); small crystals having a pearly and silky lustre. (Boutron & Pelouze.) Inodorous; tastes rather sour, leaving an after-taste like broth. (Plisson.) The crystals do not give off water at 120°. (Boutron & Pelouze; Liebig.)

¶ According to Pasteur, active aspartic acid crystallizes in indistinct forms of the rhombic [right prismatic] system; the crystals have generally the appearance of rectangular laminæ, truncated at the angles. Sp. gr. 1·6613 at 12·5°. The acid dissolved in potash, soda, or ammonia turns the plane of polarization to the left; but when dissolved in the stronger acids, to the right. The inactive acid forms very small monoclinometric [oblique prismatic] crystals, which often have a lenticular shape. Sp. gr. 1·6632. The solutions have no action on polarized light. ¶

	<i>Crystals.</i>		<i>Piria.</i>		<i>Liebig.</i>	<i>Pl. & Henry.</i>
8 C	48	36·09	35·99	36·77	37·73	
N	14	10·53	10·78	10·37	12·04	
7 H	7	5·26	5·47	5·33	5·37	
8 O	64	48·12	47·76	47·53	44·86	
C ⁸ NH ⁷ O ⁹	133	100·00	100·00	100·00	100·00	

	<i>Crystals.</i>		Butron & Pel.	Pasteur. <i>inactive acid.</i>	Wolf
8 C	48	36.09	38.77	35.6	36.2
N	14	10.53	11.27		10.3
7 H	7	5.26	5.50	5.2	5.3
8 O	64	48.12	44.46		48.2
C ⁸ NH ⁷ O ⁸	133	100.00	100.00		100.0

Aspartic acid is the amidogen-acid of malic acid, just as oxamic acid (C⁴NH³O⁶) is the amidogen-acid of oxalic acid (C²H²O⁸). (Piria.)

Decompositions. 1. The acid swells up considerably in the fire, giving off ammonia and a faint animal empyreumatic odour. When heated in vacuo, it turns first yellow, then black, giving off ammonia, hydrocyanic acid and other products, and leaves a shining charcoal. (Plisson.)— 2. When dissolved in cold nitric acid containing nitrous acid, or in pure nitric acid through which nitric oxide gas is passed, it is quickly converted, with evolution of nitrogen, into malic acid, whereas pure nitric acid has no action upon it. (Piria.)



Aspartic acid evaporated to dryness with 12 pts. of nitric acid, either remains unaltered or suffers but partial decomposition. (Plisson.)— 3. When heated with oil of vitriol, it is decomposed with formation of sulphurous acid. (Plisson.)— It is not decomposed by continued boiling with strong hydrochloric or dilute sulphuric acid. (Piria.)— When fused with excess of hydrate of potash, it is not decomposed till the heat becomes strong, acetate and oxalate of potash being then formed, with evolution of ammonia and hydrogen gas. (Piria.)

Combinations. A. *With Water.*—Aspartic acid dissolves in 128 pts. of water at 8.5°, much more copiously in hot water, from which it crystallizes on cooling. (Plisson.)— ¶ 1 pt. of the active acid dissolves in 364 pts. of water at 11°, and 1 pt. of the inactive acid in 208 pts. of water at 13.5°. When a solution saturated while hot is left to crystallize by cooling, the liquid remains supersaturated with the acid. (Pasteur.) ¶.

B. *With Acids.*—*Sulphate of Aspartic acid.*—Aspartic acid dissolves without decomposition in cold oil of vitriol. (Plisson.)— ¶. When oil of vitriol is gradually heated to 50° or 60° in a wide glass tube, aspartic acid gradually added as long as it dissolves, and the tube kept closed for a few days, large aggregated prisms of sulphate of aspartic acid are formed, which are lighter than the liquid from which they separate; they must be drained on a porous plate, quickly washed with alcohol, and dried over oil of vitriol. (Dessaignes.)

	Dessaignes.	
C ⁸ NH ⁷ O ⁸	133	57.58
2 SO ⁴ H	98	42.42
C ⁸ NH ⁷ O ⁸ .2SO ⁴ H	231	100.00

Hydrochlorate.—The solubility of aspartic acid in water is greatly increased by the presence of hydrochloric acid. (Plisson.) The solution of aspartic acid in strong hydrochloric acid, yields, by evaporation and cooling, deliquescent, very soluble laminæ, and leaves, when evaporated to dryness and further heated to 100°, an amorphous deliquescent

acid be removed from the solution by marble, the aspartic acid loses this easy solubility. (Piria.)

¶. Both active and inactive aspartic acid give, by solution in hydrochloric acid, evaporation over the water-bath, and spontaneous evaporation of the concentrated solution in a quiet place, crystalline compounds of aspartic with hydrochloric acid. These hydrochlorates are very soluble. They are identical in composition, but differ in crystalline form. The hydrochlorate formed from active aspartic acid, alone possesses the rotatory power.

a. Active Hydrochlorate. The crystals of this compound belong to the rhombic [right prismatic] system; they are prisms of about 90° , very much truncated on two opposite lateral edges, and terminated by faces inclined at an angle of about 115° , and belonging to an irregular tetrahedron. The compound rotates the plane of polarization to the right. It decomposes when dissolved in water, yielding a copious precipitate of aspartic acid; this decomposition may be prevented by the addition of a few drops of hydrochloric acid. The crystals deliquesce in the air, setting free the aspartic acid.

β. Inactive Hydrochlorate. — The crystals belong to the monoclinometric [oblique prismatic] system, and differ altogether in appearance from those of the active compound. They are permanent in the air only in summer, becoming milk-white on the surface, and losing their lustre and transparency. They decompose when dissolved in water, but as the inactive acid is more soluble than the active, no precipitation takes place; if, on the other hand, a mixture of water and alcohol be used, an abundant precipitation is formed. (Pasteur, Dessaignes.)

	Crystallized.		Pasteur.	
			active.	inactive.
8 C	48.0	28.34		
N	14.0	8.27		
8 H	8.0	4.72		
8 O	64.0	37.77		
Cl	35.4	20.90	20.9	20.7
<hr/>				
$C^8NH_7O^8, HCl$	169.4	100.00		
Or:				
$C^8NH_7O^8$	133.0	78.47		
HCl	36.4	21.53		21.24
<hr/>				
$C^8NH_7O^8, HCl$	169.4	100.00		

Both the active and inactive hydrochlorates are decomposed at the same temperature, giving off hydrochloric acid and water, and leaving the compound $C^8NH_4O^8$ (p. 214) (Pasteur):



Nitrate. Obtained like the hydrochlorate in beautiful crystals. (Dessaignes.) ¶.

C. With Salifiable Bases. Aspartic acid decomposes the alkaline bicarbonates and soap-water; it does not precipitate any of the heavy metallic salts. The aspartates of the alkalis taste like broth; when ignited, they give off ammonia, hydrocyanic acid, and other products,

and leave metallic cyanides. (Plisson.) The formula of the aspartates is C⁸NH⁶MO⁸. (Laurent, *Ann. Chim. Phys.* 23, 113.) ¶. The acid likewise forms basic salts, some having the composition C⁸NH⁶M²O⁸, others on the contrary, being composed according to the formula MO, C⁸NH⁶MO⁸. (Dessaignes, Pasteur.)

Although the formation of those basic aspartates whose formula is C⁸NH⁶M²O⁸ (*e. g.*, the baryta and lime-salts) is certainly attended with elimination of 2 At. water, Dessaignes nevertheless regards the acid as monobasic, and remarks that perfectly neutral amides,—which cannot well be regarded as monobasic acids—*e. g.*, benzamide, butyramide, urea, are capable of combining with metallic oxides, with elimination of 1 At. water.—Pasteur does not express a decided opinion regarding the basicity of aspartic acid. He states however that aspartic acid cannot be regarded as the amidogen-acid of malic acid, or asparagin as the amide of that acid, founding this opinion on certain unpublished investigations of Demondeisir.—On the other hand, Demondeisir had previously stated (*Ann. Pharm.* 80, 303,) that the artificially prepared amide of malic acid does not appear to differ from asparagin. ¶

ASPARTATE OF AMMONIA.—Crystallizes with difficulty, dissolves very readily in water, forming a solution which becomes acid by evaporation. (Plisson & Henry.)

ASPARTATE OF POTASH.—Does not crystallize; tastes sweetish, and like broth; becomes moist when exposed to the air. (Plisson.) Its formula is C⁸NH⁶KO⁸. (Laurent.) A solution of this salt evaporated to a syrup, yields crystals after a while, but they cannot be separated from the mother-liquor. (Dessaignes.)

ASPARTATE OF SODA.—Crystallizes readily; tastes like broth, and somewhat saline. (Plisson.)

¶. When active or inactive aspartic acid is neutralized with soda, or carbonate of soda, and the liquid slowly evaporated, neutral salts are formed, identical in composition and chemical reactions, but differing in crystalline form.

a. Active.—Forms needle-shaped, deeply striated prisms, belonging to the right prismatic system, and terminated by faces of a tetrahedron inclined to one another at about 106°. The four faces of this tetrahedron are either present alone, or are much more developed than those of the opposite tetrahedron, which, if equally developed with the former, would constitute a rhombic pyramid. 1 pt. of the active acid dissolves in 1.12 pts. water at 12.2°. The solution turns the plane of polarization to the left. (Pasteur.) The salt gives off 2 At. water at 160°. At 170° it turns yellow, and gives off ammonia, and at a higher temperature froths up considerably. (Dessaignes.)

β. Inactive. Crystallizes in the oblique prismatic system, and often forms macle-crystals. 1 pt. of the salt dissolves in 1.19 pts. water at 12.5°.

<i>Crystals.</i>		<i>Dessaignes active.</i>
C ⁸ NH ⁶ O ⁷	71.70	
NaO	17.90	17.44
2 HO	10.40	9.64
<hr/>		
C ⁸ NH ⁶ NaO ⁸ + 2Aq.	100.00	

The mixture formed by adding 1 At. soda to 1 At. of this salt does not crystallize even when left under a bell-jar with lime; a mixture of the solutions of 1 At. aspartate of potash and 1 At. aspartate of soda yields by evaporation nothing but aspartate of soda. ¶

like broth and not bitter; they contain 38.8 p. c. baryta. (Plisson.) Crystals soluble in water. (Boutron & Pelouze.)

¶. Aspartic acid forms with baryta a monobasic and a bibasic salt. — *a. Bibasic.* — When hydrate of baryta is gradually added to a hot and somewhat concentrated solution of the neutral salt *b*, the liquid solidifies in a crystalline mass; and on adding water to this mass, leaving it to stand for a moment, then filtering, and leaving the solution to cool out of contact of air, the basic salt is deposited in rather thick, shining prisms. These crystals remain transparent when rapidly washed and dried over sulphuric acid, give off half their water (3 At.), and become opaque when dried in vacuo, and the whole of it, amounting to 16.40 p. c. (6 At.) at 160° without decomposition. The aqueous solution of this salt has a strong alkaline reaction; carbonic acid gas passed through it, precipitates half the baryta in the form of carbonate. (Dessaignes.)

<i>Dried at 160°.</i>		Dessaignes.	
$C^8NH^6O^6$	115.0	42.45	
2 BaO	153.2	57.55	57.05
<hr/>			
$C^8NH^6Ba^2O^8$	268.2	100.00	
<i>Dried in vacuo.</i>		Dessaignes.	
$C^8NH^6O^6$	115.0	38.96	
2 BaO	153.2	51.90	51.42
3 HO	27.0	9.14	
<hr/>			
$C^8NH^6Ba^2O^8 + 3Aq.$	295.2	100.00	
<i>Crystals.</i>		Dessaignes.	
$C^8NH^6O^6$	115.0	45.74	
2 BaO	153.2	47.48	47.53
6 HO	54.0	16.78	16.40
<hr/>			
$C^8NH^6Ba^2O^8 + 6Aq.$	322.2	100.00	

b. Monobasic. Crystallizes in very fine silky needles, which give off 14.40 p. c. (nearly 4 At.) water at 160°. (Dessaignes.)

<i>Dried at 160°.</i>		Dessaignes.	
$C^8NH^6O^7$	124.0	61.88	
BaO	76.6	38.12	38.05
<hr/>			
$C^8NH^6BaO^8$	200.6	100.00	
<i>Crystals.</i>		Dessaignes.	
$C^8NH^6O^7$	124.0	52.41	
BaO	76.6	32.38	
4 HO	36.0	15.21	14.40
<hr/>			
$C^8NH^6BaO^8 + 4Aq.$	236.6	100.00	

Wolff found in the salt dried at 120°, 37.6 p. c. baryta.

ASPARTATE OF LIME. — *a. Bibasic.* — The solution of salt *b* takes up a large additional quantity of lime, and yields a crystallizable salt containing 30.65 p. c. lime. (Plisson.) Crystals soluble in water. (Boutron & Pelouze.) — ¶. The solution of *b* mixed with a slight excess of lime, then filtered, and left to evaporate over lime, yields very beautiful prisms, which may be freed from a small quantity of adhering carbonate of lime by crystallization. In vacuo it gives off water; and at 160° the loss of water amounts to 26.49 — 28.57 p. c., according as the salt is

lent in the vacuum for a longer or a shorter time. The solution of this salt has a strong alkaline reaction, and is decomposed by carbonic acid, like the basic baryta-salt. (Dessaignes.)

Dried at 160°.			Dessaignes.	
$C^{\circ}NH^{\circ}O^{\circ}$	115	67.27		
2 CaO	56	32.73	32.44	32.85
$C^{\circ}NH^{\circ}Ca^{\circ}O^{\circ}$	171	100.00		

Crystals air-dried.			Dessaignes.	
$C^{\circ}NH^{\circ}O^{\circ}$	115	47.34		
2 CaO	56	23.04	23.09	
8 HO	72	29.62	28.57	
$C^{\circ}NH^{\circ}Ca^{\circ}O^{\circ} + 8Aq.$	243	100.00		¶.

b. Monobasic. — Gummy; tastes like the soda-salt; contains 17.25 p. c. lime; gives off a large quantity of hydrocyanic acid when distilled. (Plisson.)

A neutral solution of aspartate of baryta mixed with a slight excess of lime, yielded successively basic aspartate of baryta and basic aspartate of lime, but no double salt. (Dessaignes.)

ASPARTATE OF MAGNESIA. — *Bibasic.* — The aqueous solution of salt *b* dissolves a large additional quantity of magnesia, and yields by evaporation a sharp-tasting gum, containing 22.45 p. c. magnesia. (Plisson.)

— *b. Monobasic.* — By continued boiling of asparagin with magnesia and water [is not a bibasic salt formed by this process?], and evaporation of the filtrate, a gummy mass is obtained, which tastes like the soda-salt, has an alkaline reaction, dissolves very readily in water, is insoluble in strong but soluble in weak alcohol, and contains 13.05 p. c. magnesia. (Plisson.) — If the mother-liquor left in the preparation of asparagin from marsh-mallow root after the asparagin has crystallized out of the alcoholic extracts, be further evaporated, it deposits a yellowish white powder of aspartate of magnesia, which, when recrystallized from hot water, assumes the form of crystalline crusts. These crusts yield an aqueous solution neutral to vegetable colours; they burn when heated, with evolution of ammonia but without intumescence, and leave carbonate of magnesia; they dissolve in about 16 pts. of boiling water, and pretty easily in weak alcohol, but are insoluble in absolute alcohol. (Wittstock, *Pogg.* 20, 352.)

The aqueous solution of bibasic aspartate of magnesia forms with tartar-emetic, a precipitate which dissolves in excess of either of the salts. (Plisson.)

ASPARTATE OF ZINC. — Small white opaque granules (Piria); not deliquescent; tasting first like broth, afterwards astringent.

ASPARTATE OF LEAD — ¶. *a. Bibasic.* — *a. Inactive.* — The soda-salt of inactive aspartic acid forms with an ammoniacal solution of neutral acetate of lead a curdy precipitate; and the filtrate diluted with a large quantity of water, and left at rest for a few days, deposits nacreous crystals united in very hard spherical masses having a radiated structure. This salt does not suffer any diminution in weight at 100°. (Pasteur.)

$C^{\circ}NH^{\circ}O^{\circ}$	124	...	35.6	63.9
$PbO, C^{\circ}NH^{\circ}PbO^{\circ}$	348	...	100.0	

The formula $C^{\circ}NH^{\circ}Pb^{\circ}O^{\circ}$, analogous to those of the basic aspartates of baryta and lime, would require 66.1 p.c. PbO .

β. Active. The soda-salt of active aspartic acid exhibits with ammoniacal acetate of lead, the same phenomena as that of the inactive acid, a soft precipitate being deposited, and, when the liquid is left at rest, crystals are formed united in hard radiated nodules; but these crystals consist merely of a peculiar subacetate of lead containing 65 p. c. oxide of lead. (Pasteur.) †.

b. Monobasic. — Aspartate of potash and bibasic aspartate of lime precipitate basic and neutral acetate of lead; the precipitate dissolves in an excess of either of the salts and in nitric acid. (Plisson.)

		Dried at 120°.		Plisson.	
PbO	112	...	47.46	48.81
8 C	48	...	20.34	21.35
N	14	...	5.94	6.09
6 H	6	...	2.54	2.69
7 O	56	...	23.72	21.06
$C^{\circ}NH^{\circ}PbO^{\circ}$	236	...	100.00	100.00

Nitro-aspartate of Lead. — Asparagin is heated with nitric acid quite free from nitrous acid; the liquid containing nitric acid, aspartic acid, and ammonia, mixed with nitrate of lead; and the precipitate redissolved by heat: the solution left to cool, deposits needles resembling formiate of lead. These crystals do not sustain any loss when heated to 150° in a current of air, but are decomposed with slight deflagration at a higher temperature. With oil of vitriol, they give off vapours of nitric acid, and are but slightly decomposed by cold, more completely by hot oil of vitriol. (Piria.) The formation of this salt succeeded only once; it appears to depend on the two salts being mixed in the exact proportion required, and on a proper degree of concentration of the liquid. (Piria.)

		Piria.			
2 PbO	224	...	55.72	55.47
8 C	48	...	11.94	11.98
2 N	28	...	6.96	7.28
6 H	6	...	1.50	1.62
12 O	96	...	23.88	23.65
$C^{\circ}NH^{\circ}PbO^{\circ}, PbO, NO^{\circ}$	402	...	100.00	100.00

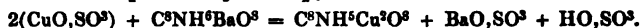
FERRIC ASPARTATE. — Sesquichloride of iron forms with basic aspartate of magnesia a precipitate which dissolves in excess of either of the two salts; with aspartate of potash it forms a deep red transparent mixture. (Plisson.)

ASPARTATE OF NICKEL. — The solution deposits by evaporation a green fissured mass. (Plisson.)

CUPRIC ASPARTATE. — Obtained by precipitating cupric sulphate with aspartate of potash. Sky-blue needles, having a silky lustre, an astringent taste, sparingly soluble in cold, easily in hot water and in aqueous aspartate of soda. (Plisson & Henry.) When 1 At. cupric sulphate is mixed with 1 At. aspartate of soda, crystals of cupric aspartate are obtained by evaporation and cooling, and the mother-liquor retains a

the soda-salt does not deposit any crystals of the copper salt by evaporation. (Plisson & Henry.)

—¶. When cupric sulphate is mixed with a solution of neutral aspartate of baryta, a rather dark violet liquid is obtained, which, on cooling, becomes filled with very light, silky, pale-blue needles of basic aspartate of copper, which are but sparingly soluble in water. The supernatant liquid has but little colour, and retains a large quantity of free sulphuric acid. Hence neutral aspartate of copper exists only in solution, and the final reaction is expressed by the equation :



The basic salt gives off 31·78 (10 At.) water at 160°.

	Crystals.		Dessaignes.	
$\text{C}^6\text{NH}^6\text{O}^8$	115	40·35		
2 CuO	80	28·07	27·98	
10 HO	90	31·58	31·65	
$\text{C}^6\text{NH}^6\text{Cu}^2\text{O}^8 + 10\text{Aq.}$	285	100·00		

This salt dissolves in aqueous aspartic acid, with aid of heat, reproducing the violet solution. (Dessaignes.) ¶

ASPARTATES OF MERCURY. — The potash-salt forms a precipitate with mercurous nitrate, and the bibasic lime-salt with corrosive sublimate. Both precipitates redissolve in excess of either salt. (Plisson.) — ¶ Mercuric oxide boiled with aspartic acid yields mercuric aspartate in the form of a white powder. (Dessaignes.)

	Dried at 100°.		Dessaignes.	
$\text{C}^6\text{NH}^6\text{O}^7$	124	36·48		
2 HgO	200	63·52	63·58	
$\text{HgO}, \text{C}^6\text{NH}^6\text{HgO}^8$	324	100·00		

The composition of this salt is analogous to that of the basic lead-salt analysed by Pasteur (p. 237).

ASPARTATE OF SILVER. — *a. Bibasic.* — Aspartate of potash and basic aspartate of lime form with nitrate of silver a white precipitate soluble in excess of either salt. (Plisson.) — ¶ Nitrate of silver added to slightly alkaline aspartate of ammonia, forms a precipitate which disappears again on stirring. After 24 hours, white heavy, entangled crystals, susceptible to light, are formed. (Dessaignes, Pasteur.) The active and inactive acids yield precisely similar results. (Pasteur.) ¶

	Liebig:		Dessaignes.		Pasteur.	
					active	inactive
2 AgO	232	66·86	66·62	66·8	66·7	66·9
8 C	48	13·84	14·07			
N	14	4·04				
5 H	5	1·43	1·47			
6 O	48	13·83				
$\text{C}^6\text{NH}^6\text{Ag}^2\text{O}^8$	347	100·00				
					Wolff.	
2 AgO	232	66·86	66·62	66·6		
8 C	48	13·84				
N	14	4·04				
5 H	5	1·43				
6 O	48	13·83				
$\text{C}^6\text{NH}^6\text{Ag}^2\text{O}^8$	347	100·00				

Liebig has not given the mode of preparation of the salt which he analysed, Laurent doubts its purity. — ¶ Liebig's result is however confirmed by those of Dessaignes, Pasteur, and Wolf. Dessaignes' salt was dried in vacuo; Pasteur's at 100°. Pasteur found in the same salt (by decomposing it with sulphuretted hydrogen, 137·99 p. c. aspartic acid (C⁶NH⁷O⁸), the formula requiring 38·33. — According to Pasteur also, the crystallized salt, after being merely pressed between paper and then dried for 24 hours at ordinary temperatures, has a composition analogous to that of the basic lead and mercury salts already described (pp. 237, 238); thus:

<i>Dried at ordinary temperatures.</i>		Pasteur.	
C ⁶ NH ⁶ O ⁷	124	34·83	
2 AgO.....	232	65·17	65·2 65·3
AgO, C ⁶ NH ⁶ AgO ⁸			
	356	100·00	

Pasteur suggests however that the salt thus dried may retain 1 At. water mechanically or chemically combined.

b. *Monobasic.* — When the mother-liquor which remains after the separation of salt *a* is left to crystallize, it deposits yellowish crystals of the monobasic salt. (Dessaignes.)

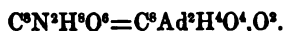
	Dessaignes.	Boutron & Pelouze.
C ⁶ NH ⁶ O ⁷	124	51·67
AgO.....	116	48·33
C ⁶ NH ⁶ AgO ⁸		
	240	100·00
		¶

Aspartic acid is less soluble in weak *alcohol* than in water, and quite insoluble in absolute alcohol. (Plisson.)

¶ *Malamate* [*Aspartate* ?] of *Ethyl.* — When malate of ethyl obtained by Demondeair's process (p. 227) is saturated with dry ammoniacal gas, the liquid becomes heated, and in the course of a day solidifies to a radiated crystalline mass, which, after being drained and then washed with common ether, consists of pure malamate of ethyl. By further treatment with ammonia, it is converted into malamide. (Pasteur, *N. Ann. Chim. Phys.* 38, 437; *Jahresber.* 1853, 411.)

β. *Amidogen-nucleus.* C⁶Ad²H⁴O⁴.

Asparagine.



VAUQUELIN & ROBIQUET. *Ann. Chim.* 57, 88.

ROBIQUET. *Ann. Chim.* 72, 143.

BACON. *Ann. Chim. Phys.* 34, 202; also *J. Chim. méd.* 2, 551; abstr. *Mag. Pharm.* 16, 140.

PLISSON. *Ann. Chim. Phys.* 35, 175; also *J. Pharm.* 13, 477; also *N. Tr.* 16, 2, 177. — *Ann. Chim. Phys.* 37, 81; also *J. Pharm.* 14, 177; also *N. Tr.* 17, 2, 165.

- PLISSON & O. HENRY. *Ann. Chim. Phys.* 45, 304; also *J. Pharm.* 16, 713; also *Schw.* 61, 314.
 WITSTOCK. *Pogg.* 20, 346.
 BOUTRON CHARLARD & PELOUZE. *Ann. Chim. Phys.* 52, 90; also *J. Pharm.* 19, 208; also *Schw.* 67, 393; also *Ann. Pharm.* 6, 75.
 LIEBIG. *Pogg.* 31, 320; also *Ann. Pharm.* 7, 146.
 REGIMBEAU. *J. Pharm.* 20, 631; abstr. *Ann. Pharm.* 13, 307.—
J. Pharm. 21, 665.
 BILTZ. *Ann. Pharm.* 12, 54.
 PIRIA. *N. Ann. Chim. Phys.* 22, 160.
 LAURENT. *N. Ann. Chim. Phys.* 23, 113; also *Compt. rend.* 22, 790.
 DESSAIGNES & CHAUTARD. *N. J. Pharm.* 13, 245.
 DESSAIGNES. *N. Ann. Chim. Phys.* 34, 143; also *Ann. Pharm.* 82, 237.

Spargelstoff, *Althäin*, *Asparamid*, *Asparagin*, *Asparamide*, *Malamide*, *Althéine* (Bacon), *Agédoile* (Caventou).—Discovered in 1805 by Vauquelin & Robiquet, who obtained it from asparagus roots. Plisson showed that the *Agédoile* discovered by Caventou in liquorice-root, and the altheine found by Bacon in marsh-mallow root, are identical with asparagine.

Sources. In the young shoots of *Asparagus off.* (Vauquelin & Robiquet); in the haulm and root of *Convallaria majalis* and *multiflora* and of *Paris quadrifolia* (Walz); in the root of *Glycyrrhiza glabra* (Caventou), of *Althæa off.* (Bacon), especially in that from Narbonne (Buchner, *Repert.* 41, 368), of *Symphytum off.* (Blondeau & Plisson, *J. Pharm.* 13, 635), of *Robinia pseudacacia* (Hlasiwetz, *J. pr. Chem.* 64, 64.) [Reinsch (*Repert. Pharm.* [2], 39, 198; *Berz. Jahresber.* 26, 524) had stated that the root of this plant contained a peculiar acid, which he named *robinic acid*; but Hlasiwetz showed that the crystals which separate from the aqueous decoction of the root after evaporation to a syrup, are not, as Reinsch supposed, the ammonia-salt of a peculiar acid, but consist of asparagine];—in the tubers of *Solanum tuberosum* (Vauquelin); in the leaves of *Atropa Belladonna* (Biltz, *Ann. Pharm.* 12, 54); in the sprouts of the hop (Leroy, *J. Chim. méd.* 16, 8); in the milky juice of *Lactuca sativa* (Aubergier); in *Ornithogalum caudatum* (Link.)—The *Cynodine* obtained by Semnola (*Berzel Jahresber.* 24, 525) from *Cynodon Dactylon* appears also to be identical with asparagine. The seeds of the following papilionaceous plants contain no asparagine, but the germs which spring from them when kept in a cellar where water has access to them, are rich in that substance. *Pisum sativum*, *Ervum Lens*, *Phaseolus vulgaris*, *Vicia Faba* and *sativa*, *Cytisus Laburnum*, *Trifolium pratense*, *Hedysarum Onobrychis*. [Also, according to Dessaignes, (*N. Ann. Chim. Phys.* 34, 183), *Lathyrus odoratus* and *latifolius*, *Genista juncea*, *Colutea arborescens*]. One litre of juice expressed from the germs yields, in the case of peas, 8.5 grammes of pure asparagine; of French beans, the juice of which likewise contains nitre, 5.5 grm.; of broad Windsor beans, 14.0 grm.; of vetches, 9.0 to 40.9 grm. The root-germs of vetches contain as much asparagine as the stem-germs; but the permanent cotyledons contain none. The corms of *Dahlia pinnata*, and the roots of *Althæa off.*, when kept in a cellar, yield germs containing asparagine; but the germs of oats, buckwheat, cucumber-seed, and potato-tubers are free from that substance. (Dessaignes & Chautard.) The germs of vetches formed in light contain just as much asparagine as those which grow in the dark; the nitrogen required for the formation of the asparagine appears to be derived, not from the air, but from the legumin of the seed; this however contains no asparagine, the plant arrived at the flowering stage contains only a trace, and

hand (*N. Ann. Chim. Phys.* 31, 70), finds, like Dessaignes & Chautard, that green vetches growing in light are free from asparagine, while those which grow in a cellar yield 5 or 6 grm. asparagine in 1 litre of juice. — Asparagine is likewise contained in chestnuts. (*Dessaigues, N. J. Pharm.* 25, 28.) ¶.

Preparation. 1. *From Asparagus.* The juice of asparagus expressed, filtered, and evaporated to a syrup, deposits, after standing quietly for some time, crystals of asparagine, which must be mechanically separated from crystals of saccharine matter which accompany them, and purified by recrystallization from water. (*Vauquelin & Robiquet.*) — As the mucus of asparagus interferes with the crystallization, it must be decomposed by fermentation, the young shoots of *Asparagus off.* or *acutifolius* (which latter yield more asparagine) being gathered in the month of May, wrapped up in damp linen, and left for about 4 days in the case of *Asparagus acutifolius*, and for 8 days in that of *Asp. off.*, moistening them frequently during the whole time, till they acquire an unpleasant odour. They must then be bruised and pressed, with addition of water; the juice heated and strained from the coagulated albumin and chlorophyl; the syrup, which must be thicker when obtained from *Asp. off.* than in the case of *Asp. acutifolius*, exposed for several days to the open air; and the resulting crystals washed with water or weak spirit. (*Reginbeau.*)

II. *From Liquorice root.* — *Robiquet* exhausts the fresh root cut into small pieces with water; precipitates the albumin from the filtrate by boiling, the glycyrrhizin by distilled vinegar, the phosphoric and malic acids together with brown colouring matter, by neutral acetate of lead, and the excess of lead by sulphuretted hydrogen; and evaporates the remaining liquid to a small bulk, whereupon it deposits crystals of asparagine after a few days. — *Plisson*, instead of acetic uses sulphuric acid, which precipitates the glycyrrhizin more quickly, and renders smaller quantities of acetate of lead and sulphuretted hydrogen sufficient in the subsequent part of the process. From 100 parts of the fresh root he obtained 0·8 pt. asparagine; the dry root yielded none.

III. *From Marsh-mallow root.* — 1. The dry root freed from the outer skin and cut in pieces is thrice exhausted at a gentle heat with four times its weight of water; and the strained infusion boiled and evaporated to a thin syrup: this, when left for some days in a cool place, yields crystals which must be washed with a little cold water, and purified by crystallization from water; they amount to 2 per cent. of the root. (*Plisson & Henry.*) — The same process is adopted by *Boutron & Pelouze*, excepting that they likewise bruise the root and exhaust it twice by 48 hours' maceration with water cooled to 70°. — *Reginbeau* objects to the bruising of the root, because it then yields a gummy infusion; he treats it with water at 1° or 2°, and adds alcohol to the evaporated infusion, to prevent decomposition. — *Larocque* precipitates the mucus contained in the watery extract by alcohol before evaporation. — 2. The dry root, cleaned and cut in pieces, is exhausted four times with cold water; the infusion evaporated in the water-bath; the very soft extract boiled with $\frac{1}{2}$ pt. alcohol of 32° Bm. (to 1 pt. of the root); the alcohol decanted; the residue thrice treated in the same manner; the extracts separately set aside for five days, whereupon they, especially the second,

deposit crystals of asparagine; the alcoholic liquid decanted therefrom abandoned to spontaneous evaporation, whereupon it deposits an additional quantity of impure asparagine in the form of a yellowish white powder; the whole of the asparagine (amounting to 0.3 per cent. of the root) washed with cold water, which removes a quantity of brown extractive matter, and boiled with 25 pts. of spirit of 20° Bm., or with 17 pts. of water; and the solution purified by treatment with animal charcoal, filtered boiling hot, and left to cool: it then deposits white crystals. (Plisson.)—In a similar manner, Blondeau obtained asparagine from *Symphytum* root.—If the extract has been too much dried, or if the alcohol has been too strong, no asparagine is extracted; if the alcohol is too weak, nothing crystallizes out. (Plisson.)—By Plisson's process, using spirit of 80 per cent., the quantity of asparagine obtained amounts to 0.3 per cent.; with 60 per cent. spirit, only $\frac{1}{4}$ of that quantity; by boiling the root with water, only a trace is obtained (Trommsdorff, *N. Tr.* 19, 1, 170;) because the gum [starch?] which dissolves in the water, converts the asparagine into aspartic acid. (Boutron & Pelouze.)—If the watery extract obtained by Plisson's process, which becomes very acid during the evaporation, be boiled five times with spirit of sp. gr. 0.835, the resulting alcoholic solution deposits on cooling, first a brown mass, and then, on decanting the liquid from this deposit, a quantity of crystallized asparagine, amounting to 0.4 p. c. of the root. But the mother-liquor, together with the portion of the extract not dissolved by the alcohol, yields, when dissolved in water, precipitated by acetate of lead, freed from lead by sulphuretted hydrogen, and then filtered and evaporated, a thick syrup, which solidifies over night in a crystalline mass, whence, by boiling with alcohol, an additional 1.2 per cent. of asparagine may be obtained, together with a small quantity of aspartate of magnesia. (Wittstock.)—If the root be exhausted with boiling spirit of sp. gr. 0.835, no asparagine is obtained, either from the alcoholic extract, or from the residue of the root when exhausted with cold water. (Wittstock.)—The root, after being twice boiled with water, yields to cold water 0.7 p. c. asparagine. (Boutron & Pelouze.) Similarly the root, after being exhausted with ether, and then with alcohol of 36° Bm., yields asparagine to lukewarm water. (Larocque, *N. J. Pharm.* 6, 352.)

IV. *From Belladonna.* The extract obtained by evaporating the expressed juice, becomes filled, when left at rest for several days, with crystals of asparagine, which may be washed with cold water and crystallized several times from hot water. (Biltz.)

V. *From the young shoots of Vetches, &c.* (p. 240).—Vetches are left to germinate on moist garden-mould or sand till the shoots are about half a metre long; the juice pressed out, evaporated, strained from the coagulated albumin, and concentrated to a syrup, which then, after standing for some time, yields brown crystals. Lastly, these crystals are washed with cold water, crystallized from hot water, and completely purified by solution in hot water, digestion with animal charcoal, and recrystallization. By this process, 100 pts. of vetches yield 4.5 pts. of brown or 3.0 pts. of pure crystals. (Piria.)

The crystals obtained by either of these processes contain 2 At. water which may be expelled by heating to 100°.

Properties, vid. Hydrated Asparagine (p. 241).

8 C	48	36·36	36·70	38·94	37·82
2 N	28	21·21	21·19	22·47	22·13
8 H	8	6·06	6·17	6·37	5·67
6 O	48	36·37	35·94	32·22	34·38

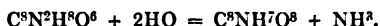
$C^8N^2H^8O^6$ 132 100·00 100·00 100·00 100·00

Asparagine is related to malic acid in the same manner as oxamide ($C^4N^2H^4O^4$) to oxalic acid ($C^2H^2O^3$). Piria. — Nevertheless, Pasteur regards malamide prepared as above from malic ether as different from asparagine (p. 227).

Decompositions. 1. From asparagine roasted till it becomes slightly brown, water extracts a small quantity of asparagine together with a bitter substance, and acquires a yellow colour by transmitted, and green by reflected light. (Plisson & Henry.) — 2. Asparagine subjected to dry distillation yields carbonate of ammonia, a colourless liquid, then a brown empyreumatic oil, and charcoal. (Trommsdorff, Biltz.) In the open fire, asparagine swells up, turns brown, gives off at first vapours having an empyreumatic, woody odour, afterwards vapours having an ammoniacal animal odour, and leaves a loosely coherent charcoal, which burns completely away. (Vauquelin & Robiquet; Plisson.) — When asparagine is heated to 200°, till it no longer evolves any ammoniacal odour, there remains a brown, sparingly soluble substance, which, when treated with hydrochloric acid, yields aspartic acid crystallized in short hard prisms. (Dessaigues; *comp.* p. 230.) — Chlorine, bromine, and iodine exert no action on asparagine. (Plisson & Henry.) — 4. Cold nitric acid containing nitrous acid quickly converts asparagine into nitrogen gas and malic acid. (Piria.)

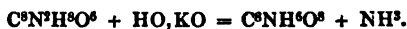


When nitric oxide gas is passed through a solution of 1 pt. asparagine in 1 pt. of pure and moderately strong nitric acid, an evolution of nitrogen gas commences immediately and rapidly increases; the liquid becomes slightly heated; and if it be then saturated with marble and filtered, it will afterwards throw down malate of lead from a solution of the acetate. (Piria.) — 5. By solution in most of the stronger acids and heating, asparagine is resolved into an ammonia-salt and aspartic acid:

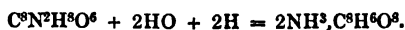


It dissolves, without effervescence, in cold nitric acid (Robiquet), forming nitrate of ammonia and aspartic acid. (Plisson & Henry.) It dissolves in 3 pts. of oil of vitriol, without blackening, forming sulphate of ammonia and aspartic acid, which when heated turns brown from decomposition. (Plisson & Henry.) Dilute sulphuric acid likewise converts it into ammonia and aspartic acid. (Piria.) Its solution in strong hydrochloric acid evaporated at a gentle heat, leaves sal-ammoniac and aspartic acid. (Plisson & Henry.) The laminæ of asparagine which form when its solution in hydrochloric acid is evaporated to a syrup after an hour's boiling, are distinguished by their deliquescence, arising from adhering hydrochloric acid; if, therefore, the liquid be saturated with pieces of marble, aspartic acid of ordinary solubility separates out. (Piria.) Concentrated acetic acid likewise forms aspartic acid and acetate of ammonia, though slowly. (Plisson & Henry.) — 6. In a similar manner, asparagine

is converted by the action of the stronger salifiable bases into a salt of aspartic acid, and ammonia which escapes (Plisson):



Aqueous ammonia produces this change slowly at a boiling heat. (Plisson & Henry.)—Hydrate of potash triturated with asparagine gives off ammonia after a while. (Robiquet.) When such a mixture is fused at a gentle heat, ammonia is evolved and aspartate of potash formed, which however, at a stronger heat, is converted, with evolution of hydrogen and ammonia, into acetate and oxalate of potash. (Piria.) Plisson & Henry, who heated the mixture to redness, likewise obtained oxalate and carbonate of potash.—Cold potash-solution eliminates ammonia from asparagine, only when very much concentrated; the hot solution effects the transformation with facility. (Plisson & Henry.)—By boiling with baryta-water, 132 pts. (1 At.) of dry asparagine are converted into 132·7 pts. (1 At.) of aspartic acid. (Boutron & Pelouze.)—Magnesia and hydrated oxide of lead likewise decompose asparagine, when boiled with it for some time in water, yielding ammonia and a salt of aspartic acid. (Plisson.)—7. Asparagine dissolved in water is very slowly converted, by boiling under the ordinary pressure, into aspartate of ammonia (Plisson & Henry); but when it is enclosed in a sealed glass tube, and heated till the pressure amounts to 3 or 4 atmospheres, the decomposition takes place immediately without formation of any permanent gas. (Boutron & Pelouze.)—On the other hand, asparagine dissolved in water is not altered by exposure to a pressure of 30 atmospheres at ordinary temperatures. (Erdmann, *J. pr. Chem.* 20, 69.)—8. The solution of pure asparagine crystals may be kept without alteration, but the solution of the crystals which still retain some degree of colour, passes into a state of fermentation, acquiring a slightly alkaline reaction and the odour of putrefying animal substances, and becoming covered with a film of infusoria, while the whole of the asparagine is converted into succinate of ammonia. (Piria.)



Consequently, 2 HO and 2 H are added to the asparagine, the hydrogen being derived from the putrefying matter. The solution of perfectly pure asparagine passes into the same state of fermentation, on addition of a small quantity of the juice expressed from the young shoots of vetches. (Piria.) Asparagine fermented under the influence of casein, is converted first into aspartate of ammonia, then into succinate. (Des-saignes, p. 110.)

Combinations. With Water.—*a. Hydrated Asparagine; crystallized Asparagine.*—*Preparation,* (p. 241.)—Transparent, colourless crystals belonging to the right prismatic system.—Rectangular octohedrons, truncated on the shorter edges of the base and at the acute angles of the base. (Vauquelin & Robiquet; Plisson.) Right rhombic prisms, $u' : u = 130$ (Vauq. & Rob.); 129·30 (Bernhardi); the acute summits and terminal edges truncated (Vauq. & Rob.); the acute summits truncated, but only two terminal edges truncated at each end, and on alternate sides: $p : a = 116^\circ 21'$ (Bernhardi). Six-sided prisms (Plisson & Henry); rhombohedrons [?] and six-sided prisms. (Leroy).—Compare Bernhardi, (*Ann. Pharm.* 12, 58; Miller, *Phil. Mag.* 6, 106; also *Pogg.* 36, 477).

The crystals of asparagine are hard and brittle (Vauquelin &

teeth. (Plisson & Henry.) Their specific gravity at 14 is 1.519. (Plisson & Henry.) They are inodorous (Plisson & Henry), and nearly tasteless (Robiquet); have a juicy taste (Plisson & Henry); a cooling but somewhat nauseating taste. (Vauquelin & Robiquet.) They do not impart any odour of asparagus to the urine, even when taken in large quantity. (Plisson & Henry.) Their aqueous solution slightly reddens litmus. (Plisson & Henry, Piria, Trommsdorf, Leroy.) They are permanent in the air. (Trommsdorf.) They soften at 100° (Plisson & Henry), becoming milk-white (Biltz), and giving off all their water (Boutron & Pelouze; Liebig), which, according to Liebig, amounts to 12.35, and according to Marchand (*J. pr. Chem.* 20, 264), to 12.20 per cent. ¶. The solution of asparagine in water or in alkalis turns the plane of polarization of a ray of light to the left, but its solution in acids turns it to the right. Like other circularly polarizing bodies, it forms crystals having hemihedral faces. (Pasteur.) ¶.

	<i>Crystals.</i>			Liebig.	Piria.	Marchand
8 C	48	32.00	32.35	31.80	32.20	
2 N	28	18.67	18.73	18.80	19.08	
10 H	10	6.67	6.84	6.85	6.60	
8 O	64	42.66	42.08	42.55	42.12	
$C^8N^2H^{20}O^6 + 2HO$	150	100.00	100.00	100.00	100.00	

b. Aqueous Asparagine. — The crystals dissolve in 11 pts. (Biltz), in about 60 pts. (Leroy), in 58 pts. (at 13°, Plisson & Henry) of cold water, and in 4.44 pts. of boiling water. (Biltz.) It dissolves in greater quantity, the more completely it is freed from aspartate of lime and magnesia. (Regimbeau.) From a saturated aqueous solution mixed with an equal quantity of alcohol, crystals of asparagine separate after a while. (Biltz.)

Asparagine cannot be melted with phosphorus; when it is melted with sulphur, it forms a red solid mass, which melts again at a stronger heat, and gives off sulphuretted hydrogen, but without decomposition of the [greater part of the] asparagine. (Plisson & Henry.)

Sulphate of Asparagine. — The solution of 1 pt. asparagine in 1 pt. dilute sulphuric acid, evaporated over oil of vitriol at ordinary temperatures, deposits crystals of asparagine, and leaves a mother-liquor, which dries up to a colourless amorphous mass, from which carbonate of lime throws down asparagine in its original state. (Dessaignes & Chautard.) ¶. With less than 2 At. sulphuric acid, crystals of asparagine always separate out; a solution of asparagine in 2 At. sulphuric acid no longer yields crystals of asparagine, but the compound cannot be obtained in crystals, even on addition of alcohol. (Dessaignes.) ¶.

Hydrochlorate of Asparagine. — *a.* A solution of 1 At. asparagine in 1 At. hydrochloric acid, evaporated over lime at ordinary temperatures, leaves a very solid, pleasantly acid gum, which contains but a mere trace of sal-ammoniac, and yields asparagine again when decomposed by carbonate of soda. (Dessaignes & Chautard.) — ¶. A crystallized compound is obtained by dissolving 1 At. asparagine in 1 At. dilute hydrochloric acid, evaporating the solution at a gentle heat, and adding alcohol. — The same compound is likewise formed by exposing hydrated asparagine in fine powder to the action of dry hydrochloric acid gas, and expelling

the excess of the gas by a stream of dry air: the asparagine then increases in weight by 23.19 per cent. The compound when exposed to moist air gives off acid vapours; and on dissolving it in hot water after the evolution of these vapours has ceased, and leaving the solution to cool, large crystals separate out, which, after rapid washing and drying, are not deliquescent. (Dessaignes.)

<i>Crystals.</i>	132.0	78.35	<i>Dessaignes.</i>
$C^6N^2H^8O^6$	36.4	21.65	21.39
$C^6N^2H^8O^6, HCl$	168.4	100.00	

b. Anhydrous asparagine absorbs dry hydrochloric acid gas. After the stream of gas had been continued for a long time, a compound was obtained, which in two instances yielded 10.02 and 10.98 p. c. hydrochloric acid. The formula $2C^6N^2H^8O^6, HCl$ requires 12.11 p. c. (Dessaignes.)

Nitrate of Asparagine. — On dissolving 1 At. asparagine in 1 At. dilute nitric acid, concentrating the solution to a syrup in vacuo over lime, and placing the residue in a gently heated drying chamber, it changes almost entirely to large non-deliquescent crystals, containing nothing but asparagine and nitric acid. (Dessaignes.) ¶.

Asparagine with Potash. — A warm aqueous solution of asparagine acquires an alkaline reaction, by addition of a mere trace of potash, and on cooling yields crystals, which, after washing, redden litmus, and are free from potash. (Plissou.) Crystals of asparagine (but not the solution), treated with a saturated solution of bicarbonate of potash, evolve bubbles of carbonic acid, but often not till gently heated. (Plisson & Henry.) — The crystalline powder of asparagine, when an alcoholic solution of potash is poured upon it, forms a soft compound, which becomes syrupy when heated, and mixes little or not at all with the supernatant liquid. This syrup repeatedly washed with water, and dried in the hot air chamber, becomes gummy, and solidifies on cooling to a transparent colourless glass, which contains 26.10 p. c. potash, and is therefore $C^6N^2H^7KO^5$. [The formula $KO, C^6N^2H^8O^6$ agrees much better with the quantity of potash found.] — The compound swells up strongly when gently heated, and gives off ammonia. (Laurent.) — ¶. On gradually adding an excess of finely pounded asparagine to an alcoholic solution of potash, gently heated in a glass tube closed with a cork, the liquid, which is at first turbid, becomes clear after a while, and the sides of the tube become covered with laminated crystals. (Dessaignes.) ¶.

Aqueous asparagine does not precipitate baryta-water. (Plisson.)

Aqueous asparagine forms with lime-water an alkaline mixture, yielding crystals of asparagine, which redden litmus again after washing, but contain a little lime. (Biltz.) — ¶. Asparagine dissolves lime, but the compound does not crystallize, and could not be obtained without excess of lime. When heated to 100° , it gives off a small quantity of ammonia. When dried in vacuo and decomposed with oxalic acid, it yielded 20.66, 20.50, and 20.62 p. c. lime, and 84.97 asparagine dried at 130° . The formula $C^6N^2H^7CaO^5$ requires 18.60 p. c. lime, and 84.41 p. c. asparagine, $C^6N^2H^8O^6$. (Dessaignes.) ¶.

Aqueous asparagine does not precipitate tartar-emetic, basic acetate

chloride of tin (Frommsdorf); or the salts of manganese of copper (Plisson & Henry).

Asparagine with Zinc-oxide. — A solution of zinc-oxide in boiling aqueous asparagine yields, on cooling, crystalline laminæ, which give off only a trace of water at 100°; they contain 25·17 per cent. of zinc-oxide, and are therefore = C⁸N²H⁷ZnO⁶. (Dessaigues & Chautard.)

¶. *Asparagine with Cadmic oxide.* — Cadmic oxide dissolves readily in aqueous asparagine; and the liquid, if filtered hot, deposits on cooling a large quantity of delicate shining prisms. (Dessaigues.)

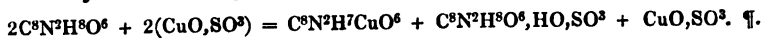
<i>Dried in vacuo.</i>		Dessaigues.	
CdO	64	34·05 34·66
C ⁸ N ² H ⁸ O ⁶	124	65·95	
C ⁸ N ² H ⁷ CdO ⁶	188	100·00	¶.

Asparagine with Lead-oxide. Asparagine boiled with an aqueous solution of neutral acetate of lead, slowly drives out the acetic acid and forms a solution, which, when evaporated over oil of vitriol, leaves a colourless gum, difficult to dry even at 100°. — The aqueous solution of 1 At. asparagine and 2 At. nitrate of lead leaves a gum but no crystals when evaporated. (Dessaigues & Chautard.)

Asparagine with Cupric Oxide. — 1. The azure-blue solution obtained by boiling asparagine with cupric oxide and water deposits an azure-blue crystalline powder. — 2. Better: A mixture of the hot-saturated solutions of asparagine and cupric acetate, yields, especially when heated, an ultramarine-coloured precipitate which increases as the liquid cools. — The compound does not give off any water when heated to 100° in a dry current of air, but decomposes at a higher temperature, with copious evolution of ammonia. It is nearly insoluble in cold water, dissolves sparingly in hot water, readily in acids and in ammonia. If the copper be thrown down from the solution of this salt by sulphuretted hydrogen, the filtrate yields by evaporation, crystallized asparagine in its original state. (Piria.)

CuO	40	24·54 Piria.
8 C	48	29·45 29·36
2 N	28	17·18 17·25
7 H	7	4·29 4·43
5 O	40	24·54 24·57
C ⁸ N ² H ⁷ CuO ⁶	163	100·00 100·00

¶. When 1 At. asparagine and 1 At. cupric sulphate were dissolved together, the mixture yielded on cooling, needles of the compound of asparagine with cupric oxide. The liquid filtered therefrom, which was blue and strongly acid, could not be made to crystallize. It contained asparagine, sulphuric acid and cupric oxide. The reaction may be represented by the following equation:



Asparagine with Mercuric Oxide. — Red oxide of mercury dissolves readily in hot aqueous asparagine, forming a colourless liquid, which after

gum. This gum swells up at 100°, assuming a dark grey colour, and if then dissolved in water, leaves a large quantity of grey powder, which, when triturated with gold and hydrochloric acid, amalgamates the gold. (Dessaignes & Chautard). — ¶. On gradually adding mercuric oxide to a hot solution of asparagine till it no longer dissolves, and then filtering and evaporating, the liquid dried up to a gummy mass, which, after drying in vacuo, contained only 41.49 p. c. mercuric oxide, instead of 46.76, the quantity required by the formula $C^8N^2H^7O^6, 2HgO$. — Asparagine was added in excess to boiling water in which mercuric oxide was suspended, and the liquid boiled, till the oxide was converted into a perfectly white powder. This, after being several times washed with boiling water, yielded results which did not agree exactly either with the formula $C^8N^2H^7O^6, 2HgO$, or with $C^8N^2H^8O^6, 2HgO$, as the following comparison will show. (Dessaignes.)

	Dessaignes.		Calculation.	
			$C^8N^2H^7O^6, 2HgO$	$C^8N^2H^8O^6, 2HgO$
Mercuric oxide	62.61	62.90	63.71	62.07
Asparagine (dried at 140°)	41.76	41.40	38.93	37.93
	104.37	104.30	102.64	100.00

Asparagine with Mercuric Chloride. — When 1 At. asparagine and 2 At. mercuric chloride were dissolved together in water, the liquid yielded on cooling, a mixture of delicate prisms and large crystals, the latter consisting of asparagine; but a solution of 1 At. asparagine and 4 At. mercuric chloride yielded a homogeneous crop of crystals resembling the slender prisms above mentioned. (Dessaignes.)

	Dried in vacuo.		Dessaignes.	
$C^8N^2H^8O^6$	132.0	19.61		
4 Hg	400.0	59.36	59.10	
4 Cl	141.6	21.03	21.62	
$C^8N^2H^8O^6, 4HgCl$	673.6	100.00		¶.

Asparagine with Silver-oxide. — Oxide of silver dissolves very readily in boiling aqueous asparagine; and the colourless filtrate evaporated in the dark over oil of vitriol, yields crystals united in fungoid masses, which are black by reflected and yellowish brown by transmitted light. After drying in vacuo over oil of vitriol, they contain 45.77 p. c. silver, and are therefore = $C^8N^2H^7AgO^6$.

Asparagine with Nitrate of Silver. — The aqueous solution of 1 At. asparagine and 1 At. nitrate of silver, yields, when evaporated in the dark over oil of vitriol, first crystals of asparagine, then dendritic crystals, which, after drying over oil of vitriol, contain 41.33 per cent. of silver. A mixture of 2 At. nitrate of silver and 1 At. asparagine, yields by evaporation, crystalline discs consisting of very fine needles, which give off nothing at 100°, contain 47.7, and, after recrystallization from water and drying at 100°, 45.29 p. c. silver: they are therefore perhaps = $C^8N^2H^8O^6, 2(AgO, NO^2)$. (Dessaignes & Chautard.)

Asparagine is insoluble in cold absolute alcohol (Plisson & Henry); it is insoluble in cold, but dissolves in 700 pts. of boiling alcohol of 98 per

alcohol of 80 per cent; and in 500 pts. of cold and 40 pts. of boiling alcohol of 60 per cent. (Biltz.)

It does not dissolve in ether, or, even with the aid of heat, in oils either fixed or volatile. (Plisson & Henry.)

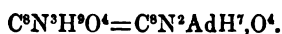
Oxalate of Asparagine. — An aqueous solution of 150 pts. (1 At.) crystallized asparagine and 126 pts. (1 At.) hydrated oxalic acid, yields by evaporation, a homogeneous mass consisting of very small crystals, which, after drying in vacuo, amount to 222 pts. and give off nothing at 100°. Consequently, 6 At. of water have escaped, and there remains the compound $C^6N^2H^8O^6$, $C^4H^2O^6$. — An aqueous solution of 2 At. asparagine and 1 At. oxalic acid in water, yields by evaporation a crystalline mixture of the same compound and pure asparagine. (Dessaigues & Chautard.)

¶. *Malamide.* $C^6N^2H^8O^6$. — *Isomeric, if not identical with asparagine.* — Obtained by the action of ammonia on malamic ether. When malamic ether is dissolved in alcohol and ammoniacal gas passed through the solution, pure malamide separates out in roundish nodules. — Or the same result may be more easily attained by mixing malic ether with strong alcohol, passing dry ammoniacal gas through the liquid and then leaving it at rest. Malamide appears to resemble asparagine in most, if not in all, its properties. Crystallizes from its aqueous solution by slow evaporation in vacuo, in right rectangular prisms with dihedral summits, whose faces meet at an angle of 92° 50'. (Demondesir, *Compt. rend.* 33, 227; Pasteur, *N. Ann. Chim. Phys.* 38, 437; *Jahresber.* 1853, 411.) ¶.

c. Nitrogen-nuclei.

a. Nitrogen-nucleus. $C^6N^2AdH^7$.

Creatine.



CHEVREUL. *J. Pharm.* 21, 234; also *J. pr. Chem.* 6, 120.

MAX PETTENKOFER. *Ann. Pharm.* 52, 97.

LIEBIG. *Ann. Pharm.* 62, 282.

HEINTZ. *Pogg.* 62, 602; 70, 460; 73, 696; 74, 125. — *Compt. rend.* 24, 500.

GREGORY. *Chem. Soc. Qu. J.* 1, 25; also *Ann. Pharm.* 64, 100.

Kreatin, Créatine. — Discovered in 1835 by Chevreul in the juice of flesh; more minutely examined by Liebig in 1847.

Sources. In the muscular flesh of mammalia, birds, amphibia, and fishes. Lean horse-flesh contains 0.070, and the flesh of poultry 0.35 per cent. That of the marten yields less than that of poultry, but more than that of other mammalia; after horse-flesh follow in decreasing series the flesh of the fox, roe-buck, stag, hare, ox, sheep, pig, calf, and pike; bullock's heart contains a large quantity of creatine. Fat animals yield

much less creatine than lean ones; *e. g.* a fox fattened on meat for 100 days, yields only $\frac{1}{10}$ as much as one that has been killed in the chase. (Liebig.) — Bullock's heart yields 0.142; the flesh of poultry 0.321; that of the pigeon 0.083, that of *Gadus morrhua* 0.170; and that of the *Raja* 0.061 per cent. (Gregory.) Human flesh yields 0.067 p. c., and that of the alligator likewise contains creatine (Schlossberger, *Ann. Pharm.* 86, 80; 49, 344.) — The flesh of the Rorqual whale (*Balaenoptera musculus*) likewise yields a small quantity of creatine. (D. Price, *Chem. Soc. Qu. J.* 3, 229.) — Pettenkofer admits the existence of creatine in human urine; Liebig, that of creatine and cratinine together; but from Heintz's experiments, it appears probable that human urine contains only cratinine, and that the precipitate obtained by treating the alcoholic extract of urine with chloride of zinc, is only a cratinine-compound, in the decomposition of which, however, part of the cratinine is converted into creatine. This however does not explain why the zinc-precipitate obtained by Liebig from fresh human urine yields creatine by decomposition as well as cratinine, whereas that which is obtained from putrid urine yields only the latter. — Heintz supposes further that creatine is a product of muscular movement, and is discharged as an excrementitious matter in the urine in the form of cratinine, and therefore cannot well be regarded as an essential nutritive constituent of meat. — Creatine is likewise found, together with cratinine and seroline in blood. (Verdeil & Marcet, *N. J. Pharm.* 20, 89.)

Formation. From cratinine (*q. v.*)

Preparation. 1. *From Muscular Flesh.* — *a.* The aqueous extract of beef is evaporated in vacuo; the residue exhausted with alcohol, and the alcohol evaporated till the creatine crystallizes out. The greater portion remains however in the mother-liquor, being prevented from crystallizing by the presence of foreign bodies. (Chevreul.) In a similar manner, Schlossberger obtained creatine from the flesh of the alligator: he purified the crystals by washing with cold alcohol.

b. The fresh lean muscular flesh of mammalia or birds, is freed as much as possible from fat, (which would stop up the press-bag when the meat is subjected to pressure,) and chopped up fine; 5 lbs. of it then well kneaded with an equal weight of water; the liquid well pressed out in a coarse linen bag; the residue twice treated with water in a similar manner; 5 lbs. of muscular flesh kneaded together with the second expressed liquid; the residue kneaded with the third expressed liquid, and then, after pressure, with 5 lbs. of pure water; and the united liquids strained through a cloth. The resulting reddish liquid, which reddens litmus, is kept at 100° in a large glass flask over the water-bath, till the albumin and blood-red have completely separated in the form of a coagulum, and a sample of the liquid remains clear when boiled. To decolorize the liquid obtained from some kinds of meat, it must be heated in a basin till it froths up. The liquid is then strained, first through linen, the coagulum being pressed out, then through paper. — The filtrate obtained from the flesh of the ox, roe-buck, hare or fox, which contains a large quantity of blood, retains a reddish tint; that from veal, poultry or pike is nearly colourless; game and poultry yield a nearly transparent filtrate, which is very favourable to the obtaining of creatine; horse-flesh and pike yield a turbid filtrate. If the filtrate were evaporated alone, even below 100°, it would become coloured, in consequence of the presence of free acid which would decompose the creatine, — and leave a dark-brown syrup having the odour of roast meat, which would yield but a very

why Berzelius (*Jahresber.* 8, 589) and Fr. Simon (*N. Br. Arch.* 26, 283) did not succeed in preparing creatine. — The filtrate is then mixed with saturated baryta-water, the addition of that liquid being continued, even after the filtrate has been rendered neutral or alkaline by it, as long as a precipitate of phosphate of baryta and phosphate of magnesia continues to form; the filtrate evaporated in a shallow basin over the water-bath to $\frac{1}{10}$; and the thickish residue set aside, first in a warm place to evaporate further, and then, after crystallization has commenced, in the cold. — The filtrate from poultry remains clear when evaporated, and becomes covered with a film of carbonate of baryta if too much baryta-water has been added; that from beef becomes covered, when concentrated to a thin syrup, with a mucous scum which swells up in water, but is insoluble and must be removed; and that from veal or horse-flesh with films which are continually renewed and must be continually skimmed off. — The needles thus obtained are separated from the mother-liquor by filtration, washed first with water then with alcohol, and dissolved in boiling water; and the solution, if coloured, digested with a small quantity of blood-charcoal, then filtered, and left to cool, whereupon it yields pure crystals of creatine. (Liebig.) — If a sufficient quantity of baryta-water has not been added, the crystals will be contaminated with phosphate of magnesia. In that case, the hot aqueous solution must be boiled with a small quantity of hydrated oxide of lead; digested, after filtration, with blood-charcoal, which removes the last traces of lead; and the filtrate again left to crystallize. (Liebig.)

c. As the chopped flesh of pike, when boiled with water, swells up to a gummy mass, from which the liquid cannot be expressed, a mixture of the chopped flesh with water must be thrown upon a funnel; small quantities of water allowed to run gradually through; and the slightly turbid, acid liquid, which smells and tastes of fish, separated from the soft, white coagulum, precipitated with baryta water, then filtered and evaporated. It then forms on cooling a colourless jelly, in which, in the course of 24 hours, crystals of creatine begin to form. (Liebig.)

The extract of the flesh of poultry or pigeons deposits brown flakes, together with the creatine crystals; — the flesh of bullock's heart often yields but few of the purer crystals, but a considerable quantity of brown flakes, from which boiling water extracts a large additional quantity of creatine. From skate and cod the juice may be easily expressed, after the flesh has been mixed with rather more than equal quantity of water; the jelly ultimately obtained from it, in which the creatine-crystals form, dissolves readily in cold water, and deposits more crystals; the flesh of cod yields the whitest creatine. — From the syrupy mother-liquors of crude creatine, chloride of zinc does not deposit any chloride of zinc and cratinine, or only a trace; but the mother-liquors obtained in the recrystallization of crude creatine yield this precipitate on addition of chloride of zinc. (Gregory.)

2. *From Chloride of Zinc and Cratinine.* — a. The solution of this compound in boiling water is digested with hydrated oxide of lead, till it acquires a strong alkaline reaction; filtered from the oxide of zinc and basic hydrochlorate of lead-oxide; digested with a little blood-charcoal, which removes the small remaining quantity of lead, together with fibrin; the filtrate evaporated to dryness; and the remaining mixture of creatine and cratinine, treated with an eightfold quantity of boiling alcohol to dissolve out the latter: the alcohol, on cooling, likewise deposits crystals of creatine, which are added to the undissolved residue of creatine, and

the whole purified by recrystallization. (The alcohol filtered after cooling deposits cratinine.) (Liebig.)—*b*. The boiling aqueous solution of the zinc compound is treated with baryta-water, which precipitates zinc-oxide, together with the greater part of the adhering fibrin; carbonic acid gas passed through the filtrate; the liquid again filtered to separate carbonate of baryta; the filtrate evaporated to dryness in vacuo; the residue exhausted with alcohol; the baryta which has been taken up by the alcohol as chloride of barium, precipitated by sulphuric acid; the liquid again filtered, boiled with oxide of lead, treated with absolute alcohol to precipitate all the chloride of lead, and filtered from chloride and sulphate of lead; any lead that may yet remain dissolved, removed by sulphuretted hydrogen; and the filtrate evaporated to dryness in the water-bath. (Pettenkofer.) The residue thus obtained contains cratinine as well as creatine. (Liebig.)—*c*. The boiling aqueous solution of the zinc-compound is mixed with ammonia till it begins to show turbidity, and then precipitated with hydrosulphate of ammonia; the filtrate evaporated to a small bulk, and mixed with absolute alcohol; and the crystals of creatine, which separate from the liquid after long standing in the cold, purified by recrystallization from water. (Heintz.)—[The cratinine remains in the alcoholic mother-liquor.]

The crystals of creatine obtained by either of these processes may be freed from water of crystallization by heating them to 100°. (Liebig.)

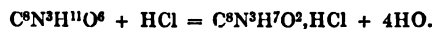
Properties. White opaque mass. (Liebig.) Inodorous, without perceptible taste. (Chevreul.) Has a somewhat bitter taste, and scratches in the throat. (Liebig.) Neutral to vegetable colours. (Chevreul.)

Dried at 100°.		Liebig.		Heintz.	
		<i>a.</i>	<i>b.</i>	<i>c.</i>	
8 C	48	36·64	36·66	36·90	36·39
3 N	42	32·06	32·15	32·61	31·64
9 H	9	6·87	6·96	7·07	6·86
4 O	32	24·43	24·23	23·42	25·11
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C ⁸ N ² H ⁹ O ⁴	131	100·00	100·00	100·00	100·00

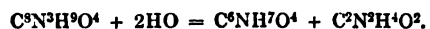
a was obtained from meat; *b* and *c* from the chloride of zinc and cratinine prepared from human urine.

Decompositions. 1. Hydrated creatine when heated, first gives off its water of crystallization with decrepitation; then melts without becoming coloured; afterwards emits an odour of ammonia, hydrocyanic acid and phosphorus; and, lastly, gives off yellow fumes, which condense partly to an oil, partly to needle-shaped crystals, and leaves a small quantity of charcoal. (Chevreul.) The charcoal is difficult to burn. (Schlossberger.)—2. The solution of creatine in aqueous hypermanganate of potash is decolorized by continued digestion, without evolution of gas, the creatine being decomposed and carbonate of potash formed. (Liebig.) The aqueous solution of creatine is not decomposed by boiling with peroxide of lead. (Liebig.) It is not coloured by boiling with mercuric nitrate. (Chevreul.)—3. Creatine dissolved in strong nitric, sulphuric, phosphoric, or hydrochloric acid, is converted into cratinine by abstraction of 2HO, the cratinine then combining with the acid. (Liebig.)—But if these acids are dilute, the creatine remains unaltered, even after long boiling, and the solution in cold hydrochloric acid leaves, by spontaneous evaporation, crystals of pure creatine.

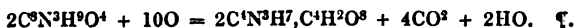
of hydrated creatine heated to 100° in Liebig's drying apparatus, the weight first increases by absorption of hydrochloric acid; but if dry air be then passed through the apparatus for some time, water is continuously given off, and the compound diminishes in weight, till it amounts to only 154·16 pts. and contains 38·05 pts. (a little more than 1 At.) hydrochloric acid. Hence 36 pts. (2 At.) of water of crystallization, and 2 At. more produced from the creatine, have been given off, and on the other hand, 38·05 pts. (1 At.) hydrochloric acid have entered into combination with the hydrated creatine :



131 pts. (1 At.) of dry creatine similarly treated with hydrochloric acid gas take up about 18·04 pts., because, in this case, only 18 pts. (2 At.) water are given off for every 36·4 pts. (1 At.) hydrochloric acid taken up. (Liebig.) — The colourless solution of creatine in nitric acid of sp. gr. 1·34 gives off nitrous fumes when heated in the water-bath, and leaves on evaporation a colourless residue [of nitrate of creatinine?], which dissolves in water, separates out therefrom in small granules, and does not precipitate bichloride of platinum. (Chevreul.) — 4. By boiling with a small quantity of baryta dissolved in water, creatine is resolved into sarcosine (ix. 432), and urea, which is then quickly resolved by the baryta into carbonic acid and ammonia. (Liebig):



An aqueous solution of creatine saturated at a boiling heat, and mixed with crystals of baryta amounting to 10 times the weight of the creatine, remains clear at first, but, if the boiling be continued, gives off abundance of ammonia; deposits carbonate of baryta at the same time; and, if fresh baryta be added from time to time, is ultimately found to contain scarcely any thing but sarcosine and carbonate of baryta; and, if the operation be interrupted during the strongest evolution of ammonia, likewise a little urea. A small quantity of another substance, probably urethane (ix. 274), is however produced at the same time; for if the alcohol from which the sulphate of sarcosine has crystallized out (ix. 433) be mixed with water, neutralized with carbonate of baryta, filtered and evaporated to a thin syrup, colourless needles and laminae are obtained, which redden litmus very slightly, fuse and volatilize when heated, without leaving baryta, dissolve in water, in alcohol, and in 30 pts. of ether, and whose aqueous solution does not precipitate the salts of baryta lime or silver, or neutral acetate of lead, or corrosive sublimate. (Liebig.) — 5. The aqueous solution becomes turbid by long standing (if, according to Liebig, it contains a trace of foreign organic matter), and evolves a sickening ammoniacal odour. (Chevreul.) — ¶. 6. When nitrous gas is passed into a solution of creatine in nitric acid, an alkali is formed, having the composition C^6NH^8 . (Dessaignes, *Compt. rend.* 38, 839; see also ix. 378.) — 7. When an aqueous solution of creatine is heated with mercuric oxide, carbonic acid is evolved, and methyluramine ($\text{C}^4\text{N}^2\text{H}^7$) obtained in the form of an oxalate. (Dessaignes, ix. 357):



Combinations. a. With Water. — a. *Hydrated Creatine, Crystals of Creatine.* — Creatine crystallizes from its aqueous solution in trans-

parent, colourless, highly lustrous, oblique rhombic prisms and needles, resembling in form those of neutral acetate of lead (Liebig). (*Fig. 91*, together with the *t*-face; $i : t = 108^\circ 55'$; $u : u = 46^\circ 58'$: Heintz). In nacreous rectangular prisms (Chevreul); in cubes (Schlossberger). — Their specific gravity lies between 1.35 and 1.84. (Chevreul.) When covered with a non-exhausted bell-jar, they effloresce on the surface, and become covered with a mealy powder, giving off 2.84 p. c. water (Heintz); at 100° they become quite opaque, and give off 12.17 p. c. (Liebig); 13.08 p. c. (Heintz.)

	Crystals.		Liebig.		Or:	
8 C	48	32.22	32.70			
3 N	42	28.19	28.32	C ⁸ N ³ H ⁹ O ⁴	131	87.92
11 H	11	7.38	7.36			
6 O	48	32.21	31.62	2HO.....	18	12.08
C ⁸ N ³ H ¹¹ O ⁵	149	100.00	100.00		149	100.00

β. Aqueous Creatine. — Creatine dissolves in 83 pts. of water at 18° (Chevreul), in 74.4 pts. (Liebig); it dissolves abundantly in hot water, so that a solution saturated at the boiling heat solidifies on cooling in a mass of delicate needles.

b. With Acids. Creatine dissolves slowly in oil of vitriol and without colour in strong hydrochloric acid. (Chevreul) It does not neutralize the weakest acid, even when added in very large quantity. (Liebig.)

¶. *Sulphate of Creatine.* C⁸N³H⁹O⁴, HO, SO³, and the *Hydrochlorate* C⁸N³H⁹O⁴, HCl, are obtained in fine prisms by dissolving creatine in the proper quantity of acid, and evaporating the solution at 30° or in vacuo; they are soluble in water but not deliquescent. (Dessaignes.)

Nitrate of Creatine. — 1. Obtained by dissolving crystallized creatine in the requisite quantity of nitric acid, and evaporating the solution at 30°. — 2. By passing a rapid stream of nitrous gas through water containing an excess of creatine in suspension. The creatine dissolves with tolerable rapidity, and a considerable quantity of small shining crystals of the nitrate are formed, which, when recrystallized by dissolving them in lukewarm water and cooling, form thick short prisms. This salt is less soluble in water than the sulphate or hydrochlorate. The solution has a very sour taste, and is decomposed by ammonia with precipitation of creatine. (Dessaignes.) *Compt. rend.* 38, 839; *Ann. Pharm.* 92, 409.

	Crystals.		Dessaignes.	
C ⁸ N ³ H ⁹ O ⁴	131	67.53		
HO, NO ⁵	54	32.47	32.36	
C ⁸ N ³ H ⁹ O ⁴ , HO, NO ⁵	185	100.00		

By dissolving 1.057 grm. of creatine in a quantity of nitric acid containing 0.447 grm. HO, NO⁵, and evaporating at 30°, Dessaignes obtained 1.373 grms. of crystallized nitrate; the formula requires 1.376. ¶.

From a solution in warm baryta-water creatine crystallizes on cooling without taking up any baryta. (Liebig.)

The aqueous solution of creatine does not precipitate: Chloride of barium, subacetate of lead, ferric sulphate, cupric sulphate, nitrate of silver, or bichloride of platinum. (Chevreul.) — It does not precipitate chloride of zinc, unless it contains cratinine. (Heintz.) — The warm non-

down any crystalline compound, but yields the creatine in the separate state on cooling. (Liebig.) On boiling the mixture, the zinc-precipitate is formed (Heintz), probably from conversion of the creatine with cratinine.

Creatine dissolves in 2000 pts. of alcohol of sp. gr. 0.810 at 15° (Chevreul); it dissolves in 9410 pts. of cold absolute alcohol, more readily in hydrated alcohol. (Liebig.)

It is nearly or quite insoluble in ether. (Heintz.)

β. Nitrogen-nucleus. $C^8N^3H^6O^3$.

Cratinine.



LIEBIG. *Ann. Pharm.* 62, 298 and 324.

HEINTZ. *Pogg.* 62, 602; 73, 595; 74, 125.

Kratinin, Kreatinin, Créatinine. On account of the too great similarity between the words *creatine* and *cratinine*, which might lead to confusion, I propose to drop the *e* in the first syllable of the latter. (Gm.)—Heintz and Pettenkofer in 1844, and nearly at the same time, discovered in human urine a nitrogenous substance which formed a crystalline precipitate with chloride of zinc. The crystalline substance separated from this precipitate was regarded by Pettenkofer as a peculiar compound = $C^8N^3H^6O^3$ [plainly a mixture of creatine and cratinine], by Heintz, at first as an acid, and afterwards as creatine,—till Liebig, in 1847, showed that it was a mixture of creatine and cratinine together,—which cratinine he had just before discovered and investigated, having obtained it by decomposing creatine with concentrated acids.

Sources.—1. In human urine to the amount of 0.5 per cent. (Pettenkofer), and, according to Heintz, likewise in the urine of horses and other mammalia. Socoloff has likewise found it in the urine of horses and of calves.—2. In muscular flesh. As it occurs in the mother-liquor of the creatine prepared from flesh, and as dilute acids do not convert creatine into cratinine, we cannot suppose that this cratinine of muscular flesh is formed by heating the decoction of the flesh. (Liebig.)—3. In blood. (Verdeil & Marcet; see p. 250.)

Formation. From creatine, by the action of the stronger mineral acids.

Preparation—1. *From human urine.*—*a.* Fresh human urine is neutralized with carbonate of soda, and evaporated below 100° to a syrup (till the salts crystallize out, according to Liebig); this syrup exhausted with alcohol; the filtrate mixed with a concentrated solution,—(alcoholic, according to Heintz), of chloride of zinc, which at first throws down a brown amorphous precipitate containing zinc (phosphate of zinc, according to Heintz), then after several hours, crystalline grains; the whole of the precipitate, after standing for some time collected on a filter, (Heintz washes it with weak alcohol;) boiled with water, which leaves the amorphous precipitate undissolved; and the filtrate

evaporated, — whereupon it yields yellow crystals, which may be freed from adhering salts by repeated boiling with strong alcohol. (Pettenkofer.) — *b.* Fresh human urine is neutralized with milk of lime; chloride of calcium added as long as a precipitate of phosphate of lime continues to form; the filtrate evaporated till the salts crystallize out; 32 pts. of the mother-liquor mixed with 1 pt. of chloride of zinc dissolved in the smallest possible quantity of water; the mixture set aside for four days; and the zinc-compound which separates in nodules washed with cold water. (Liebig.) — *c.* Putrid human urine is boiled with excess of milk of lime till it no longer gives off ammonia; the filtrate evaporated to a syrup; and mixed as above with chloride of zinc; and the crystals which form after long standing, washed. (Liebig.)

To purify the crystals, it is not good to use bone-charcoal, which occasions great loss; but they must be dissolved in hot water; the solution mixed with ammonia till a precipitate begins to form; the precipitation completed by means of hydrosulphate of ammonia; the filtrate highly concentrated and mixed with absolute alcohol; the nearly white crystals of creatine and cratinine which are obtained by cooling the solution to a low temperature, dissolved in the smallest possible quantity of boiling water; the solution mixed with alcoholic chloride of zinc and alcohol; and the precipitate which forms on setting the liquid aside in a cold place, washed with alcohol. The above-mentioned mother-liquor of creatine, which likewise contains sal-ammoniac, also yields with alcoholic chloride of zinc, a precipitate, which, when purified by crystallization from boiling water, yields the zinc-compound in white crystals. (Heintz.)

The zinc-compound is further treated in the manner described on page 251, 252; the cratinine is then found in the mother-liquor of the creatine.

¶. 2. *From Horse-urine.* — The urine, which has an alkaline reaction, is neutralized with hydrochloric acid, evaporated to a small bulk, and then mixed with an additional quantity of hydrochloric acid; the liquid separated from the precipitated hippuric acid, neutralized with milk of lime, and evaporated nearly to dryness over the water-bath; the residuo repeatedly boiled out with alcohol; and the alcoholic solution mixed with a small quantity of chloride of zinc: it then gradually deposits a brownish yellow precipitate of chloride of zinc and cratinine, from which creatine and cratinine may be obtained as above. (Socoloff, *Ann. Pharm.* 78, 243.)

3. *From Calves' urine.* — The fresh urine evaporated to a small bulk over the water-bath, and filtered while hot from the amorphous precipitate thereby formed, yields, after a few days, a crystalline mass consisting of allantoin, together with a large quantity of phosphate of soda and ammonia; and on washing this crystalline mass with cold water, and recrystallizing the residue, crystals of pure allantoin are obtained. The mother-liquor filtered from the allantoin is mixed with alcohol, which throws down sulphates, mucous matter, the greater part of the phosphates, and a large quantity of colouring matter; and the filtrate which is still considerably coloured, is freed from the remainder of the phosphoric acid by means of chloride of calcium, and lastly mixed with a concentrated solution of chloride of zinc: it then yields a precipitate of chloride of zinc and cratinine, which continues to increase for several days. (Socoloff.)

litres) is freed from fibrin and blood-corpuscles by stirring, and from albumin by heat, then filtered through linen, and evaporated over the water-bath with addition of a little powdered gypsum, which removes an albuminous substance not coagulable by heat, as well as some additional blood-corpuscles, and precipitates the saponifiable fats. The liquid is then evaporated to $\frac{1}{4}$ of its bulk, again filtered, and the colourless filtrate evaporated to dryness at a very gentle heat, whereupon nearly all the chloride of sodium crystallizes out. On treating the residue with small quantities of absolute alcohol till nothing more is dissolved, and expelling the greater part of the alcohol by heat, the solution yields on cooling, Boudet's *Serolin* (*Ann. Chim. Phys.* 52, 337), the quantity of which increases on addition of a small quantity of water. — The liquid filtered from the serolin, yields, on addition of a small quantity of solution of chloride of zinc, sometimes immediately, sometimes after a few hours, a partly crystalline, partly amorphous precipitate, which is but partially soluble in boiling water. The insoluble portion is resinous, and appears to be a compound of chloride of zinc with a peculiar organic substance: the soluble portion consists of chloride of zinc and cratinine. The quantity thus obtained is however but small. (Verdeil & Marcet, *N. J. Pharm.* 20, 89.) ¶.

5. *From Muscular Flesh.* — The mother-liquor of creatine (p. 251) is treated with alcohol to precipitate the inosinate of potash or baryta; the filtrate evaporated over the water-bath; the residue boiled out with alcohol, which takes up all the cratinine, together with a little creatine, and leaves a residue consisting chiefly of chloride of potassium and lactate of potash; the filtrate mixed with chloride of zinc; and the crystals of chloride of zinc and cratinine, which form after a while, decomposed as above with hydrated oxide of lead. (Liebig.)

6. *From Creatine.* — *a.* Hydrochloric acid gas is passed to saturation over creatine heated to 100° in a Liebig's drying apparatus, then dry air as long as water continues to escape; — or the solution of creatine in strong hydrochloric acid is evaporated to dryness in the water-bath. — The hydrochlorate of cratinine obtained by either of these methods is then dissolved in 24 pts. of water; the solution kept at the boiling heat in a basin; perfectly pure hydrated oxide of lead macerated in water added to it by small portions till it becomes neutral or slightly alkaline, and then three times as much of the hydrated oxide of lead, until the liquid becomes pasty from formation of quadribasic hydrochlorate of lead-oxide. The liquid is then filtered and the precipitate well washed; the filtrate treated with a small quantity of blood-charcoal to remove any lead that may still remain dissolved; the liquid again filtered; and the filtrate evaporated and cooled to the crystallizing point. (Liebig.) — *b.* The solution of 1 pt. creatine in 1 pt. oil of vitriol and 3 pts. water is evaporated till all moisture is removed; the remaining sulphate of cratinine boiled with water and very pure carbonate of baryta, till it becomes alkaline; and the solution filtered and left to crystallize. (Liebig.)

Properties. Colourless oblique rhombic prisms belonging to the oblique prismatic system; *Fig.* 91, with *t*-face; $i : t = 110^{\circ} 30'$ ($110^{\circ} 3'$, according to Heintz); $u : w = 81^{\circ} 40'$; $u : t = 130^{\circ} 50'$. (Kopp.) — The same form therefore as that of creatine, excepting that in cratinine the

incarnation of the ammonia into the creatine, $u : u' = 46^{\circ} 58'$. (Heintz.)—Cratinine in the state of concentrated solution has a caustic taste, like that of dilute ammonia. It blues reddened litmus, and reddens turmeric (Liebig.)

		Liebig.		
		from urine	from flesh.	from creatine.
8 C	48	42.48	42.64	42.54
3 N	42	37.17	37.41	37.20
7 H	7	6.19	6.23	6.38
2 O	16	14.16	13.72	13.88
<hr/>				
$C^8N^3H^7O^2$	113	100.00	100.00	100.00

Decompositions. Cratinine, under certain circumstances, takes up 2 At. water, and is reconverted into creatine. The dilute solution of hydrochlorate or sulphate of cratinine slightly supersaturated with dilute ammonia and evaporated, yields a few crystals of creatine (Heintz; see also *Chloride of Zinc and Cratinine.*)—Cratinine is decomposed by mercuric oxide in the same manner as creatine (p. 253), yielding methyluramine. (Dessaignes.)

Combinations. Cratinine dissolves in 11.5 pts. of water at 16° , and much more abundantly in hot water. (Liebig.)

Sulphate of Cratinine.—An aqueous solution of cratinine saturated at a boiling heat and mixed with dilute sulphuric acid till it acquires a strong acid reaction, leaves on evaporation a white mass, whose solution in hot alcohol becomes turbid on cooling, then becomes clear and deposits transparent, colourless, quadratic tables which remain transparent at 100° . (Liebig.)

		Crystals.	Liebig.
8 C	48	29.63	29.33
3 N	42	25.93	25.44
8 H	8	4.94	5.03
3 O	24	14.81	15.56
SQ^8	40	24.69	24.64
<hr/>			
$C^8N^3H^7O^2, HO, SO^2$	162	100.00	100.00

Hydrochlorate of Cratinine.—*Preparation* (ix. 257, 6). Crystallizes from solution in boiling alcohol, in transparent colourless prisms, and by evaporation of the aqueous solution, in transparent laminæ which redden litmus. Dissolves very readily in water. (Liebig.)

		Crystals..	Liebig.
8 C	48.0	32.13	32.48
3 N	42.0	28.11	28.27
8 H	8.0	5.35	5.30
2 O	16.0	10.71	10.54
Cl	35.4	23.70	23.41
<hr/>			
$C^8N^3H^7O^2, HCl$	149.4	100.00	100.00

Chloride of Zinc and Cratinine.—*Preparation.* 1. (p. 256).—2. By mixing cratinine and chloride of zinc, in the state of concentrated aqueous solutions. Both processes yield, with greater rapidity as the mixture is more concentrated, delicate needles united in nodules, or oblique rhombic prisms (Pettenkofer) belonging to the oblique prismatic system, with

Pharm. 61, 332.) The crystals give off only a trace of hygroscopic water at 120°. When the cratinine is separated from this compound by means of hydrated oxide of lead or hydrosulphate of ammonia (p. 251), more than $\frac{1}{2}$ of it is found to be converted into creatine, and in larger proportion, apparently, as the solution of the zinc-compound used was more dilute. If therefore, after the creatine has been separated from the resulting liquid by evaporation and cooling, with addition of alcohol, the mother-liquor containing the rest of the cratinine be repeatedly precipitated with chloride of zinc, and the precipitate decomposed, &c.—nearly all the cratinine may be converted into creatine. (Heintz.)—Chloride of zinc and cratinine dissolves sparingly in alcohol, but is insoluble in strong alcohol and ether. (Pettenkofer.)

<i>Crystals.</i>	Heintz.			
			<i>from urine.</i>	<i>from flesh.</i>
8 C.....	48·0	26·58	26·29	
3 N.....	42·0	23·25	23·54	
7 H.....	7·0	3·88	3·96	
2 O.....	16·0	8·86	9·31	
Zn.....	32·2	17·83	17·74	17·87
Cl.....	35·4	19·60	19·16	19·18
<hr/>				
C ⁸ N ³ H ⁷ O ⁸ , ZnCl.....	180·6	100·00	100·00	

With *Cupric salts*, cratinine forms crystallisable double salts of a fine blue colour. (Liebig.)

When mixed in aqueous solution with *Corrosive sublimate*, it immediately forms a white curdy precipitate, which changes in a few minutes to a mass of delicate colourless needles. (Liebig.)

With concentrated *Silver solution* it coagulates immediately into a mass of delicate white needles, which dissolve readily in hot water, and crystallize out again unchanged on cooling. (Liebig.)

The clear mixture of dilute hydrochlorate of cratinine and *Bichloride of Platinum* (or of hydrochloric acid, creatine, and bichloride of platinum), yields, by slow evaporation, transparent, aurora-red prisms, and by quicker evaporation, granules which dissolve readily in water, less quickly in alcohol, and contain 30·53 p. c. platinum, whence they probably consist of C⁸N³H⁷O⁸, HCl + PtCl². (Liebig.)

Cratinine dissolves in 102 pts. of absolute *alcohol* at 16°, and more abundantly in hot alcohol, from which it crystallizes out on cooling. (Liebig.)

γ. *Nitrogen-nucleus.* C⁸N²Ad²H²O⁴.

Allantoin.



VAUQUELIN & BUNIVA. *Ann. Chim.* 33, 269; also *Scher. J.* 6, 211.

C. G. GMELIN. *Gilb.* 64, 350.

LASSAIGNE. *Ann. Chim. Phys.* 17, 301; also *J. Phys.* 92, 406.

LIEBIG. *Pogg.* 21, 34.

LIEBIG & WÖHLER. *Ann. Pharm.* 26, 244; also *Pogg.* 41, 561.

PELOUZE. *N. Ann. Chim. Phys.* 6, 70; also *Ann. Pharm.* 48, 107;
J. pr. Chem. 28, 18.

SCHLIEPER. *Ann. Pharm.* 67, 216.

WÖHLER. *Ann. Pharm.* 70, 229.

LIMPRICHT. *Ann. Pharm.* 88, 94.

Amniotic acid, Allantoic acid, Amniosäure, Allantoinensäure, Allantoine, Acide amniotique, Acide allantoïque.— Found by Vauquelin & Buniva in 1800 (probably mixed with allantoic liquid) in the amniotic liquid of the cow; wherein, however, neither Dzondi (*N. Gehl.* 2, 52) nor Prout (*Ann. Phil.* 5, 416) was able to find it again; afterwards Lassaigne showed that it is contained, not in the amniotic but in the allantoic liquid. It was also artificially prepared and accurately investigated by Liebig & Wöhler.

Sources. In the allantoic liquid of the cow (Lassaigne), and in the urine of calves. (Wöhler.)

Formation. In the decomposition of uric acid by heating with peroxide of lead and water (Liebig & Wöhler), or with ferricyanide of potassium and potash-ley. (Schlieper.)

Preparation. 1. The allantoic liquid (mixed with amniotic liquid) is evaporated down to $\frac{1}{2}$, and cooled to the crystallizing point. (Vauquelin & Buniva.) The allantoin is likewise deposited when the liquid is left to stand for some time, and must be purified by solution in hot water, filtering, and recrystallizing. (C. G. Gmelin.)

2. The urinary bladder of a calf is tied at the lower part previous to slaughtering; the urine obtained from it evaporated below 100° to a syrup; and set aside for several days in the cold to crystallize; the liquid then diluted with water; the gelatinous precipitate, consisting chiefly of urate of magnesia, separated by elutriation from the crystals of allantoin and phosphate of magnesia; the crystals washed with a little cold water, and boiled with water and a small quantity of good blood-charcoal; the liquid filtered at the boiling heat from the greater part of the phosphate of magnesia; the filtrate mixed with a few drops of hydrochloric acid, so that the phosphate of magnesia contained in it may remain dissolved; and colourless allantoin obtained from it by cooling (Wöhler):— For another mode of preparation from calves' urine, *vid.* Socoloff (p. 256).

3. Uric acid is pulverized, and suspended in a small quantity of water, the liquid heated nearly to the boiling point; finely pulverized peroxide of lead added to it by small portions and with frequent stirring, till the last portions added no longer turn white; the liquid filtered hot; and crystalline allantoin obtained from it by cooling, and also by further evaporation and cooling of the mother-liquor, while the more soluble urea, which is likewise present, remains in the last mother-liquor: the allantoin must be freed from it by recrystallization from water. (Liebig, Wöhler.)

4. The same process is followed as in the preparation of lantanuric acid (ix. 445, the first 17 lines), and the crystals of allantoin, which are contaminated with red flakes, purified by solution in cold potash-ley, filtering, quickly supersaturating with acetic acid, and recrystallizing the precipitated allantoin from hot water. (Schlieper.)

(Vauquelin & Buniva), and four-sided prisms. Prisms whose primitive form is a rhombohedron. (Liebig & Wöhler.)—Crystals belonging to the doubly oblique prismatic system (*Fig.* 124); $v : u = 56^\circ 42'$; $v : y = 95^\circ 15'$; $u : y = 91^\circ 40'$; the y -faces have the strongest lustre. (Delffs, *Jahrb. prakt. Pharm.* 8, 378.)—Single oblique prismatic system; *Fig.* 93, with z -face between u and u' ; $i : u$ backwards $= 88^\circ 14'$; $f : u$ backwards $= 96^\circ 17'$; cleavage easy parallel to f . (Dauber, *Ann. Pharm.* 71, 68.) The crystals obtained by (2) are thinner and united in tufts, in consequence of the admixture of a trace of foreign matter; from this they are freed by combination with oxide of silver, separation therefrom by hydrochloric acid, and then crystallized in the ordinary way. (Wöhler.)

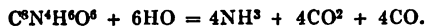
Tasteless (Lassaigne), and neutral to litmus. (Liebig & Wöhler.) Tastes slightly acid and reddens litmus slightly. (Vauquelin & Buniva.) Permanent in the air (Vauquelin); anhydrous (Liebig).

	Lieb.&Wöhl.		Schliep.		Städeler.		Lassaigne.	
		(3)		(4)		(2)		(1)
8 C.....	48	30·38	30·50	30·02	30·15	28·15		
4 N.....	56	35·44	35·34	35·17	35·25	25·24		
6 H.....	6	3·80	4·04	4·04	3·81	14·50		
6 O.....	48	30·38	30·12	30·77	30·79	32·11		
$C^8N^4H^6O^6$	158	100·00	100·00	100·00	100·00	100·00	100·00	

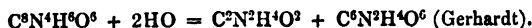
The bracketed numbers refer to the mode of preparation.

Decompositions.—Allantoin yields by dry distillation, carbonate and hydrocyanate of ammonia, a small quantity of empyreumatic oil, and a very porous charcoal. (Lassaigne.)—2. Over the open fire it swells up, blackens, gives off the odour of ammonia and hydrocyanic acid, and leaves a tumefied charcoal. (Vauquelin & Buniva.)

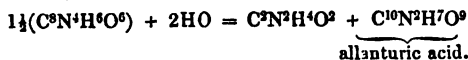
3. Heated with oil of vitriol, it yields sulphate of ammonia and a mixture of carbonic acid and carbonic oxide gases. (Liebig & Wöhler.)



4. Allantoin gently heated with nitric acid of sp. gr. 1·2 to 1·4, does not give off any gas, but yields crystalline nitrate of urea on cooling; on evaporating the solution to dryness, nitrate of urea and allanturic acid (ix. 447) remain (Pelouze):

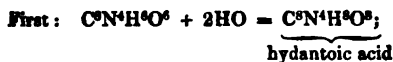


Pelouze gives the equation:



5. Allantoin is likewise resolved into urea and allanturic acid by heating with hydrochloric and other aqueous acids. The same decomposition also takes place when allantoin is heated with water in a sealed glass tube to $110^\circ - 140^\circ$, excepting that in this case the urea is further resolved into ammonia and carbonic acid. (Pelouze.)—6. Allantoin is also resolved into allanturic acid and urea by the action of peroxide of lead and water at ordinary temperatures. (Pelouze.) [According to what equation?]

7. The solution of allantoin in cold potash-ley, deposits all the allantoin if immediately mixed with acids; but in the course of 24 to 48 hours, it changes spontaneously into hydantoate of potash, and is then no longer precipitated by acids, gives off but little ammonia when boiled, and does not at the same time form any oxalic acid; by the further action of potash, the hydantoate of potash is resolved into lantanurate of potash (ix. 445) and urea (Schlieper):



8. Allantoin boiled with aqueous potash or baryta is completely resolved into ammonia and oxalic acid (Liebig & Wöhler):



¶ 9. A solution of allantoin mixed with yeast and exposed to a temperature of 30°, becomes on the fourth day strongly ammoniacal, and no longer contains allantoin, but urea and the ammonia-salts of oxalic acid, carbonic acid, and an acid which may be obtained in the form of a sour syrup. (Wöhler, *Ann. Pharm.* 88, 100.) ¶.

Combinations. Allantoin dissolves in 400 pts. of cold water (Lassaigne); in 160 pts. of water at 20° (Liebig and Wöhler); in 30 pts. of boiling water, and crystallizes on cooling.

According to Liebig & Wöhler, allantoin does not combine with any base excepting oxide of silver. C. Gmelin and Liebig & Wöhler were not able to obtain the allantoates described by Lassaigne. From solution in hot dilute alkalis, the allantoin crystallizes in the free state. — ¶. The following compounds have however been obtained by Limpricht.

Zinc-compound. — $2\text{ZnO}, \text{C}^6\text{N}^4\text{H}^8\text{O}^6 = \text{ZnO}, \text{C}^6\text{N}^4\text{H}^8\text{ZnO}^6$. — When allantoin is boiled with zinc-oxide and the liquid filtered, the filtrate yields crystals of allantoin, and there remains a syrupy mother-liquor, which, when mixed with absolute alcohol, yields a precipitate containing, after drying at 100°, 36.5 per cent. of zinc-oxide: the above formula requires 35 p. c. (Limpricht.)

Cadmium-compound. — $\text{CdO}, \text{C}^6\text{N}^4\text{H}^8\text{O}^6 = \text{C}^6\text{N}^4\text{H}^8\text{CdO}^6$. Syrupy mass, which, on addition of alcohol, solidifies to a white crystalline powder. The powder thus precipitated does not redissolve completely in water, but leaves a compound richer in cadmium. The crystalline powder yields by analysis, 28.04 p. c. CdO, the above formula requiring 30 per cent. (Limpricht.)

Lead compound. — $3\text{PbO}, 2\text{C}^6\text{N}^4\text{H}^8\text{O}^6$ — First observed by Lassaigne. — A solution of lead oxide in allantoin deposits the compound by evaporation in crusts, which yield by analysis 52.5 and 52.8 p. c. lead-oxide; the formula requires 52.9. Acids poured upon the compound produce a slight effervescence; the carbonic acid of the air seems also to exert a decomposing action upon it. (Limpricht.)

solves at the boiling heat, in a solution of allantoin, forming a blue liquid, which deposits green crystals by evaporation. These give in two analyses 7·23 and 7·36 p. c. CaO, while the formula requires 8·2 p. c.

Mercury-compounds. — When an aqueous solution of allantoin is boiled with excess of mercuric oxide, a certain quantity of the oxide dissolves, and two compounds are formed.

a. $5\text{HgO}, 3\text{C}^6\text{N}^4\text{H}^6\text{O}^6$. — This compound separates from the liquid filtered at a boiling heat, and left to stand for several hours. It is a white amorphous powder, which melts and intumesces when heated. It is insoluble in cold water and in alcohol, but dissolves sparingly in hot water, readily in hydrochloric, nitric, and sulphuric acid. (Limpricht.)

<i>Dried at 100°.</i>		<i>Limpricht (mean).</i>	
24 C	144	14·59	14·27
12 N	168	17·02	
15 H	15	1·52	1·56
15 O	120	12·16	
5 HgO	540	54·71	54·83
<hr/>			
$5\text{HgO}, 3\text{C}^6\text{N}^4\text{H}^6\text{O}^6$	987	100·00	

b. $3\text{HgO}, 5\text{C}^6\text{N}^4\text{H}^6\text{O}^6$. — The mother-liquor of *a* filtered and evaporated at 100° to a small bulk, deposits this compound, after 24 hours, in the form of a mass, having the consistence of turpentine, and drying up over sulphuric acid to a brittle, glassy solid, which blackens at 100°. (Limpricht.)

<i>Dried at 60°.</i>		<i>Limpricht.</i>	
40 C	240	22·45	21·23
20 N	280	26·19	
25 H	25	2·34	2·74
25 O	200	18·71	
3 HgO	324	30·31	29·06
<hr/>			
$3\text{HgO}, 5\text{C}^6\text{N}^4\text{H}^6\text{O}^6$	1069	100·00	

The mother-liquor of *a* left to evaporate spontaneously, deposits crystalline crusts of variable composition. (Limpricht.)

c. $4\text{HgO}, 3\text{C}^6\text{N}^4\text{H}^6\text{O}^6$. — When water is poured upon the compound *b*, it swells up and is converted into a white pulverulent mass, which blackens when heated a little above 100°. (Limpricht.)

<i>Dried at 100°.</i>		<i>Limpricht.</i>	
24 C	144	16·38	16·12
12 N	168	19·11	
15 H	15	1·71	1·75
15 O	120	13·66	
4 HgO	432	49·14	49·6
<hr/>			
$4\text{HgO}, 3\text{C}^6\text{N}^4\text{H}^6\text{O}^6$	879	100·00	

d. $5\text{HgO}, 2\text{C}^6\text{N}^4\text{H}^6\text{O}^6$. — An aqueous solution of allantoin is not precipitated by corrosive sublimate; but mercuric nitrate, even when very dilute, forms with it a bulky non-crystalline precipitate exhibiting this composition. (Limpricht.)

		Dried at 100°.		Limpricht.	
16 C	96 11·46	11·14 to 11·35
8 N	112 13·37	
10 H	10 1·19	1·03 1·04
10 O	80 9·54	
5 HgO	540 64·44	63·97 65·07
<hr/>					
5H ₂ O, 2C ⁸ N ² H ² O ⁴	838 100·00	

Allantoin behaves, in fact, with corrosive sublimate and mercuric nitrate, in the same manner as urea. (Limpricht.) ¶.

Silver-compound.— A hot aqueous solution of allantoin mixed with nitrate of silver, and then with ammonia as long as any precipitate is formed, yields a white micaceous powder, which, when examined by the microscope, appears to consist of globules. It is decomposed by all acids with separation of allantoin. (Liebig & Wöhler.)

		Liebig & Wöhler.		Wöhler.	
8 C	48 18·12	18·18
4 N	56 21·13	21·04
5 H	5 1·88	1·94
Ag	108 40·75	40·44 40·78
6 O	48 18·12	18·40
<hr/>					
C ⁸ N ² H ² AgO ⁶	265 100·00	100·00

Allantoin dissolves in *alcohol* more readily than in water. (Vauquelin & Buniva.)

Hydantoic Acid.



SCHLIEPER. (1848.) *Ann. Pharm.* 67, 232.

Formation (p. 262). — *Preparation.* A solution of allantoin in strong potash-ley is set aside for two days, {then supersaturated with acetic acid and diluted; hydantoate of lead precipitated from it by addition of neutral acetate of lead; the precipitate washed, suspended in water, and decomposed by sulphuretted hydrogen; and the strongly acid filtrate evaporated in the water-bath. During the evaporation, a certain amount of decomposition appears to take place.

Properties. Thick, uncrystallizable, very acid syrup, which, when moistened with alcohol, is converted into a very friable mass.

Decompositions. The acid treated with cold potash-ley, evolves ammonia, probably because it has been already partially decomposed by evaporation, and yields white flakes when evaporated with it. It does not form oxalic acid by boiling with potash-ley.

Combinations. The acid deliquesces in the air.

When neutralized with aqueous *ammonia*, it gives off ammonia on evaporation, and again becomes acid.

solution of allantoin in potash with acetic acid after two days, and then precipitating with alcohol, in the form of an oily liquid which refracts light strongly.

The acid mixes without effervescence with carbonate of soda; the liquid, when heated, deposits yellowish white flakes.

The acid does not become turbid when mixed with baryta or lime-water; but, on the addition of alcohol, white flakes are deposited, which redissolve in water.

The lead-salt (*vid. sup.*) is deposited, after a while, on the sides of the vessel as a thick white precipitate, and afterwards fills the entire mixture with thick white flakes, which, after washing, dry up to a white powder, readily soluble in nitric, but very sparingly soluble in acetic acid, even when hot.

				Schlieper (at 100°.)
PbO.....	112	40·15 39·09
8 C.....	48	17·20 16·75
4 N.....	56	20·07 19·04
7 H.....	7	2·51 2·90
7 O.....	56	20·07 22·22
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C ⁶ N ⁴ H ⁷ PbO ⁸	279	100·00 100·00

[The salt probably contains 1 At. more water at 100°.]

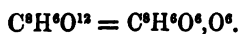
Silver-salt. — The oily potash-salt dissolved in water, forms with nitrate of silver a thick white precipitate, which turns black when boiled. The free acid forms, with nitrate of silver, a white precipitate, which dissolves partially when heated. This precipitate contains 13·12 p. c. (5 At.) nitrogen to 45·31 p. c. (2 At.), silver-oxide, a proof that the acid has been to some extent decomposed by evaporation.

The acid is insoluble in alcohol. (Schlieper.)

Primary-nucleus. C⁶H¹².

Oxygen-nucleus. C⁶H⁶O⁶.

Tartaric Acid.



RETZIUS & SCHEELE. *Abh. der Schwed. Akad. der Wiss.* 1770, p. 207; also *Crell. Chem. J.* 2, 179.

MATTH. A. PAECKEN (properly KLAPROTH). *Diss. de sale essentiali tartari* Gottl. 1779.

RICHTER. *Neuere Gegenst.* 6, 39.

THENARD. *Ann. Chim.* 38; 30; also *Scher. J.* 8, 630.

OSANN. *Kastn. Arch.* 3, 204 & 369; 5, 107.

BERZELIUS. *Ann. Chim.* 94, 177. — *Pogg.* 19, 305; 36, 4. — *Ann. Chim. Phys.* 67, 303; also *J. pr. Chem.* 14, 350.

DULK. *Schw.* 64, 180, & 193; abstr. *Ann. Pharm.* 2, 39.

DUMAS & PIRIA. *Ann. Chim. Phys.* 5, 353; also *Ann. Pharm.* 44, 66; also *J. pr. Chem.* 27, 321.

WERTHER. *J. pr. Chem.* 32, 385.

LAURENT & GERHARDT. *Compt. chim.* 1849, 1 & 97; also *Ann. Pharm.* 70, 348; also *J. pr. Chem.* 46, 300.

Tartarsäure, Tartrylsäure, Weinsäure, Weinsteinssäure, wesentliches Weinsteinssalz, Sal essentielle tartari, Acide tartarique.—Tartaric acid was first obtained in the separate state by Scheele in 1770, but its existence in tartar had been previously assumed by Duhamel, Marggraf, and Rouelle the younger.

Sources. Partly free, partly combined with bases: in tamarinds (Retzius), in the unripe berries of the mountain-ash; the berries of *Rhus typhinum* and *glabrum*, in the wood of *Quassia amara*, the bark of *Quassia Simaraba*, the root of *Nymphæa alba*, the herb of *Chelidonium majus*, the root of *Rubia tinctorum*, in potatoes, cucumbers, the root of *Leontodum taraxacum*, the corms of *Helianthus tuberosus*, camomile flowers (Bindheim), in the herb of *Rumex acetosa*, in mulberries, pine-apples, the leaves of *Agave mexicana* (Hoffman), and in senna-leaves (Casselmann); in black pepper, the bulb of *Scilla maritima*, the root of *Triticum repens*, Iceland moss, and *Lycopodium complanatum*. Dessaignes (*N. J. Pharm.* 25, 24), found this acid in considerable quantity in the decoction of pelargoniums; also, together with malic acid, in the berries of *Mahonia aquifolia*; the residue obtained by evaporating the juice of the vine-stock, he found to consist chiefly of tartrate of lime.

Formation. 1. In the preparation of potassium, (iii. 5), the metal which sublimes is accompanied by a carbonaceous mass, whose aqueous solution contains tartrate of potash, together with croconate and oxalate. (Liebig.) [The author did not succeed in the preparation of the tartrate from this mass.]—2. When lemon-juice is kept for a year in bottles, the greater part of the citric acid is converted into tartaric. (Schindler, *Ann. Pharm.* 31, 280.)—3. When pyroxilin is dissolved in potash-ley, tartaric acid, or a similar acid appears sometimes to be produced. (Kerckhoff & Reuter, *J. pr. Chem.* 40, 284.)

Preparation. 1. To 1 pt. of crude or purified tartar suspended in boiling water, 0.27 pt. or a somewhat larger quantity, of powdered chalk, marble, or oyster-shells is added, and the mixture boiled till the effervescence entirely ceases, and the liquid no longer reddens litmus. Or tartar suspended in boiling water is exactly neutralized with milk of lime. The tartrate of lime, which settles to the bottom, is separated from the neutral tartrate, which remains in solution, by decanting the liquid and washing the deposit on linen.—*a.* The tartrate of lime thus obtained, is decomposed by digestion for a day or two with oil of vitriol, amounting to 0.4 pt. of the dried tartrate of lime, or equal to the carbonate of lime used, and in any case not less than sufficient for the complete saturation of the lime, and with 12 times its weight of water. The liquid is separated from the gypsum by filtration; evaporated to a thin syrup; separated from the precipitated gypsum by straining through linen; and then further concentrated, whereupon it yields crystals of tartaric acid, either by standing for some time in the cold, or by further evaporation.—If these operations have been performed in vessels of tin or copper, the metals thereby dissolved must be precipitated from the slightly cou-

acid, by a small quantity of sulphide of calcium, and the evaporation finished in vessels of glass or porcelain. — If the quantity of sulphuric acid used is not sufficient for the complete decomposition of the tartrate of lime, the tartaric acid obtained is mixed with a certain quantity of acid tartrate of lime, which prevents the crystallization of the acid, but may easily be decomposed by a small additional quantity of sulphuric acid, which throws down the lime as sulphate. — If the acid liquid contains free sulphuric acid, this acid remains in the mother-liquor, which may then be used for the decomposition of fresh portions of tartrate of lime. The sulphuric acid still adhering to the crystals, may be removed either by recrystallization, or by digestion with a small quantity of oxide of lead, the filtrate being subsequently treated with sulphuretted hydrogen. — The brown colour of the liquid, which is particularly strong when crude tartar is used, is partially removed by digestion with charcoal powder; the greater portion of the colouring matter, however, remains in the mother-liquor. This liquid may be decolorized by $\frac{1}{1175}$ of chlorate of potash. (Berzelius, Wittstein, *Repert.* 57, 228.) — *b.* The solution of neutral tartrate of potash separated from the tartrate of lime, yields, when precipitated by hydrochlorate or acetate of lime, or when decomposed by half an hour's boiling with sulphate of lime (Desfosses, *J. Pharm.* 15, 613), an equal quantity of tartrate of lime, which may be washed and treated as above. Compare Lowitz, *Crell. Ann.* 1799, 1, 99; Buchholz, *A. 7r* 7, 1, 21; Grindel, *Schw.* 13, 355.)

2. One part of tartar is neutralised with carbonate of potash; the aqueous mixture boiled for an hour with 8 pts. of burnt lime; the decoction, which contains caustic potash free from lime, filtered while still hot; and the precipitated tartrate of lime washed, freed from excess of lime by means of hydrochloric or acetic acid, and treated as above. (Osann, *Kastn. Arch.* 5, 107.)

3. Tartar is gradually added in excess to a boiling mixture of 1 pt. oil of vitriol and 3 pts. water; the excess of tartar (together with gypsum,) left to crystallize out by cooling; the remaining liquid evaporated to a small bulk, and the tartaric acid removed from it by cold alcohol, while bisulphate of potash remains. (Fabroni, *Ann. Chim. Phys.* 25, 9.) — [The alcohol may produce tartrovinic acid, in which case continued boiling with water will be required to expel it.]

Properties. Large, transparent, colourless prisms belonging to the oblique prismatic system. *Fig.* 109; no cleavage: $i : u$ or $u' = 97^{\circ} 10'$; $u : u' = 88^{\circ} 30'$; $i : a = 128^{\circ} 15'$; $i : c = 134^{\circ} 50'$; $i : m = 100^{\circ} 47'$; $i : f$; backwards = $122^{\circ} 45'$; one of the u -faces is often disproportionately large. (Brooks, *Ann. Phil.* 22, 118.) — *Fig.* 109, together with truncation-faces between a and i and between u and i ; $i : u = 97^{\circ} 10'$; $i : a = 128^{\circ} 34'$; $i : f = 122^{\circ} 30'$; $i : e = 135^{\circ} 0'$; $u : f = 121^{\circ} 4'$; $u : e = 125^{\circ} 15'$; $u : a = 129^{\circ} 20'$; $a : a = 102^{\circ} 51'$; $e : f = 102^{\circ} 30'$; cleaves easily parallel to i . (Prevostage, *N. Ann. Chim. Phys.* 3, 129.) — They are oblique rhombic prisms, about = *Fig.* 86, with one other face x , between i and m ; but of the four h -faces, only the two on the right side are present, above and below, not those on the left, whereby the crystals are rendered unsymmetrical, a fact which is connected with their thermo-electric properties (and with their optical relations, according to Pasteur). $i : m = 81^{\circ}$; $i : x = 145^{\circ} 15'$; $u : u = 99^{\circ} 45'$; $i : h = 136^{\circ}$, (Hankel, *Pogg.* 49, 500; — compare also Haberle, *Taschenb.* 1805, 160; Soret, *Taschenb.*

1823, 141; Bernhardt, *N. Tr.* 7, 2, 40; Peclet, *Ann. Chim. Phys.* 31, 78; Em. Wolff, *J. pr. Chem.* 28, 138; Rammelsberg, *Pogg.* 96, 23). — Sp. gr. 1.75. (Richter.) — The acid shines when rubbed in the dark, like sugar. (Bouchardat, *N. J. Pharm.* 15, 440.) — Melts at 170° to a transparent colourless liquid. Tastes strongly but pleasantly sour, and reddens litmus. Its concentrated solution yields, with quantities of ammonia and potash not sufficient to neutralize it, granular precipitates, and with excess of lime-water, white flakes soluble in excess of the acid and in sal-ammoniac.

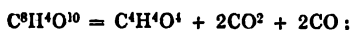
	<i>Crystallized.</i>		Prout.	Herrmann.	Döbereiner.	Ure.	Berthollet.
8 C.....	48	32	32	32.50	32.42	31.42	24.41
6 H.....	6	4	4	4.19	2.94	2.76	5.57
12 O.....	96	64	64	63.31	64.64	65.82	70.02
C ⁸ H ⁶ O ¹²	150	100	100	100.00	100.00	100.00	100.00

The radical theory assumes a hypothetical anhydrous tartaric acid = C⁸H⁶O⁸ = T.

Decompositions. 1. Tartaric acid heated merely till it melts, which takes place at 170° to 180°, is converted, without perceptible loss, into metatartaric acid (Laurent & Gerhardt); when melted for a longer time, or at a stronger heat, it is converted chiefly into tartralic acid, then, with loss of 2 At. water, into tartrellic acid and tartaric anhydride. (Braconnot, Fremy, Laurent & Gerhardt.) According to Weniselos (*Ann. Pharm.* 15, 133,) the acid begins to boil at 150°.

2. When the acid is gradually heated to 220°, it swells up considerably, and is very apt to froth over; becomes continually browner; then loses its viscosity, so that it boils without tumefaction; continually gives off carbonic acid gas, loaded with vapours of acetic and pyroracemic acids; and yields a colourless watery distillate, which smells of acetic acid and empyreumatic oil, has a sharp sour taste, continually becomes more concentrated, and only towards the end acquires a yellowish colour, and contains a small quantity of empyreumatic oil, which causes it to become turbid when mixed with water. This distillate, when very slowly distilled over the water-bath, yields acetic, (no formic,) and then pyroracemic acid, together with a trace of wood-spirit, or something of that kind, and leaves a thick brown syrup containing crystals of pyrotartaric acid. The residue left at 220° in the distillation of tartaric acid, is black, semifluid, hard after cooling, has the appearance of charcoal, and at a higher temperature, yields marsh-gas and empyreumatic oil, while a soft bulky charcoal remains. (Berzelius.) — The acid distilled between 170° and 190° yields large quantities of carbonic acid, water, and pyrotartaric acid, but very little olefiant gas, acetic acid, empyreumatic oil, and charcoal; if the distillation takes place between 200° and 300°, the first three products diminish and the last three increase; and by distillation over the open fire, very little pyrotartaric acid is obtained, together with small quantities of water and carbonic acid, but on the other hand, highly concentrated acetic acid, and large quantities of olefiant gas, empyreumatic oil, and charcoal. (Pelouze, *Ann. Chim. Phys.* 56, 297.) — 100 pts. of tartaric acid yield, when distilled with various degrees of rapidity, 28 to 70 pts. of watery distillate, (containing 0.3 to 0.5 pyrotartaric acid,) 4.7 to 0.8 pts. empyreumatic oil, and 12.5 pts. or a much smaller quantity, of charcoal. (Gruner, *N. Tr.* 24, 2, 57.)

less empyreumatic oil. (Arppe.) — Tartaric acid subjected to dry distillation with spongy platinum, yields pure carbonic acid gas, and a transparent, colourless, crystallizable distillate. (Reiset & Millon, *N. Ann. Chim. Phys.* 8, 285.) — ¶. The distillate obtained at 200° is colourless, and leaves, when evaporated, a scarcely perceptible residue of pyrotartaric acid; the gas evolved at and below that temperature is carbonic acid, with but little carbonic oxide. At 220°, the fused tartaric acid becomes more viscid, and acquires a yellow-brown colour; the pale-yellow distillate contains but little pyrotartaric acid, and the evolved gas consists of carbonic acid with $\frac{1}{3}$ to $\frac{1}{4}$ carbonic oxide. At 220° the decomposition of the tartaric acid is still incomplete; at higher temperatures, the distillate is more highly coloured, and the evolved carbonic acid is accompanied by increasing quantities of carbonic oxide (the proportion ultimately reaching the half); no hydrocarbons are formed. Small quantities of tartaric acid may be completely decomposed in the oil bath at 300°, leaving only a very small quantity of carbonaceous residue. When the acid is distilled over the open fire, the distillate consists chiefly of acetic and pyroracemic acids, together with aldehyde, acetone, and other substances, as in the distillation of sugar: on rectifying this distillate, the portion which goes over between 105° and 120°, consists chiefly of acetic acid; that between 130° and 180°, of pyroracemic acid; and that between 180° and 190°, of pyroracemic and pyrotartaric acids. From these results it appears, that anhydrous tartaric acid is resolved by strong and sudden heating into acetic acid, carbonic acid, and carbonic oxide:



but by slower and more gentle heating, into hydrated pyroracemic and carbonic acid:



the two processes may take place together. (Völckel. *Ann. Pharm.* 89, 57; see also ix. 418.) ¶.

3. Tartaric acid heated in the air, froths up, emits an odour of burnt sugar, takes fire, and leaves a soft charcoal. — 4. Tartaric acid mixed with spongy platinum and heated in a stream of oxygen gas, begins to form carbonic acid and water at 160°, and at 250°, is completely resolved into these two products. (Reiset & Millon.)

5. Chlorine scarcely exerts any decomposing action on the aqueous acid. (Liebig.) — 6. Hot nitric acid decomposes tartaric acid into acetic, oxalic, and saccharic acid. (Hermbstadt.) The nitric acid solution mixed with basic acetate of lead, and heated, deposits crystals of oxalonnitrate of lead. (Johnston.) — ¶. Finely pulverized tartaric acid dissolves quickly in 4½ times its weight of mono-hydrated nitric acid; and on agitating the solution with an equal volume of sulphuric acid, it forms a crystalline pulp, which, after the sulphuric acid has been absorbed by continued pressure between porous plates, forms a loose, white, silky, mass, emitting white fumes in the air. This product consists of nitrotartaric acid. (Dessaigues, *Compt. rend.* 34, 731.) ¶. — 7. Boiling aqueous iodic and periodic acids slowly decompose tartaric acid, with formation of tartaric acid and liberation of iodic. (Benckiser, Millon.)

8. Tartaric acid gently heated with a three or fourfold quantity of oil of vitriol, till sulphurous acid is about to escape, is partly converted into

tartralic and tartrelic acids. (Fremy.)—When strongly heated with a small quantity of oil of vitriol, the acid yields carbonic oxide, carbonic acid, and sulphurous acid, and leaves a black mixture; but when subjected to a gradually increasing heat in contact with a large excess of fuming oil of vitriol, it yields at first, without any blackening, carbonic oxide and sulphurous acid gases (without any carbonic acid) in the ratio of 4 : 1, and ultimately carbonic oxide, carbonic acid, and sulphurous acid, in the proportion of 3 : 1 : 2 (Dumas & Piria):



but at the temperature which is ultimately attained, 1 vol. of carbonic oxide out of the four is oxidised by the sulphuric acid to carbonic acid, and 1 vol. more of sulphurous produced thereby at the same time. (Dumas & Piria.) The evolution of carbonic oxide had been previously observed by Döbereiner. (*Gül.* 72, 201.)

9. A cold mixture of equal parts of tartaric acid and *bichromate of potash* and a small quantity of water, assumes a dark greenish brown colour; becomes gradually heated to the boiling point; gives off a large quantity of carbonic acid; and leaves a dark greenish brown, nearly black liquid containing formic acid. (Winckler, *Repert.* 46, 466; 65, 189.—10. Tartaric acid reduces *vanadic acid* to vanadic oxide. (Berzelius.)—11. Heated with *peroxide of manganese* and water, it becomes hotter, and gives off carbonic and formic acids with strong effervescence, while formiate and tartrate of manganese remain in solution; on addition of sulphuric acid, the tartaric acid is completely decomposed, and all the formic acid expelled, with formation of sulphate of manganese. (Döbereiner, *Gül.* 71, 107; also *Schw.* 35, 113; Persoz.)—12. Crystallized tartaric acid, to the amount of 150 pts. (1 At.) triturated with 480 pts. (4 At.) *peroxide of lead* at 16°, rises in a few seconds to a red heat, and burns away with a glimmering light, giving off carbonic acid gas with an odour of formic acid. (Walcker, *Pogg.* 5, 536.)—Böttger (*J. pr. Chem.* 8, 477) prefers 5 pts. of well-dried tartaric acid and 16 pts. of the peroxide.—When 1 pt. of tartaric acid, 5 pts. of peroxide of lead, and 10 pts. of water are mixed at ordinary temperatures, pure carbonic acid is evolved, and a solution of formiate of lead obtained, while the undecomposed portion of peroxide of lead is often mixed with tartrate and carbonate of lead. (Persoz, *Compt. rend.* 11, 522; also *J. pr. Chem.* 23, 54; Böttger, *Beitr.* 2, 124.)—13. Tartaric acid boiled with *silver-solution* reduces the silver; if it be boiled with potash and oxide of silver as long as the latter continues to be reduced, the acid is converted into oxalic acid with evolution of carbonic acid. (Erdmann, *Ann. Pharm.* 21, 14.)—14. Tartaric acid neutralized by alkalis (but not the free acid) reduces *gold* from the chloride without evolution of carbonic acid (Pelletier), and *platinum* from the bichloride in the form of platinum-black, with evolution of carbonic acid. (R. Phillips, *Phil Mag. J.* 2, 94.)—Neutral tartrate of potash added to solution of *mercuric chloride* forms a precipitate of calomel, even in the dark. (Brandes, *Ann. Pharm.* 11, 88.)

15. Heated potassium and sodium decompose the acid with strong effervescence, the latter also with slight emission of light, yielding charcoal and alkali. (Gay-Lussac & Thénard.)

16. Aqueous tartaric acid decomposes by keeping, but only in the dilute state, producing a small quantity of acetic acid; when digested for some weeks with alcohol, it is converted into vinegar. (Bergman.)—¶. According to Wittstein (*N. Jahrb. Pharm.* 2, 229), the aqueous solu-

is commonly supposed: a solution of tartaric acid in 5 times its weight of water exhibited after the lapse of a year—during which a fungus had formed in it—the original amount of acid.—According to Städeler & Kranse (*Chem. Gaz.* 1855, 67), a fresh solution of tartaric acid does not reduce an alkaline solution of cupric oxide at a boiling heat; but a solution which has been kept for some time effects the reduction, and with greater rapidity as it is more dilute.

17. When a solution of neutral tartrate of potash is subjected to the action of a powerful voltaic current, the gas evolved at the positive pole contains carbonic acid and carbonic oxide, resulting from the combustion of the acid by oxygen evolved at that pole from the water. (*Martens, Instit.* 1853, 117.) ¶.

Combinations. With Water. — Aqueous Tartaric acid.—The acid dissolves in $\frac{1}{3}$ pt. of cold and in a still smaller quantity of boiling water. The concentrated solution has the consistence of a syrup.

100 pts. of the aqueous solution contain of the crystallized acid:

According to Richter.			
Sp. gr.	Acid.	Sp. gr.	Acid.
1·36	64·56	1·16	32·06
1·32	58·75	1·12	24·98
1·28	52·59	1·08	17·45
1·24	46·03	1·04	9·06
1·20	39·04		

According to Osann (*Kastn. Arch.*, 3, 396.)

Sp. gr.	Acid.	Sp. gr.	Acid.
1·274	51·42	1·109	22·27
1·208	40·00	1·068	14·28
1·174	34·24	1·023	5·00
1·155	30·76	1·008	1·63
1·122	25·00		

The acid dissolved in water turns the plane of polarization of a luminous ray to the right (vii. 65), the angle of deviation corresponding exactly to the quantity of acid traversed by the ray (Biot, *Compt. rend.* also *Pogg.* 38, 179).—¶. The greater number of optically active substances exhibit the same *specific rotatory power*,* whether they are used in the pure state, or diluted to any extent with optically inactive solvents. But tartaric acid and its compounds form an exception to this rule. The optical power of the molecules of tartaric acid is continually increased by addition of water, and in a still greater degree by the addition of extremely small quantities of boracic acid, which is itself inactive.—The dispersion of the planes of vibration of the different coloured rays by circular polarization likewise exhibits exceptional relations in the case of tartaric acid. In all other substances, the deflection increases with the refrangibility of the ray; but in tartaric acid, the plane

* Let α denote the deviation of the plane of vibration of the ray in its passage through a stratum of liquid of length l and density δ , and ϵ the quantity of the optically active substance in the unit of weight of the solution: then:

$$[\alpha] = \frac{\alpha}{l \epsilon \delta}$$

is the specific rotatory power for the given coloured ray. (Biot.)

of vibration of the green ray is more strongly deflected than those of the red and blue, and that of the violet least of all. Moreover, the ratios of these angles of deviation are altered by addition of water and boracic acid, being thereby brought nearer to the ordinary deviations produced by other bodies. Even $\frac{1}{100}$ of boracic acid is sufficient to reduce the abnormal dispersion-relations of tartaric acid to the normal relations observed in quartz, sugar, &c. Hence it appears that the molecules of tartaric acid are altered in their chemical nature by addition of water, and still more of boracic acid, without however undergoing actual decomposition. (Biot, *N. Ann. Chim. Phys.* 36, 257; abstr. *Compt. rend.* 35, 233; *Instit.* 1852, 349; *Ann. Pharm.* 84, 160; *Jahresber.* 1852, 165.) ¶

Tartaric acid with Boracic acid.—The two crystallized acids triturated together while warm, unite even out of contact of air, into a pasty mass, which solidifies on cooling, and deliquesces in the air. (Thevenin, *J. Pharm.* 2, 421.)—A mixture of pulverized tartaric and boracic acids deliquesces in air saturated with moisture, in which either of the two acids in the separate state would remain dry. Boracic acid dissolves more abundantly in water containing tartaric acid than in pure water, though the solubility does not increase exactly in proportion to the quantity of tartaric acid present. By repeated crystallization, all the boracic acid may be recovered from the solution. (Soubeiran, *J. Pharm.* 10, 395; also *Mag. Pharm.* 8, 221.)—According to Wittstein (*Pharm. Centr.* 1851, 61), boracic acid does not form a chemical compound with tartaric acid without the intervention of a base. The deliquescence of a mixture of the two acids arises from the boracic acid abstracting from the tartaric acid a portion of its water, and thereby converting it into hygroscopic tartaric acid.

Tartaric acid with Nitric oxide.—The aqueous acid saturated at 37° (but not the pulverized acid) absorbs a considerable quantity of nitric oxide gas. The colourless liquid, after a while, deposits needles which appear to consist merely of tartaric acid; it evolves no gas even when boiled, but produces a deep brown colour with protosulphate of iron. (Reinsch, *J. pr. Chem.* 38, 394.)

Tartrates.—The acid has a powerful affinity for bases. Its alcoholic solution does not decompose carbonates unless water be present (Pelouze), because tartrates are insoluble in alcohol. (Braconnot.)—The acid forms chiefly *neutral salts* = $C^6H^4M^2O^{12}$, and *acid salts* = $C^6H^6MO^{12}$. Respecting the salts in which the metallic oxide contains 3O, see especially those of uranic and antimonic oxide.—Like free tartaric acid, all tartrates dissolved in water turn the plane of polarization of light to the right; only the concentrated solution of tartrate of alumina in water, and the solution of tartrate of lime in hydrochloric acid, exhibit rotation to the left. (Biot, *J. Chim. méd.* 12, 8.) With this is connected the fact that the crystals of all tartrates are hemihedral, and exhibit unsymmetrical faces on the right side, excepting the neutral tartrate of lime, which likewise exhibits the opposite optical relation. (Pasteur, *N. Ann. Chim. Phys.* 24, 442;—*Compt. rend.* 29, 297; *Chem. Soc. Qu. J.* 3, 79; further, *N. Ann. Chim. Phys.* 38, 437; *Compt. rend.* 35, 176; *Ann. Pharm.* 84, 157.)—The tartrates yield by dry distillation the same products as the free acid, viz. carbonic acid, and a carburetted hydrogen gas, acetic acid, pyro-

leave a carbonaceous, often pyrophoric residue. When heated they emit an odour of malic acid. Their dilute solutions are in become mouldy. A dilute solution of tartrate of potash, mixed with a small quantity of ferment, e. g. an aqueous extract of almond, prepared in the cold and left in a warm place, is quickly converted into carbonate. (Buchner, *Ann. Pharm.* 78, 203.)—The soluble form with tartaric acid, neutral salts which are easily soluble and acid salts which are sparingly soluble. The neutral tartarates and other bases are insoluble or sparingly soluble in water, but on addition of tartaric acid. These salts likewise dissolve in hydrochloric or nitric acid. All tartrates dissolve in excess of ammonia, potash, or soda, excepting the silver-salt, which is insoluble in potash and soda, and the mercury-salts, which are not soluble of the three alkalis. From the solution of a tartrate in water bisulphate of potash throws down, after a while, a precipitate of bisulphate of potash. — Tartaric acid forms a great number of double salts.

TARTRATE OF AMMONIA. — *a. Neutral.* — The aqueous acid saturated with carbonate of ammonia, is evaporated, with frequent addition of carbonate of ammonia, and cooled to the crystallising point. The parent, colourless prisms belonging to the oblique prismatic system, *Fig. 89*; but instead of the *f*-face there is an *e*-face between the *i* and *m* faces. $i : m = 91^\circ 51'$; $i : e = 127^\circ 40'$; $e : m = 140^\circ 29'$; $a : a = 124^\circ 55'$; $a : h$ below = $124^\circ 24'$; $a : a$ at the side = $116^\circ 50'$; $i : h = 88^\circ 58'$; $e : a = 137^\circ 39'$; $m : a = 110^\circ 28'$. The *a*-faces at one end are enlarged so as to cover the *a* and *h* faces. (Prevostaye, *N. Ann. Chim. Phys.* 3, 126) crystals are therefore hemihedral; they cleave easily parallel to *i*. (comp. Neumann, *Schw.* 64, 197; Rammelsberg, *Pogg.* 96, 23) according to Pasteur also (*N. Ann. Chim. Phys.* 42, 418; *Compt. Rend.* 20; *Jahresber.* 1854, 395) this salt is dimorphous. From a solution of the acid ammonia-salt supersaturated with ammonia, it separates above-described crystals of the oblique prismatic system; but solution of that salt mixed with neutral malate of ammonia (active or inactive, but most readily with the latter), the neutral malate of ammonia separates in crystals having the same compositional properties as the preceding, but belonging to the right prismatic system. (See also *N. Ann. Chim. Phys.* 38, 437.)—The salt tastes lil effloresces in the air from loss of ammonia, is decomposed and dissolves readily in water. — Its solution, exposed to light for a year, exhibits scarcely any turbidity, but becomes alkaline. (*Br. Arch.* 4, 257.)

<i>Crystals.</i>			Dumas & Piria.	Rammelsberg
8 C.....	48	26.09	25.7	26.22
2 N.....	28	15.22		14.88
12 H.....	12	6.52	6.6	6.55
12 O.....	96	52.17		52.35
<hr/>				
$C^8H^4(NH^4)^2O^{14}$	184	100.00		100.00
<hr/>				
Or:				Dulk.
2NH ³	34	18.48		16.16
C ⁸ H ⁴ O ¹²	150	81.52		
<hr/>				
		184	100.00	

b. *Acid*. — The concentrated aqueous solution of salt *a*, or aqueous ammonia, mixed with an excess of concentrated tartaric acid, yields so copious a precipitate of the sparingly soluble acid salt in the form of delicate needles, that it solidifies. — The transparent, colourless crystals belong to the right prismatic system; *Fig. 56*, but with *m*-faces in addition, and always two faces between *u* and *t*; *i* : *i* = 110° 32'; *i* : *a* = 141° 12'; *a* : *a* behind = 127° 12'; *u* : *u'* = 70° 44'; *t* : *a* = 116° 24'; *t* : *u* = 125° 22'. (Prevostaye.) According to Pasteur, the crystals exhibit hemihedry to the right by bevelling in opposite directions, somewhat as in *fig. 72*, so that, standing opposite to *t*, the upper bevelling face lies to the right. ¶. According to a later investigation of Pasteur's (*N. Ann. Ch. Phys.* 38, 446; *Jahresber.* 1853, 415) the crystals of this salt belong to the oblique prismatic system; and are holohedral when obtained from a solution in pure water or weak nitric acid, but hemihedral when crystallised from a solution mixed with a considerable quantity of acid tartrate of soda. ¶¶.

Crystals.		Dum. & Piria.	
8 C	48	28·74	28·8
N	14	8·38	
9 H	9	5·39	5·6
12 O	96	57·49	

Or:

C ⁶ H ⁶ (NH ⁴)O ¹²	167	100·00	
NH ³	17	11·08	Dulk. 10·68
C ⁶ H ⁶ O ¹²	150	89·82	
C ⁶ H ⁶ (NH ⁴)O ¹²	167	100·00	

¶. *Acid Tartromalate of Ammonia*. — Acid tartrate of ammonia combines with the acid ammonia-salt of optically active malic acid in equal numbers of atoms. From a solution of the two salts in this proportion in a large quantity of hot water, the acid tartrate crystallizes on cooling: the mother-liquor when evaporated and cooled, yields the double salt in indistinct prisms (thick acuminated prisms); and from the mother-liquor decanted from these crystals, and again evaporated and cooled, the same double salt is deposited in white warty nodules; the last mother-liquor yields nothing but acid malate of ammonia. — From a solution of equal numbers of atoms of acid tartrate and acid malate of ammonia in only four times their weight of hot water, the double salt crystallizes on cooling, mixed with acid tartrate of ammonia, every two tables of the double salt having a narrower table of pure acid tartrate of ammonia inserted between them. — The double salt is best obtained by dissolving 1 pt. of acid tartrate and 2 pts. of acid malate of ammonia in 15 pts. of hot water, and leaving the solution to crystallize. — It dissolves in 11·8 pts. of water at 15°. The solution acts upon polarized light exactly in the same manner as a mixture of the two simple salts in equal numbers of atoms. When recrystallised, it undergoes partial decomposition. (Pasteur, *N. Ann. Chim. Phys.* 38, 437; *Jahresber.* 1853, 417.)

Calculation, according to Pasteur.

C ⁶ H ⁶ (NH ⁴)O ¹²	167	52·51
C ⁶ H ⁶ (NH ⁴)O ¹⁰	151	47·49
C ⁶ H ⁶ (NH ⁴)O ¹² , C ⁶ H ⁶ (NH ⁴)O ¹⁰	318	100·00

carbonate of potash or carbonate of lime till it is neutralised. On evaporating the solution, it is obtained in the form of a white powder, having a saline bitterish taste. Crystallizes by slow evaporation in transparent, colourless prisms belonging to the oblique prismatic system. Nearly the form of *Fig.* 109, without *a*-faces; *i* : *f* behind = 142° 13'; *i* : *c* = 127° 17'; *c* : *f* = 89° 30'; *u* : *m* = 112° 35'; *u* : *c* = 103° 35'; *u* : *i* = 95° 35'. (Prevostaye.) Brooke (*Ann. Phil.* 23, 161), according to whom the crystal is cleavable in the direction of *f* and *c*, places the figure in a different manner, but gives also the angles, 142° 13'; 127° 17'; 89° 30'; and 103° 40'; compare also Bernhardt (*N. Gehl.* 8, 417, and *N. Tr.* 7, 2, 51); Hankel (*Pogg.* 53, 620); Rammelsberg (*Pogg.* 96, 19). These crystals, according to Hankel, Pasteur, and Rammelsberg, likewise exhibit hemihedry. — The crystals do not give off any thing at 100°; but at 180° they part with 3·8 per cent. of water, and between 200° and 220°, they give off, without any colouring, from 5 to 5·5 per cent. more of acetone and other products, while a large quantity of carbonate of potash remains in the residue. (Dumas & Piria.) At higher temperatures, the salt melts and decomposes with intumescence. By dry distillation, it yields 37·5 per cent. of watery distillate (containing 0·05 p. c. of pyrotartaric acid, besides acetic acid, resin, &c.) and 6·25 per cent. of brown oil. (Gruner.)

From the aqueous solution of this salt, most acids (even a stream of carbonic acid, according to Dive, *J. Pharm.* 7, 489; also *Schw.* 34, 261) throw down the bitartrate; according to N. E. Henry (*J. Pharm.* 12, 80) the precipitate formed by sulphuric, hydrochloric, or nitric acid redissolves in an excess of the acid. Bromine likewise precipitates the bitartrate, with formation of bromide of potassium, and without exerting any decomposing action on the tartaric acid. (Cahours, *N. Ann. Chim. Phys.* 19, 507.) The salt triturated with $\frac{1}{10}$ of iodine assumes a pale red, and on addition of water, a brown colour. (Vogel.) — 1 pt. of the salt dissolves at 2° in 0·75, in 14° in 0·66, at 23° in 0·63, and at 64° in 0·47 of water. (Osann.) In air completely saturated with aqueous vapour, it deliquesces, taking in 53 days 82·3 per cent. of water. (Brandes, *Schw.* 51, 426.) It dissolves in 240 pts. of boiling alcohol. (Wenzel.)

		<i>Anhydrous.</i>		Thomson.		Thénard.			
2 KO	94·4	41·69	42	43	
8 C	48·0	21·20				
4 H	4·0	1·77				
10 O	80·0	35·34				
<hr/>		<hr/>		<hr/>		<hr/>		<hr/>	
$C^6H^4K^2O^{13}$		226·4	100·00				
		<i>Crystals.</i>		Dumas & Piria.		Berzelius.		Rammelsberg.	
2 KO	94·4	40·10	41·31	40·07	
8 C	48·0	20·39	20·17	20·40	
5 H	5·0	2·13	2·22	2·13	
11 O	88·0	37·38			37·40	
<hr/>		<hr/>		<hr/>		<hr/>		<hr/>	
$C^6H^4K^2O^{13} + Aq.$		235·4	100·00				100·00

b. Acid. — *Tartar*, *Weinstein*, *Tartarus*. — Occurs most abundantly in grapes. — When tartaric acid and potash in aqueous solution are mixed together, with the acid in excess, there is generally formed after a

while — provided the solutions are not too dilute, the temperature not too high, and there is not too great an excess of any of the stronger mineral acids present, — a precipitate of the acid tartrate of potash consisting of small crystals. In a similar manner, tartaric acid throws down the acid tartrate from all potash-salts dissolved in not too large a quantity of water; and, according to Pettenkofer, it affords for these salts a more delicate reagent than bichloride of platinum, inasmuch as tartaric acid at 10° precipitates a solution of carbonate of potash (subsequently neutralised with acetic acid) in 700 to 800 parts of water in 12 to 18 hours, whereas chloride of platinum gives no precipitate in a solution containing more than 500 pts. of water; but in presence of common salt, the precipitation, either by tartaric acid or by chloride of platinum, does not take place, unless the proportion of water is limited to 100 pts., or even less. — Perchlorate of potash is not precipitated by tartaric acid, since, on the other hand, perchloric acid throws down perchlorate of potash from a saturated solution of the acid tartrate (Serullas, *Ann. Chim. Phys.* 46, 297); bisulphate of potash also, according to Jacquelin, yields no precipitate of acid tartrate with tartaric acid. — Moreover, the stronger acids added to a solution of the neutral tartrate, throw down the acid tartrate, and according to Berzelius, bisulphate of potash precipitates it from solutions of other tartrates.

The crude *Tartar, Argol, roher Weinstein, Tartarus crudus*, containing the colouring matter deposited from the wine, the ferment, and about 6 per cent. of tartrate of lime, is converted by solution in hot water, filtering, crystallisation, and treatment with clay in copper vessels, into *Purified Tartar, Cream of Tartar, Crystals of Tartar, Cremor Tartari, Tartarus depuratus*. — This purified tartar often contains copper, and constantly also tartrate of lime to the amount, according to Vauquelin (*Ann. Chim.* 63, 33,) of 5 to 7, and sometimes according to Duflos (*N. Br. Arch.* 23, 302,) even of 16 per cent. The quantity of lime is best determined by ignition, solution in hydrochloric acid, and precipitation with oxalate of ammonia. To remove it, 12 pts. of purified tartar are treated for 24 hours, at 20° to 25° , with a mixture of 1 pt. commercial hydrochloric acid and 6 pts. water, and after draining, well washed with cold water. (Duflos.) — ¶. Gadicke, (*Arch. Pharm.* [2], 67, 44,) recommends for the purification of calcareous tartar, to dissolve it in $1\frac{1}{4}$ times its weight of hydrochloric acid of sp. gr. 1.145, diluted with an equal weight of water, strain the liquid through linen, and mix it with such a quantity of milk of lime or solution of carbonate of soda, that sufficient hydrochloric acid may remain free to hold the tartrate of lime in solution. ¶.

White, hard, transparent prisms (translucent if they contain tartrate of lime,) having a sourish taste, and permanent in the air. They belong to the right prismatic system. *Fig. 56.* They cleave very easily parallel to *m*, (that is, to the edge between *u* and *u* backwards and perpendicular to *t*); less easily parallel to *t*, *u'*, and *u*; $u' : u = 107^\circ 30'$; $u' : t = 126^\circ 15'$; $u : a = 117^\circ 2'$; $i : t = 125^\circ 30'$; $i : i$ backwards = 109° ; *a* to the left above : *a* to the right below = 77° . Generally some of the faces, especially *a*, are disproportionately large, while others disappear. (Brooke, *Ann. Phil.* 23, 161.) Similarly, Prevostaye, according to whom the acid tartrate of potash is isomorphous with acid tartrate of ammonia, but not with tartaric acid, whence K or NH^4 appears not to be isomorphous with H. (*Comp. Wollaston Ann. Phil.* 10, 37; Schabus, *Wien. Akad. Ber.* 1850, 42; *Jahresber.* 1850, 377.)

	Wardenburg.					Man.	Harr.
KO.....	47.2	25.08	24.80	24.94	26.6	23	33
C ⁸ H ⁴ O ¹⁰	132.0	70.14	70.45	70.82	73.4	77	57
HO	9.0	4.78	4.75	4.24			

C⁸H⁴KO¹² 188.2 100.00 100.00 100.00 100.00 100 97

The crystals cannot be further dehydrated by heat. (Phillips.) But crystals which have been merely dried in the air give off, when heated, 4 per cent. of hygroscopic water, which they absorb again in 16 days, if exposed to a thoroughly moist atmosphere. (Brandes, *Schw.* 51, 425). — 100 pts. of purified tartar yield by dry distillation 37.9 pts. of a mixture of carbonic acid, carbonic oxide, carburetted hydrogen, and olefiant gas; 14.0 pts. of watery distillate, in which, as the distillation proceeds, the amount of formic acid continually increases; pyrotartaric acid, which, towards the end of the distillation, sublimes in yellowish white needles; 4.2 pts. of empyreumatic oil, which at first passes over light and pale yellow, then continually browner, heavier, and more viscid, and at last tarry; and as residue, 40.9 pts. of a mixture of charcoal and carbonate of potash. (Göbel.) — 100 pts. yield by rapid distillation 33 pts. of watery liquid, containing a large quantity of acetic (but no formic) acid, and 11 pts. of pyrotartaric acid. — As Weniselos also did not obtain formic acid, it is probable that Göbel's formic acid was merely acetic. — 100 pts. of tartar leave 40 pts. of a mixture of 31.25 pts. of carbonate of potash and 8.75 pts. of carbonate of lime, and charcoal impregnated with sulphide of calcium (Brunner.) — Cream of tartar free from lime yields 36.37 pts. of carbonate of potash. (Melandri Contessi, *Ann. Pharm.* 5, 311.) — Crude tartar does not yield any pyrotartaric acid. (V. Rose, Gruner.) As it contains a certain quantity of wine-lees, it leaves a small quantity of cyanide of potassium, as well as charcoal and carbonate of potash. (Hassenfratz, *Berthollet, Statique chim.* 2, 232; Gm.) — Cream of tartar mixed with nitre detonates slightly when touched with a red-hot coal. *Salt of Tartar, Black and White Flax* (iii. 19, 20). — Cream of tartar, kept for years in a moist state, undergoes decomposition, and yields crystals of carbonate of potash. (Hecht, *Bull. Pharm.* 2, 206.) Its aqueous solution becomes mouldy, and yields carbonate of potash with a small quantity of oil. (Berthollet. *Mém. Paris*, 1782.) — When boiled with lime in water, it gives up all its acid to the lime. (Scheele, Osann.) Triturated with $\frac{1}{10}$ of iodine, it yields a violet powder, which becomes brownish when moistened with water. (Vogel.) — It dissolves in 240 pts. of water at 10° (Pettenkofer); and in 14 pts. (Wenzel), 15 pts. (A. Vogel, Brandes,) of boiling water. — It dissolves in 238 pts. of water at 27°; in 190 pts. at 13°; in 54 pts. at 40°; and in 20 pts. at 68° (Osann); in 195 pts. at 19°; in 89 pts. at 25°; in 47.5 pts. at 37.5°; in 37.8 pts. at 50°; in 22 pts. at 75°; in 16.8 pts. at 87.5°; and in 15 pts. at 100° (Brandes & Wardenburg); in 178 pts. at 17.5°, and in 15.3 pts. at 100° (Melandri Contessi). — Hydrochloric acid greatly increases the solvent power of water upon cream of tartar; then follow in order: sulphuric, nitric, oxalic, phosphoric, and citric acids; acetic acid has very little influence; tartaric acid appears rather to act in the contrary way. From the solution in water containing hydrochloric acid, alcohol throws down cream of tartar; from water containing sulphuric acid, it precipitates sulphate of potash, and from water containing nitrate of potash, it throws down nitre. (Destouches, *Bull. Pharm.* 1, 468.)

Tartrate of Boracic acid and Potash. — *Tartarus borazatus* or *Cremor Tartari salubilis* of the French. — Obtained by heating cream of tartar for some time with water and boracic acid, which latter, assuming the part of a salifiable base, takes up half the tartaric acid, and thereby forms a kind of double salt. Boracic acid is rendered much more soluble in water by the presence of cream of tartar, and the latter also by the presence of boracic acid. If the boracic acid is in excess in the compound, that is to say, if there be less than 188 pts. (1 At.) cream of tartar to 61·8 pts. (1 At.) crystallized boracic acid, it may be extracted by alcohol; when, on the other hand, the cream of tartar is in excess, that is, when there is more than 565 pts. (3 At.) cream of tartar to 123·6 pts. (2 At.) boracic acid, this excess remains for the most part undissolved on digesting the mixture with a small quantity of cold water. The two following definite compounds appear to be distinguishable.

a. $KO, BO^3, C^8H^{10} = C^8H^4(BO^3)O^{12}$ — When 61·8 pts. (1 At.) boracic acid are digested for 24 hours, at 60° to 70° , with 247·2 pts. of cream of tartar, the mixture then evaporated to dryness, the residue dissolved in a little cold water, and the solution filtered, 188·49 pts. (1 At.) cream of tartar remain in solution; and on evaporating and drying the residue for a considerable time, 214·2 pts. (1 At.) of tartrate of boracic acid and potash are obtained; and this, when burnt, leaves 84·4 pts. (a little more than 1 At.) of monoborate of potash; or, according to another experiment, 100 parts of the dry double salt, leave 38 pts. of borate of potash free from carbonate. The salt contains, therefore, 1 At. potash, 1 At. boracic acid, and 1 At. tartaric acid. — When boracic acid is heated to the boiling point for 10 minutes with excess of cream of tartar, a double quantity of the latter is dissolved, and the filtrate does not deposit anything till it is evaporated and cooled, when it deposits nearly half the cream of tartar. (Duflos, *Schw.* 64, 188, and 335.)

A solution of 1 pt. crystallized boracic acid and 2 pts. cream of tartar in 24 pts. of boiling water is evaporated; the compound precipitated from the concentrated liquid by alcohol; and the soft mass triturated in the heated liquid, dissolved three or four times more in a small quantity of water, and precipitated each time in the same manner by alcohol. (Soubeiran.) — Since 188·2 pts. (1 At.) cream of tartar require only 61·8 pts. (1 At.) crystallized boracic acid, 2 pts. of cream of tartar cannot require more than 0·66 pt. of crystallized boracic acid. The precipitations with alcohol serve to remove the excess of boracic acid; if the solution of boracic acid and cream of tartar be evaporated to dryness, and the pulverized residue repeatedly boiled with alcohol, the alcohol may remove a portion of the boracic acid, even from the compound *a*, thereby producing the compound *b*. (Soubeiran.)

The compound obtained by evaporation is a colourless, gummy, amorphous mass, which softens when heated, has a very sour taste, and dissolves very readily in water, but is insoluble in alcohol. Mineral acids added to the aqueous solution do not precipitate either cream of tartar or boracic acid; tartaric acid throws down cream of tartar after a few minutes. Alcohol of sp. gr. 0·81 removes from the compound both boracic and tartaric acid. (Duflos.)

	<i>Dried at 100°.</i>	<i>Soubeiran.</i>
KO'	47·2	22·06
BO ³	34·8	16·26
C ⁸ H ⁶ O ¹⁰	132·0	61·68
C ⁸ H ⁴ K(BO ³)O ¹²	214·0	100·00

decomposition, 8.10 p. c. (2 At.) water, so that there remains $\text{KO}, \text{BO}^2, \text{C}^6\text{H}^6\text{O}^2$, as in the case of strongly heated tartar-emetic (q. v.)

b. $2\text{C}^6\text{H}^4\text{K}(\text{BO}^2)\text{O}^{12} + \text{C}^6\text{H}^6\text{KO}^{12}$. — 1 pt. of crystallized boracic acid and 12 pts. of cream of tartar are boiled for 6 hours with a large quantity of water; the liquid evaporated down to a small quantity; the mother-liquor decanted from the cream of tartar which crystallizes out on cooling, evaporated to dryness; the residue dissolved in a small quantity of cold water; the filtrate again evaporated; the residue redissolved in water, &c. &c. as long as any cream of tartar remains behind; and the mass obtained by evaporation repeatedly washed with boiling alcohol. (Soubeiran.) — Of the same composition appears to be Meyrac's crystalline salt, obtained by evaporating an aqueous solution of 1 pt. of dry boracic acid and 8 pts. of cream of tartar within a bell-jar over lime. Colourless, very acid crystals, which dissolve readily in water, very sparingly in alcohol of at most 25° Bm. Their aqueous solution subjected to the action of the electric current yields boracic acid with a small quantity of tartaric acid at the positive pole, and acid tartrate of potash at the negative pole. When mixed with neutral tartrate of potash, it deposits the acid tartrate. Alcohol added to it throws down the salt in the form of a viscid mass, which, under the further influence of the alcohol, becomes white and solid from loss of water. (Meyrac.)

	<i>Dried at 100°.</i>		<i>Soubeiran.</i>
2 BO^2	69.6	11.30	11.43
2 $\text{C}^6\text{H}^4\text{KO}^{12}$	358.4	58.16	-
$\text{C}^6\text{H}^6\text{KO}^{12}$	188.2	30.54	
616.2 100.00			

1 pt. of crystallised boracic acid with 4 pts. of cream of tartar yields 4.5 pts. of dry salt (a mixture of *a* and *b*), which tastes very acid, does not give up any boracic acid to alcohol, and when ignited leaves borate of potash with a small quantity of carbonate. From its hot aqueous solution, the stronger acids—but not tartaric acid—throw down boracic acid, which then crystallises out on cooling. The salt is not deliquescent, but dissolves in $\frac{2}{3}$ pt. of cold and $\frac{1}{4}$ of boiling water. The hot solution does not deposit cream of tartar on cooling, but solidifies in a gelatinous transparent mass containing 34 per cent. of water. (A. Vogel.) — Sometimes the dry mass is insoluble in cold water, but becomes soluble in it, after immersion for a few seconds in boiling water. (Soubeiran.)

With 5 or more parts of cream of tartar to 1 pt. of crystallised boracic acid, a mass is obtained which, when dissolved in a small quantity of cold water, leaves behind a portion of the cream of tartar. (A. Vogel, Soubeiran.)

Compare Destouches (Bull. Pharm. 1, 468), Thevenin. (J. Pharm. 2, 423), Meyrac (J. Pharm. 3, 8). A. Vogel (Schw. 18, 189). Soubeiran (J. Pharm. 10, 399; 11, 560; 25, 241.) Soubeiran & Capitaine (J. Pharm. 25, 741; also Ann. Pharm. 34, 206). Dulk. Duflos (Schw. 64, 188 and 333). Wittstein (Repert. Pharm. [3] 6, 1; Pharm. Centr. 1851, 61; Jahresber. 1850, 378.)

A mixture of 3 pts. cream of tartar and 1 pt. borate of potash is viscid, very sour, and deliquescent. (A. Vogel.)

The hot aqueous solution of 1 At. tartaric acid and 1 At. chlorate of potash does not deposit cream of tartar on cooling, but yields a double salt. (De Vry, *Ann. Pharm.* 61, 248.)

Tartrate of Potash and Ammonia. — *Soluble Tartar, auflöslicher Weinstein, Tartarus solubilis ammoniacalis, Tartarus ammoniacus.* — Obtained by neutralising cream of tartar with ammonia or carbonate of ammonia. — Pulverised cream of tartar is dissolved in a slight excess of cold, moderately strong ammonia; the solution filtered from any tartrate of lime that may have separated; then evaporated, fresh ammonia added till an alkaline reaction is produced, and the liquid left to cool; or cream of tartar is heated with excess of aqueous carbonate of ammonia, and the process completed in the same manner. The lower the temperature, the larger and more solid are the crystals obtained: *Comp. Wittstein (Repert. 61, 215); Fr. Bucholz (N. Br. Arch. 11, 232); Veling (N. Br. Arch. 37, 38); Rammelsberg (Pogg. 96, 25).* — Transparent, colourless prisms, isomorphous with neutral tartrate of potash. (Prevostaye, *comp. Pasteur, N. Ann. Chim. Phys.* 38, 437.) The crystals have a cooling, pungent taste; become opaque in the air from loss of ammonia (Lassone, *Crell. Chem. J.* 5, 76); give off, when heated to 140° in a current of air, 12.4 p. c. therefore perhaps NH^4O , while pure cream of tartar remains in a very friable state (Dumas & Piria); and dissolve very readily in water.

	<i>Crystals.</i>		Dulk.		
NH ³	17.0	8.29	7.84
KO	47.2	23.00	21.35
C ⁸ H ¹⁰ O ¹¹	141.0	68.71		
C ⁸ H ⁴ (NH ⁴)KO ¹² 205.2 100.00					

¶ Rammelsberg obtained a salt isomorphous with the neutral potash salt, and in which $\frac{2}{3}$ of the potash in that salt are replaced by oxide of ammonium.

	<i>Crystals.</i>		Rammelsberg.		
$\frac{2}{3}$ NH ⁴ O	31.2	14.86	14.70 14.17
$\frac{1}{3}$ KO	37.7	17.97	18.44 18.55
C ⁸ H ⁴ O ¹⁰	132.0	62.88		
HO	9.0	4.29		
C ⁸ H ⁴ (NH ⁴) $\frac{2}{3}$ K $\frac{1}{3}$ O ¹² + Aq. 209.9 100.00					

In consequence of the smaller solubility of the ammonia-salt, a solution containing 1 At. of each of the two salts yields at first crystals containing a larger amount of ammonia than those which are afterwards deposited. (Rammelsberg.) ¶

2 pts. of cream of tartar and 1 pt. of borate of ammonia dissolved together in water and evaporated, leave a gummy acid compound. Lassone, *Crell. Chem. J.* 5, 86; A. Vogel.)

TARTRATE OF SODA. — *a. Neutral.* — Tartaric acid is neutralised with carbonate of soda, or 3 pts. of tartrate of lime are decomposed by boiling with 2 pts. of carbonate of soda dissolved in water; or neutral tartrate of potash is decomposed by an excess of sulphate of soda. Transparent, colourless prisms belonging to the right prismatic system. *Fig. 65*, with an *m*-face between *u'* and *u*; *y* : *y* = $132^\circ 19'$ (133° according to Haberle; $132^\circ 44'$ according to Prevostaye); *y* : *t* = $113^\circ 50'$; *u'* : *u* = $77^\circ 19'$; *u'* : *u* behind = $102^\circ 41'$ ($104^\circ 30'$ according to Haberle; $104^\circ 50'$ according to Prevostaye); *u* : *t* = $141^\circ 20'$ ($124^\circ 25'$ according to Prevostaye). Bernhardt (*N. Tr.* 7, 2, 35). *y* : *u* = $108^\circ 30'$; *u* : *m* = $127^\circ 35'$ (Prevostaye.) According to Haberle (*A. Gehl.* 5, 538), the salt likewise forms rhombic prisms of about $92\frac{1}{2}^\circ$ and $87\frac{1}{2}^\circ$, and rectangular prisms (*vid.* also

erzeugter Producte, Wien, 1855, S. 63; Jahresber. 1854, 696.) — By rapid crystallisation, the salt is sometimes obtained in needles united in bundles. The crystals are permanent in the air and melt in their water of crystallisation when quickly heated. (Herzog, *N. Br. Arch.* 31, 1.) At 200°, they begin to show colour, and give off 16 p. c. water. (Dumas & Piria.) They dissolve in 5 pts. of cold and in every proportion of hot water, but are insoluble in absolute alcohol (Bucholz, *A. Gehl.* 5, 520); in 3.46 pts. of water at 6°; in 2.28 pts. at 24°; in 1.75 pt. at 38°; in 1.5 pt. at 42.5 (Osann); in 2 pts. of cold water. (Herzog.)

Crystals.			Dumas & Piria.	
2 NaO	62.4	27.09		
8 C	48.0	20.83	20.06	
8 H	8.0	3.47	3.56	
14 O	112.0	48.61		

Or:

$C^8H^8Na^2O^{12} + 4Aq.$			230.4	100.00		
					Bucholz.	Herzog.
2 NaO	62.4	27.09	26.8	26.97		
$C^8H^8O^{10}$	132.0	57.29				
4 HO	36.0	15.62	16.9	15.56		
$C^8H^8Na^2O^{12} + 4Aq.$			230.4	100.00		

b. Acid. — Separates on cooling from the hot solution of the neutral salt mixed with $\frac{1}{2}$ pt. tartaric acid. Transparent, colourless prisms belonging to the right prismatic system. The primary form is a right rhombic prism, *Fig.* 61, with lateral edges of 140° and 40°; but the acute lateral edges are obliquely truncated, so that the resulting irregular six-sided prism exhibits two lateral edges of 140°, two of 120° 30', and two of 101° [these angular magnitudes are not exact]; moreover, as in *Fig.* 68, two small faces *y* forming with *p* an angle of 110°, and two faces *i*, which form with *p* an angle of 120°. (Haberle.) According to Pasteur, they are right rhombic prisms, bevelled in opposite directions, as in *Fig.* 72, but without the *t*-face. According to Bernhardt, they are twelve-sided prisms. — The salt has a very sour taste, and dissolves in 9 pts. of cold water (12, according to Vogel), in 1.8 pt. of boiling water, but is insoluble in absolute alcohol. (Bucholz.)

Crystals.			Dumas & Piria.	
NaO	31.2	16.40		
8 C	48.0	25.24	24.81	
7 H	7.0	3.68	3.89	
13 O	104.0	54.68		

Or:

$C^8H^8NaO^{12} + 2Aq.$			190.2	100.00		
					Bucholz.	
NaO	31.2	16.40	17.5			
$C^8H^8O^{11}$	141.0	74.14				
2 HO	18.0	9.46	15.1			
$C^8H^8NaO^{12} + 2Aq.$			190.2	100.00		

The crystals heated to 108° in a current of air, give off 9.5 per cent. of water. (Dumas & Piria.)

Tartrate of Boracic acid and Soda. — When 75.74 pts. ($\frac{1}{2}$ At.) of tartaric acid dissolved in water are neutralised by carbonate of soda,

soda, 61·8 pts. (1 At.) of crystallised boracic acid, the solution then evaporated, and the residue dried at 100°, the quantity of salt thus obtained amounts to 199 pts. From the solution of this salt in water, mineral acids do not throw down anything; but tartaric acid, after some time, throws down acid tartrate of soda. (Duflos.)

Acid tartrate of soda forms, both with borax and with borate of ammonia, a gummy, amorphous and deliquescent salt (A. Vogel; see also Wittstein, *Jahresber.* 1850, 378.)

Tartrate of Soda and Ammonia. — Isomorphous with tartrate of soda and potash. (Pasteur.) Sp. gr. 1·58. The formula of the salt is $C^8H^4Na(NH^4)O^{12} + 8Aq.$ (Mitscherlich, *Pogg.* 57, 484.)

Tartrate of Soda and Potash. — *Rochelle salt, Seignette salt, Sal polychrestum Seignette.* — Cream of tartar is neutralised with carbonate of soda, the solution filtered to separate tartrate of lime, then evaporated, and left to crystallise in the cold. The salt may also be obtained by decomposing 1 At. neutral tartrate of potash with 1 At. sulphate of soda or common salt, in which case, however, the sulphate of potash or chloride of potassium formed at the same time must be separated by crystallisation. Or sulphate of soda may be ignited with charcoal, the product digested in water, and the filtrate saturated with cream of tartar (Bauer, *Repert.* 25, 438); or sulphate of baryta may be ignited with charcoal, the baryta precipitated as carbonate from the aqueous sulphide of barium by carbonate of soda, and the filtrate neutralised with cream of tartar. (Weitzel, *Ann. Pharm.* 5, 294.) — If the solution of Rochelle salt contains tartrate of lime, the crystals are turbid; but on heating the solution for some time to 50° — 60°, the greater part of the tartrate of lime separates out. (Geiger, Weitzel.)

Large, transparent, colourless prisms of 4, 6, 8, 10, 12, or 16 sides, and belonging to the right prismatic system. *Fig.* 80; $u' : u = 100^\circ$ ($100^\circ 24'$, Bernh.); $u : n = 163^\circ$ (160° , Bernh.); $p : i = 138^\circ 50'$; often only half developed, so that the face m or t is situated at the top. (Brooke, *Phil. Ann.* 21, 451; *comp.* Bernhardi. *N. Tr.* 7, 2, 55). The half crystals are simple, and the entire ones maced, and consequently thermo-electric. (Hankel, *Pogg.* 49, 502). Rochelle-salt likewise exhibits hemihedry to the right, the two upper truncations of terminal edges being in opposite directions to the two lower. (Pasteur.) ¶. According to a later observation of Pasteur's (*N. Ann. Chim. Phys.* 38, 451), the salt rarely exhibits hemihedral faces when crystallized from pure water, but the crystals obtained from a solution mixed with acid tartrate of potash or ammonia, are generally hemihedral. The crystals effloresce when exposed to the air, but only on the surface. They melt when heated, then remain liquid for 4 to 8 hours after cooling, and afterwards crystallise on the surface; the fused mass poured into cold water remains for a long time soft and capable of being drawn out into threads. (Marx, *J. Pharm.* 22, 143.) — The crystals heated in the water-bath give off 17·5 per cent. of water, and if then exposed to an atmosphere saturated with moisture, absorb 26·75 p. c. in 8 days. (Brandes, *Schw.* 51, 432.) They do not part with their last atom of water till they are heated to 130° (Berzelius, *Pogg.* 47, 316.) At the temperature of the water-bath, they give off only 6 At. water out of the 8 At. which they contain. (Schaffgotsch, *Pogg.* 57, 485.) — Heated to 155° in a current

(Dumas & Piria.)— They melt between 70° and 80° to a transparent colourless liquid which boils at 120°; becomes viscid with formation of large bubbles at 170° to 180°; then flows clearly and quietly; and boils again between 190° and 195°, the ebullition then continuing to 215°, by which time all the water, amounting to 25·09 per cent. is driven out. The residue is a viscid mass, which remains transparent when cold; absorbs water from the air; turns brown and swells up at 220°; and at a higher temperature, is converted, with emission of an odour of burnt sugar, into a mixture of charcoal and carbonate of potash and soda. The crystals give off 23·26 p. c. water at 180°, or at 100° if they are mixed with sand. (Fresenius, *Ann. Pharm.* 53, 234.)

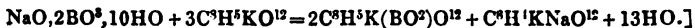
The dry salt dissolves in 2·62 pts. of water at 6°. (Fresenius.) The crystals dissolve, according to Osann, in 3·3 pts. of water at 3°, in 2·4 pts. at 11°, and in 1·5 pt. at 26°; according to Brandes, in 2 pts. at 5·6°, in 1·2 pt. at 12·5°, in 0·42 at 25°, and in 0·3 at 37·5°. The solution saturated at 8° has a density of 1·254. The solution precipitates bichloride of platinum, and forms a precipitate of cream of tartar with sulphuric or tartaric acid. (Widmann, Buchner, Kaiser, *Repert.* 22, 257.)

Crystals.		Dumas & Piria.		Fresenius.	
KO.....	47·2	16·71			
NaO	31·2	11·05			
8 C	48·0	17·00	17·1	17·06
12 H	12·0	4·25	4·3	4·33
18 O.....	144·0	50·99			
<hr/>					
C ⁶ H ⁴ KNaO ¹² + 8Aq.		282·4	100·00	

Or:

		Schaffgotsch.		Fresenius.	
KO.....	47·2	16·71	16·60	
NaO	31·2	11·05	11·18	
C ⁶ H ⁴ O ¹²	132·0	46·74			
8 HO	72·0	25·50		25·09
<hr/>					
C ⁶ H ⁴ KNaO ¹² + 8Aq.....		282·4	100·00	

Tartrate of Borax and Potash.— *Tartarised Borax, Boraxweinstein, Tartarus boraxatus, Cremor tartari solubilis, Borax tartarisata* of the Germans.— Obtained by dissolving 1 pt. of common borax and 3 pts. of cream of tartar in warm water, filtering if necessary from tartrate of lime, and evaporating to dryness.— If 5 pts. of cream of tartar are taken to 1 pt. of borax, the mass, when redissolved in cold water, leaves 2 pts. of cream of tartar behind. (Duflos, *Schw.* 64, 333.)— With 1 pt. of borax to 2 pts. of cream of tartar, the mass is alkaline and less soluble, and with equal parts, even the borax crystallizes out separately. (A. Vogel, *J. Pharm.* 3, 1.) The residue obtained with 1 pt. borax to 3 pts. cream of tartar amounts, after drying at 100°, to 3·6 pts. (A. Vogel), to 3·53 pts. (Duflos). [Since 1 : 3 as 190·8 (the atomic weight of 10-hydrated borax) : 572·4, and since 3 : 188·2 (the atomic weight of cream of tartar) = 564·6, it follows that this tartarised borax must contain 1 At. borax and 3 At. cream of tartar, and may be regarded as a mixture of 2 At. tartrate of boracic acid and potash *a.* (page 278), and 1 At. tartrate of soda and potash;



Dumas had previously estimated the proportions of the constituents correctly, inasmuch as he supposed the compound to contain 3 At. potash, 1 At. soda, 2 At. boracic acid, and 3 At. tartaric acid. [According to the above equation, 190·8 borax with 3·188·2 cream of tartar (making together 765·4 pts.) should part with $13 \cdot 9 = 117$ pts. of water, and therefore 4 pts. (1 pt. borax to 3 pts. cream of tartar) should give off 0·62 pt. water. Duflos supposed the loss of water to amount to only 0·47 pts.; but it must be remembered that 3 pts. cream of tartar to 1 pt. borax is rather too much, and that the cream of tartar which is in excess does not give off any water.—It might be objected to the equation above given, that the Rochelle salt supposed to exist in the mixture would crystallise out; but the large quantity of the tartarised borax likewise supposed to exist in it, which in the state of concentrated solution has a viscid consistence, may prevent the crystallisation.]

¶. According to Wackenroder (*Arch. Pharm.* [2] 58, 4; *Jahresber.* 1849, 306), a concentrated solution of 1 pt. borax and 3 pts. of purified tartar (still, however, containing lime) gradually deposits a finely divided crystalline powder containing 19·2 p. c. potash, 4·3 lime, 1·0 soda, 61·3 anhydrous tartaric acid ($C^6H^4O^{10}$), 2·0 boracic acid, and 12·2 water. In tartarised borax thus prepared, $\frac{1}{2}$ of the tartar is in excess and merely mixed with the true double-salt, and gradually separates from the solution. As the best mode of preparing tartarised borax, Wackenroder recommends to dissolve 24 pts. (2 At.) crystallised borax and 59 pts. (5 At.) dry pulverised cream of tartar, purified as completely as possible with hydrochloric acid, in 180 pts. of water at a gentle heat, then filter and evaporate; the product dried at 50° to 130° , till it no longer diminishes in weight, may afterwards be preserved unaltered (tartarised borax prepared with 1 pt. borax to 3 pts. cream of tartar is also not subject to deliquescence or alteration, unless it has been but imperfectly dried). The product, when perfectly dried, gives off such a quantity of water, that 4 At. tartaric acid may be supposed to be converted into $C^6H^2O^8$.—According to Wittstein, (*Repert. Pharm.* [3] 6, 1; *Jahresber.* 1850, 378,) 1 At. borax converts at most 2 At. cream of tartar into an easily soluble double salt, which when perfectly dry has the composition $C^6H^4(BO^2)KO^{12}$ [?]. ¶.

Similar compounds are obtained with borate of potash and acid tartrate of soda, and with acid borate of soda and cream of tartar. (Hagen.)

The mass obtained with 1 pt. borax and 3 pts. cream of tartar is gummy, amorphous, and rather acid. When burnt, it leaves a mixture of borate and carbonate of potash. (Duflos.)—[As 2 At. boracic acid, 3 At. potash, and 1 At. soda are present, and 2 At. boracic acid take up only 2 At. alkali, the residue must consist of 2 At. borate of potash with 2 At. carbonate].—Absolute alcohol does not extract from it either boracic or tartaric acid; sulphuric, hydrochloric, or nitric acid throws down from it, not cream of tartar, but boracic acid, which may be dissolved out by alcohol; tartaric acid on the other hand precipitates cream of tartar. (A. Vogel.) Alcohol of sp. gr. 0·81 dissolves out boracic and tartaric acid. (Duflos.)—The mass dissolves in 1 pt. of cold and $\frac{1}{2}$ pt. boiling water; but is insoluble in alcohol. (A. Vogel.) It deliquesces in damp air, and becomes solid again in a dry atmosphere. (Meyrac.)

The aqueous solution was once observed to exhibit luminosity when evaporated. (Herberger, *Repert.* 55, 59); compare also Dulk.

TARTRATE OF LITHIA.—*a. Neutral.*—Remains on evaporating the solution, as a white, opaque, non-crystalline, deliquescent mass, which

dried salt yields, when burnt, 44.44 per cent. of carbonate of lithia. (Dulk.)

b. Acid. — Uncrystallisable, still more soluble. (C. Gmelin.) White, shining, very small, easily soluble crystals, which when ignited, leave 20.22 p. c. carbonate of lithia, and, when dried in vacuo with twice their weight of lead-oxide and a small quantity of water, give off 19.22 p. c. water. (Dulk.)

Crystals.		Dulk.	
LiO.....	14.4	7.89	7.60
C ⁸ H ⁴ O ¹⁰	132.0	72.37	
4 HO.....	36.0	19.74	19.22
<hr/>			
C ⁸ H ⁵ LiO ¹² + 3Aq.	182.4	100.00	

Tartrate of Lithia and Potash. — Obtained by saturating cream of tartar with carbonate of lithia. Large rectangular, slightly displaced four-sided prisms, having a saline, bitter taste, slightly effervescent, readily soluble in water. (C. Gmelin.) Melts when heated. (Dulk.)

Crystals.		Dulk.	
KO.....	47.2	22.30	22.17
LiO.....	14.4	6.81	6.54
C ⁸ H ⁴ O ¹⁰	132.0	62.38	
2 HO.....	18.0	8.51	8.71
<hr/>			
C ⁸ H ⁴ KLiO ¹² + 2Aq.	211.6	100.00	

Tartrate of Lithia and Soda. — Obtained by saturating acid tartrate of soda with carbonate of lithia. Long rectangular prisms, often with obliquely set terminal faces; efflorescent only on the surface; easily soluble in water. (C. Gmelin.)

Indistinct Crystals.		Dulk.	
NaO.....	31.2	14.61	14.72
LiO.....	14.4	6.74	6.57
C ⁸ H ⁴ O ¹⁰	132.0	61.80	
4 HO.....	36.0	16.85	15.43
<hr/>			
C ⁸ H ⁴ NaLiO ¹² + 4Aq.	213.6	100.00	

TARTRATE OF BARYTA. — Baryta-water is precipitated by tartaric acid, but recovers its transparency on addition of excess of acid. Neutral tartrate of potash forms with chloride of barium, white flakes which become crystalline in 12 hours. (Wittstein, *Repert.* 57, 22.) Highly concentrated solutions yield a crystalline, dilute solutions a pulverulent precipitate; moreover, the precipitate redissolves spontaneously, when to the solution of the potash-salt in not more than 30 parts of water, there is added a quantity of chloride of barium, much less than sufficient to precipitate the whole of the tartaric acid. The same reaction is exhibited by tartrate of potash and ammonia and by tartrate of soda and potash. (Bush, *Br. Arch.* 24, 244.) — The precipitated neutral salt is a white loosely coherent (Richter) or crystalline powder. — It yields by dry distillation, empyreumatic oil and acetic acid, but no pyrotartaric acid. (Gruner.) — The carbonaceous residue takes fire after cooling in the air. (Böttger.) It is decomposed by aqueous sulphate of potash or soda. (Kölrnter.) — It dissolves in 400 to 1000 pts. of water, but less easily

aqueous sal-ammoniac. (Dreit, *Ann. Mag.* 5: 16, 33.) Wittstein, it does not. It dissolves in cold potash-ley, forming a liquid which coagulates by heat; this liquid may also be prepared with baryta-water and neutral tartrate of potash or soda. (Osann, *Gilb.* 69, 290.)

<i>Dried warm in vacuo.</i>				<i>Bolle.</i>		<i>Dulk.</i>	
2 BaO	153·2	53·72	52·79	53·06
C ⁸ H ⁴ O ¹⁰	132·0	46·28				
<hr/>							
C ⁸ H ⁴ BaO ¹²	285·2	100·00				

Tartrate of Baryta and Potash. — A solution of cream of tartar mixed with not too large a quantity of baryta-water, does not form any precipitate. (Thénard.) By evaporating the clear mixture, a neutral pulverulent double salt is obtained, sparingly soluble in water. (Dulk.)

<i>Air-dried powder.</i>				<i>Dulk.</i>	
KO	47·2	17·24	17·00
BaO	76·6	27·98	27·50
C ⁸ H ⁴ O ¹⁰	132·0	48·21		
2 HO	18·0	6·57	5·42
<hr/>					
C ⁸ H ⁴ KBaO ¹² + 2Aq.....	273·8	100·00		

Tartrate of Baryta and Soda. — Precipitated on mixing an aqueous solution of Rochelle salt with chloride of barium, chloride of potassium then remaining in solution; if the liquid be very dilute, the double salt is precipitated after some time only, and takes the form of needles. Dissolves sparingly in water, more readily in the aqueous solution of Rochelle salt. (Kaiser.)

<i>Crystals.</i>				<i>Dulk.</i>	
NaO	31·2	12·11	11·82
BaO	76·6	29·71	29·34
C ⁸ H ⁴ O ¹⁰	132·0	51·20	53·02
2 HO	18·0	6·98	5·82
<hr/>					
C ⁸ H ⁴ NaBaO ¹² + 2Aq.....	257·8	100·00	100·00

TARTRATE OF STRONTIA. — Tartaric acid forms a cloud in strontia-water, but an excess removes it. Strontia-water neutralised with tartaric acid yields, by gentle evaporation, small rectangular tables belonging to the right prismatic system, and bevelled at the edges. (Dulk & Neumann.) The aqueous solution of neutral tartrate of potash forms with chloride of strontium, white flakes which become crystalline in a minute. (Wittstein.) With nitrate of strontia it forms a slight precipitate, which dissolves on the application of a gentle heat, but is copiously deposited in shining crystals on boiling. (Vauquelin.) These crystals, however, according to Dulk, are contaminated with nitre. The cold aqueous mixture of neutral tartrate of potash and nitrate of strontia yields oblique rhombic prisms belonging to the oblique prismatic system. *Fig. 81, i : u = 92° 35'; u : u = 125° 20'* (Teschmacher, *Phil. Mag. Ann.* 3, 29; also *Kastn. Arch.* 13, 198.) — The salt, when ignited in a close vessel, leaves a pyrophoric residue. (Böttger.) It dissolves in 147 pts. of water at 16°. (Dulk.) Dissolves rapidly in aqueous hydrochlorate and succinate of ammonia, slowly in nitrate of ammonia. (Wittstein.)

$C^8H^4O^{10}$	132	...	42.86	
8 HO	72	...	23.37	21.51
<hr/>				
$C^8H^4Sr^2O^{12} + 8Aq.$	308	...	100.00	

Tartrate of Strontia and Potash. — Similar to the tartrate of baryta and potash. (Thénard.)

When prepared like the corresponding baryta-salt, it exhibits, after drying in the air, the following composition :

				Dulk.
KO	47.2	...	18.94	18.53
SrO	52.0	...	20.86	20.42
$C^8H^4O^{10}$	132.0	...	52.97	
2 HO	18.0	...	7.23	6.76
<hr/>				
$C^8H^4KSrO^{12} + 2Aq.$	249.2	...	100.00	

Tartrate of Strontia and Soda. — Acid tartrate of soda, neutralised with strontia-water and evaporated, leaves a gummy mass, which melts when heated, and gives off 8.05 p. c. (2 At.) water. It dissolves in 1.4 pt. water at 15°, and in all proportions of hot water. (Dulk.)

				Dulk.
	<i>Dried.</i>			
NaO	31.2	...	14.50	14.66
SrO	52.0	...	24.16	22.74
$C^8H^4O^{10}$	132.0	...	61.34	
<hr/>				
$C^8H^4NaSrO^{12}$	215.2	...	100.00	

Tartrate of strontia forms with cold aqueous potash or soda a solution which coagulates every time it is heated; but if the heating be continued too long, the precipitate does not disappear on cooling. (Osann.)

TARTRATE OF LIME. — *a. Neutral.* — Occurs in many plants, especially in grapes, and mixes with the tartar, sometimes, according to Walchner, covering it with crystals. Also in considerable quantity in senna-leaves. (Casselmann.) — Lime-water forms with tartaric acid an abundance of white flakes, which sometimes become crystalline; they dissolve immediately in excess of the acid, the solution, after a while, depositing the neutral salt. Neutral tartrate of potash forms with chloride of calcium a crystalline pulverulent precipitate. (Wittstein.) In dilute solutions, the precipitate appears after some minutes only; in solutions diluted with 600 to 120 pts. of water, after 12 to 48 hours only, and is then more distinctly crystalline; when the tartrate of potash is dissolved in not more than 20 pts. of water, an insufficient quantity of chloride of calcium forms a precipitate which redissolves. (Busch, *Br. Arch.* 24, 244.) The salt is obtained in the process of preparing tartaric acid (p. 266). It presents itself, sometimes as a white tasteless powder, sometimes in small rectangular octohedrons, having the solid angles at the base truncated. *Fig. 47*, with *i*- and *m*-faces; $y : y = 100^\circ$; sometimes lengthened horizontally into a prism. (Walchner, *Schw.* 44, 133.) Right rhombic prisms with octohedral summits; *Fig. 64*, without the *i*- and *ii*-face; $u : u = 82^\circ 30'$. Angle of the octohedron = $122^\circ 15'$; no hemihedry. (Pasteur.) The crystals, when heated, give off water and lose their transparency. (Walchner.) When strongly heated, they swell

quantity of acid distillate (Walchner) containing acetic but no pyrotartaric acid. (Gruner.) The residue is pyrophoric. (Böttger.) The salt, when heated with potassium, decomposes, with faint emission of light, and yields charcoal and alkali; with sodium it decomposes in a similar manner, but with stronger emission of light. (Gay-Lussac & Thénard, *Recherch.* 2, 302.) ¶ When gradually heated in a tube after addition of ammonia and of nitrate of silver in small fragments, it covers the sides of the tube with a metallic speculum of silver, just like that produced by aldehyde-ammonia. A very small quantity of the lime-salt is sufficient to produce this reaction, but it is essential that the nitrate of silver be added in small pieces; if it be added in solution, the reduced silver is merely deposited in a grey powder. Racemate of lime produces the same reaction. (A. Casselmann, *Arch. Pharm.* 83, 148; *Chem. Soc. Qu. J.* 8, 306.) ¶ For the decomposition by putrefaction, see ix. 414.

The salt dissolves in 1995 pts. of water at 8° and in 906 pts. at 80° (Osann); in 600 pts. of boiling water; in 1210 pts. of cold, and 350 pts. of boiling water. (Casselmann.) It dissolves readily in mineral acids, acetic acid, and cream of tartar. From its solution in hydrochloric acid it is not precipitated by ammonia (Gay-Lussac); for, according to Brett, it dissolves in aqueous hydrochlorate or nitrate of ammonia; only however while the precipitate is still flocculent, not after it has become crystalline. (Wittstein.) The solution of the salt in hydrochloric acid does not form an immediate precipitate with ammonia (unless it be very highly concentrated), but after a while it deposits crystals of the salt (Berzelius); and when chloride of calcium is precipitated by neutral tartrate of potash, the flocculent precipitate dissolves readily in sal-ammoniac, but after a while the crystalline salt again makes its appearance, at least in concentrated solutions. (Gm.) [Hence the crystalline salt appears to be less soluble in sal-ammoniac than the flocculent salt.]—The salt dissolves abundantly in cold solution of caustic potash (*vid. inf.*); it dissolves pretty readily in a concentrated aqueous solution of neutral tartrate of potash, tartrate of potash and ammonia, or tartrate of soda and potash, whence it separates for the most part on dilution with water, and likewise on evaporating the solution and treating the residue with water. (Hornemann, *Berl. Jahrb.* 1822, 1, 81; Busch.)

<i>Dried at 160°.</i>		Gay-Lussac & Thénard.	
2 CaO	56	21·54	22·42
8 C	48	18·46	18·66
12 H	12	4·62	5·14
18 O	144	55·38	53·78
<hr/>			
C ⁸ H ⁴ Ca ² O ¹² + 8Aq.	260	100·00	100·00

Or:

		Berzelius. Meissner.	
2 CaO	56	21·54	24·64
C ⁸ H ⁴ O ¹⁰	132	50·77	21·60
8 HO	72	27·69	27·81
<hr/>			
C ⁸ H ⁴ Ca ² O ¹² + 8Aq.	260	100·00	27·71

The crystals contain the same amount of water. (Dumas & Piria.)

b. Acid.—Obtained by John (*Chem. Schriften*, 4, 175), from the fruit of *Rhus typhinum*, and erroneously regarded by Meissner (*Schw.* 45, 104,) as the neutral salt.—When lime-water is mixed with a suffi-

mixture set aside, it deposits the neutral salt; but by immediate evaporation, crystals of the acid salt are obtained. (Dulk.) Right prismatic system. *Fig. 44*; the obtuse terminal edges of the octohedron rest on the narrow lateral edges of the right rhombic prism. Angle of the acute terminal edges of the octohedron = $82^{\circ} 50'$; angle of the obtuse terminal edges, which are truncated = 153° nearly. (Neumann.) The crystals are transparent, redden litmus, dissolve sparingly in water, and their solution is precipitated by alkaline carbonates, oxalic acid, and neutral acetate of lead, but not by ammonia, nitrate of baryta, or nitrate of silver. (John.) They dissolve in 140 pts. of water at 16° , more readily in hot water. (Dulk.)—Lime-water mixed with tartaric acid till its transparency is restored, is not rendered turbid by ammonia. (Thénard.)

	<i>Crystals.</i>	<i>Dulk.</i>
CaO	28	17.44
C ² H ⁴ O ¹¹	141	83.43
C ² H ⁴ CaO ¹³	169	100.00

Tartrate of Lime and Potash. — a. Basic. — Tartrate of lime dissolves after some time in moderately warm aqueous potash. (Osann.) The same solution is obtained by moderately heating hydrate of lime with water and cream of tartar, or with neutral tartrate of potash, tartrate of potash and ammonia, or tartrate of potash and soda. It is mobile and caustic. Carbonate of potash with the aid of heat precipitates all the lime from it. (Lassone, *Crell. Chem. J.* 4, 109.) The perfectly saturated solution deposits part of the tartrate of lime, even on addition of water. (Osann.) It solidifies every time it is heated, provided it be not too concentrated, to a turbid, pasty mass. (Lassoue, Osann.) If it be then filtered while hot, there remains on the filter a compound of about 3 At. lime to 1 At. tartaric acid. (Osann.)—The cold liquid appears to be a solution of neutral tartrate of lime in potash; the potash at the boiling heat abstracts from the lime a portion of the tartaric acid, and throws down a basic salt. In the cold, this basic salt again takes from the potash the tartaric acid which the latter had abstracted from it, and is thereby again rendered soluble. (Osann, *Gibb.* 96, 291; *Kastn. Arch.* 3, 204; *Pogg.* 31, 36; *comp. Funcke, Repert.* 12, 337.)

b. Neutral. — a. With equal numbers of Atoms. — Separates gradually from a mixture of aqueous cream of tartar with not too large a quantity of lime-water. (Thénard.)

β. With excess of Tartrate of Potash. — The solution of neutral tartrate of potash in an equal weight of water, boiled down with excess of tartrate of lime, dissolves 27 per cent. of that salt. The solution remains clear and liquid in the cold; but when evaporated to a syrup, the greater part of it solidifies on cooling to a mass consisting of needles, which becomes somewhat moist in the air, dissolves completely in boiling water, but is decomposed by cold water, which dissolves its own weight of the salt, with separation of all the lime excepting $1\frac{1}{2}$ per cent., and this quantity is afterwards completely precipitated on diluting the solution with 9 pts. of cold water. (Hornemann, *Berl. Jahrb.* 1822, 1, 81.)

c. Acid. — The solution of 1 pt. borax and 3 pts. cream of tartar containing tartrate of lime, in not too small a quantity of water, deposits

is nearly insoluble in cold water, and is resolved by boiling water into cream of tartar which dissolves, and tartrate of lime which remains behind; when burnt, it leaves 13 p. c. carbonate of lime, and 22.4 p. c. carbonate of potash (no boracic acid), and therefore contains 35.80 p. c. neutral tartrate of lime with 63.63 p. c. acid tartrate of potash [about equal numbers of atoms]. (Th. Martius, *Kunst. Arch.* 19, 361.)

Tartrate of Lime and Soda. — a. Basic. — An aqueous solution of 31.2 pts. (1 At.) dry soda dissolves but a small quantity of tartrate of lime, at ordinary temperatures, but when moderately heated, takes up 101.1 pts. [less than $\frac{1}{2}$ At.]. Hydrate of lime is dissolved by aqueous tartrate of soda. These solutions coagulate whenever they are heated, still more strongly than those which contain potash, and form a stiff jelly. A solution diluted beyond a certain point does not coagulate; the stronger it is, the higher is the temperature at which it coagulates. The precipitate formed on heating the liquid is basic tartrate of lime. This precipitate dissolves more readily in a concentrated liquid and at a temperature a little below the point of coagulation, than in a dilute solution and in the cold. When the coagulated mass is evaporated to a small bulk, it forms, first a yellow transparent liquid, then a white mass. (Osann, *Gilb.* 69, 290.)

b. Neutral. — Precipitated on mixing Rochelle salt with chloride of calcium in white flakes, which afterwards become granular; or, if the solutions are very dilute, the double salt is precipitated after some minutes in numerous small needles, which dissolve sparingly in water, more readily in excess of Rochelle-salt, and still more readily in chloride of calcium. (Kaiser, *Repert.* 22, 280.)

TARTRATE OF MAGNESIA. — a. Neutral. — Dilute tartaric acid digested with excess of *Magnesia alba*, yields a filtrate which, by cooling and evaporation, deposits a crystalline crust, soluble in 122 pts. of water at 16°. (Dulk.) The residue obtained by ignition is pyrophoric. (Böttger.) The solution has but little taste. (Aviat, *J. Chim. méd.* 23, 447.) Aqueous sal-ammoniac dissolves the salt readily. (Brett.) — Magnesia-salts mixed with tartaric acid are not precipitated by excess of ammonia, potash, or soda, or their carbonates. (H. Rose.)

	Crystals.			Dulk.
2 MgO	40	16.39	17.65
C ⁶ H ⁴ O ¹⁰	132	54.10	
8 HO	72	29.51	29.30
<hr/>				
C ⁶ H ⁴ Mg ² O ¹² + 8Aq.....	244	100.00		

b. Acid. — Obtained by using a larger quantity of acid. Transparent, colourless, short, six-sided prisms, which intumescence when heated and are soluble in water. (Bergman.) Crystalline crust, soluble in 52 pts. of water at 16°. (Dulk.)

	Crystals.			Dulk.
MgO	20	12.42	12.88
C ⁶ H ⁴ O ¹¹	141	87.58	
<hr/>				
C ⁶ H ⁴ MgO ¹²	161	100.00		

tartrate with excess of *magnesia alba* and water, and evaporating the filtrate. (Thénard, Dulk.) At first small crystals are obtained which intumescce strongly in the fire, and do not become moist in the air; and the mother-liquor, when subsequently evaporated, leaves a gummy mass. (Dulk.) Thénard obtained only an amorphous salt, which became glutinous when heated, turned moist in the air, and was precipitated by potash. [Is this amorphous compound a basic salt?]

Crystals.		Dulk.	
KO.....	47.2	17.41	17.44
MgO	20.0	7.37	6.97
C ⁶ H ⁴ O ¹⁰	132.0	48.67	
8 HO.....	72.0	26.55	25.36
<hr/>			
C ⁶ H ⁴ MgO ¹² + 8Aq.....	271.2	100.00	

Tartrate of Magnesia and Soda. — The clear aqueous mixture of Rochelle salt and chloride of magnesium yields by evaporation, efflorescent rhombic prisms belonging to the oblique prismatic system; they must be freed from adhering chloride of calcium by washing. (Dulk.) About the shape of *Fig. 97*, without the *f*-face; $u : u = 51^\circ$; $i : t = 108^\circ$. (Neumann.)

Crystals.		Dulk.	
NaO	31.2	11.42	12.32
MgO	20.0	7.32	6.72
C ⁶ H ⁴ O ¹⁰	132.0	48.32	
10 HO.....	90.0	32.94	32.47
<hr/>			
C ⁶ H ⁴ NaMgO ¹² + 10Aq.	273.2	100.00	

CEROUS TARTRATE. — Tartrate of potash, but not the free acid, forms a white precipitate with cerous salts. The slight solubility of this precipitate in water is not increased by addition of tartaric acid. It dissolves readily in potash and soda, and still more readily in ammonia; this solution yields a gummy mass by evaporation. (Berzelius.)

TARTRATE OF LANTHANUM. — Soluble in ammonia. (Berzelius.)

TARTRATE OF YTTRIA. — *a. Neutral.* — Tartrate of potash forms with yttria-salts a precipitate which dissolves sparingly in water, readily in alkalis. (Klaproth, Berzelius.) The bulky precipitate dries up after washing to a white loose powder, which contains no water, decomposes very slowly by ignition, and is insoluble in water. (Berlin.)

b. Acid. The first quantities of the salt *a*, which are added to the aqueous acid, dissolve sparingly; the following acquire, after a while, a crystalline aspect, being converted into the acid salt. (Berlin.)

TARTRATE OF GLUCINA. — Crystallizes with difficulty by slow evaporation. Readily soluble. (Vauquelin.)

TARTRATE OF ALUMINA. — Occurs in *Lycopodium clavatum*. — Gummy mass, which has a rough sweetish taste, does not deliquesce in the air, and dissolves readily in water. (v. Paecken.) — Neither *tartrate of alumina*, nor any other salt of alumina mixed with tartaric acid, is precipitated by alkalis or alkaline carbonates. (Thénard, H. Rose.)

Tartrate of Alumina and Ammonia. Amorphous. (L. A. Buchner, *Repert.* 78, 320.)

Tartrate of Alumina and Potash.—*a. Basic.* An aqueous solution of neutral tartrate of potash (or of Rochelle salt), dissolves, when heated, a large quantity of alumina, without becoming alkaline. (Thénard.) The aqueous solution deposits, on addition of alcohol, oily drops, which unite into a layer, and whose aqueous solution dries up on evaporation to a gum containing potash and soda. (Werther.)

b. Neutral? A solution of cream of tartar dissolves hydrate of alumina, and is converted into an amorphous mass, which is not precipitated by alkalis. (Thénard.) The aqueous solution, of sp. gr. 1.477, rotates the plane of polarization to the left, but acquires greater dextro-rotatory power the more it is diluted. (Biot.)

When 1 pt. of cream of tartar is boiled with 4 pts. of water, the addition of $\frac{1}{2}$ pt. alum causes the whole to dissolve; as the liquid cools, small quantities of cream of tartar and of alum are precipitated; and the remaining very acid liquid yields, by evaporation, a white saline mass, which becomes gummy on exposure to the air, and dissolves in a very small quantity of water. (A. Vogel.)

TARTRATE OF THORINA.—*a. Neutral.*—Remains in the form of white flakes, which dissolve but slowly and partially in ammonia, when hydrate of thorina is treated with a quantity of tartaric acid not sufficient to dissolve it.—Thorina-salts mixed with tartaric acid, are not precipitated by ammonia. (Berzelius.)

b. Acid.—Found in the solution obtained in the preparation of salt *a*. This solution has rather an acid than a rough taste; is not precipitated by ammonia; and when evaporated yields crystals, which are resolved by alcohol into the salt *a*, and a soluble and still more acid salt *b*. (Berzelius.)

Tartrate of Thorina and Potash.—Obtained by digesting hydrate of thorina with aqueous cream of tartar. Crystallizable, sparingly soluble, not precipitated by alkalis. (Berzelius.)

TARTRATE OF ZIRCONIA.—Tartrate of ammonia forms with zirconia-salts, a precipitate which dissolves in potash and in excess of tartaric acid, and is not precipitated from the latter solution, either by caustic alkalis or their carbonates. (Berzelius.)

TITANIC TARTRATE.—Hydrochlorate of titanic oxide is precipitated by tartaric acid. The precipitate, which resembles titanic oxalate, yields, when ignited in a covered crucible, a black metallic powder, which, when heated in the air, slowly turns white. Acid solutions of titanic oxide which contain free tartaric acid, are not precipitated by ammonia, carbonate of ammonia, or potash; tincture of galls forms with these solutions a white precipitate, but the precipitation is incomplete, so that the liquid remains coloured. (H. Rose, *Gilb.* 73, 74; *Pogg.* 3, 165.)

According to Wollaston, tartaric acid dissolves hydrated tantallic oxide; but according to Gahn, Berzelius & Eggertz, it does not.

Potassio-tantallic Tartrate—A boiling solution of cream of tartar dissolves dry tantallic acid in a small quantity only, but the hydrated acid

potash or carbonate of ammonia, solidifies on cooling. (Gahn, Berzelius, & Eggertz.)

MOLYBDOUS TARTRATE. — Like the oxalate.

Potassio-molybdous Tartrate. — The solution of molybdic acid in aqueous cream of tartar is digested with zinc, whereby the molybdic acid is reduced to molybdic oxide; a little hydrochloric acid then added, and the digestion with zinc continued; the molybdic oxide is thereby reduced to molybdous oxide, which falls down in the form of a pulverulent double salt, to be washed upon the filter. This salt, when ignited in an open crucible, yields fused molybdate of potash. It dissolves sparingly in water, forming a purple solution; easily, and with dark purple colour, in aqueous ammonia, whence it is deposited on evaporation. (Berzelius, *Pogg.* 6, 379.)

MOLYBDIC TARTRATE. — The aqueous solution dries up to a pale red gummy mass, which is very apt to assume a green and blue colour. With alkalis it forms, without precipitation, deep red solutions, which become colourless on exposure to the air. (Berzelius, *Pogg.* 6, 348.)

Potassio-molybdic Tartrate. — *a. Basic.* — Cream of tartar forms with excess of hydrated molybdic oxide, a brown pulverulent salt, which dissolves sparingly in water, readily in alkalis. — *b. Neutral.* The solution dries up to a yellow mass, which dissolves readily in water, forming a solution which yields a yellow precipitate with tincture of galls. (Berzelius.)

Tartrate of Molybdic acid. — The colourless solution yields by evaporation a blue non-crystalline mass, which dissolves completely in water and alcohol.

Tartrate of Molybdic acid and Potash. — Of all solvents, a boiling aqueous solution of cream of tartar dissolves molybdic acid, even when ignited and sublimed, with the greatest facility. The solution dries up to a gummy mass. (Berzelius.)

VANADIC TARTRATE. — The beautiful medium blue solution dries up to a blue, translucent, fissured mass, which dissolves very slowly in cold water, more quickly in ammonia, forming a purple solution, the colour of which quickly disappears on exposure to the air, from formation of vanadic acid. (Berzelius.)

Potassio-vanadic Tartrate. — The blue solution of vanadic acid (which is thereby reduced to oxide), yields by evaporation with aqueous cream of tartar, a reddish blue extract, which becomes fissured; the same solution forms with ammonia a purple mixture without precipitation. (Berzelius.)

Tartrate of Vanadic acid. — The yellow solution of vanadic acid in aqueous tartaric acid, which, however, if it contains excess of tartaric acid, soon becomes green and afterwards blue, from formation of vanadic oxide. (Berzelius.)

CHROMIC TARTRATE. — a 1 At. Chromic oxide to 1 At. Tartaric acid. — Potassio-chromic tartrate is precipitated by neutral acetate of lead, the lead-salt suspended in water and decomposed by sulphuretted hydrogen, and the solution filtered. (Köchlin, *Bull. scienc. mathem.* 1828, 132; Berlin, *Berz. Lehrb.*) The green filtrate leaves when evaporated, a green vitreous mass = $Cr^2O^3, C^6H^6O^6$. (Berlin.) — Köchlin regards the salt as a *Chromotartaric acid*, which he supposes to form green and violet salts with bases. But these salts are really, as affirmed by Berzelius (*Pogg.* 16, 100), double salts; and the fact of the so-called chromotartaric acid not being precipitated by alkalis proves nothing, seeing that so many bases are protected by the presence of tartaric acid from precipitation by alkalis.

b. 2 At. Chromic oxide to 3 At. Tartaric acid. — The solution of hydrated chromic oxide in aqueous tartaric acid, is dark green by reflected, and violet-red by transmitted light; it reddens litmus slightly; is not decomposed by alkalis, and leaves a dark green saline crust when evaporated. (Brandenburg.) — The violet solution, which is not precipitated by alkalis, dries up to a violet mass containing 2 At. chromic oxide to 3 At. tartaric acid. (Berlin.) — By slowly evaporating the solution, violet-red octohedrons are obtained, which slowly effloresce, become nacreous and friable at a moderate heat, and dissolve readily in water. (Moser.)

Ammonio-chromic Tartrate. — Amorphous. (Buchner.)

Potassio-chromic Tartrate. — Formed, with evolution of heat and carbonic acid, on mixing tartaric acid with bichromate of potash. — In this decomposition, not only are carbonic acid and water formed, but likewise formic and oxalic acids, which remain, together with the tartaric acid, in combination with the chromic acid and potash. Pure potassio-chromic tartrate is therefore not yet known. (Lövel, *Compt. rend.* 16 862.) — The salt is not obtained by boiling hydrated chromic oxide with aqueous cream of tartar. (Berlin.)

Fischer (*Kastn. Arch.* 14, 169), mixes 1 pt. of a saturated aqueous solution of bichromate of potash with 2 pts. of a saturated solution of tartaric acid. The mixture quickly turns yellowish red, brown, greenish brown, and lastly violet; deposits cream of tartar on cooling, often mixed with brown oxide of chromium; and the filtrate, when evaporated at a gentle heat, leaves a violet, glassy, slightly transparent, amorphous mass, which dissolves slowly in cold, but quickly and abundantly in hot water. — Berlin adds to a hot aqueous solution of bichromate of potash, pulverised tartaric acid in successive small portions, but only so long as carbonic acid continues to escape, because a larger quantity of tartaric acid would throw down some of the potash in the form of acid tartrate; — and by evaporating the dark green solution, obtains a blackish green vitreous mass, which contains 1 At. potash, 1 At. chromic oxide, and 1 At. tartaric acid; dissolves readily in water; and is precipitated therefrom by alcohol. On mixing the solution of this mass with a concentrated solution of neutral tartrate of potash, it deposits dark green crystalline grains, containing 3 At. potash to 1 At. chromic oxide. (Berlin.) — According to Malaguti (*Compt. rend.* 16, 457; also *J. pr. Chem.* 29, 294), the salt obtained with bichromate of potash and tartaric acid is: $KO, Cr^2O^3, C^6H^6O^6 + 7Aq$; he does not, however, regard it as a double salt, but agrees with Köchlin in viewing it as chromotartrate of potash. — An aqueous solution of cream of tartar saturated with hydrated

red-hot coals, gives off the same odour as other tartrates, which is not the case with chromotartrate of potash. (Malaguti.)

URANOUS TARTRATE.—Tartaric acid forms with protochloride of uranium, a copious greyish green precipitate which is easy to wash. The air-dried salt gives off 11·76 per cent. of water at 100°. It dissolves in hydrochloric acid, and is precipitated therefrom by ammonia, unless an additional quantity of tartaric acid is added, in which case ammonia merely colours the solution brownish yellow. It dissolves sparingly in aqueous tartaric acid, forming a non-crystallisable liquid which is not precipitated by alkalis. (Rammelsberg, *Pogg.* 59, 81.)

Dried at 100°.		Rammelsberg.	
3 UO.....	204	59·13	59·57
8 C.....	48	13·91	13·12
4 H.....	4	1·16	1·08
10 O.....	80	23·19	21·81
HO.....	9	2·61	3·76
<hr/>		<hr/>	
UO, C ⁸ H ⁴ U ² O ¹² , HO.....	345	100·00	99·34

URANIC TARTRATE.—An aqueous mixture of chloride of uranic oxide and neutral tartrate of potash deposits very small, pale-yellow, sparingly soluble crystals. (V. Rose, Richter.) The yellow solution of pure uranic oxide in aqueous tartaric acid yields: (a) by warm evaporation, crystals with a smaller amount of water; and (b) by spontaneous evaporation, crystals with a larger amount. The latter give off in vacuo or at 150° in a current of dry air, 10·3 p. c. (6 At.) water, whereby they are converted into salt a, which suffers no further loss at 200°. (Peligot, *N. Ann. Chim. Phys.* 12, 463; also *J. pr. Chem.* 35, 153.)

Salt a.		Peligot.	
2 U ² O ³	288	65·76	65·30
8 C.....	48	10·95	10·85
6 H.....	6	1·37	1·45
12 O.....	96	21·92	22·40
<hr/>		<hr/>	
2U ² O ³ , C ⁸ H ⁴ O ¹²	438	100·00	100·00

Salt b.		Peligot.	
2 U ² O ³	288	58·54	58·60
8 C.....	48	9·76	9·86
12 H.....	12	2·44	2·38
18 O.....	144	29·26	29·16
<hr/>		<hr/>	
2U ² O ³ , C ⁸ H ⁴ O ¹² + 6Aq.....	492	100·00	100·00

Uranic salts are precipitated by alkalis, even after addition of tartaric acid. (H. Rose.)

Potassio-uranous Tartrate.—1. Uranous tartrate while still moist is dissolved in a warm concentrated solution of neutral tartrate of potash, the dark brown solution left to evaporate spontaneously, then decanted from the crystallised acid tartrate of potash, and completely dried.—2. Recently precipitated hydrated uranic oxide is boiled with cream of tartar and water, and the rest of the process conducted as above.—Black, shining, amorphous mass, which, after drying over oil of vitriol,

contains 13·15 p. c. KO and 48·52 UO, and whose aqueous solution is precipitated by potash but not by ammonia or by alkaline carbonates. (Rammelsberg.)

MANGANOUS TARTRATE. — A hot aqueous mixture of chloride of manganese and neutral tartrate of potash, first deposits cream of tartar, and afterwards, on cooling, manganous tartrate in small white crystals which are resolved by water into a soluble *acid* and an insoluble *basic* salt. (Pfaff, *Schw.* 4, 377.)

MANGANIC TARTRATE. — A cold concentrated solution of tartaric acid forms with manganose-manganic oxide, a brown solution which is decomposed by evaporation, and when supersaturated with potash remains brown without yielding any deposit. (Fromherz, *Schw.* 44, 338.)

Potassio-manganous Tartrate. — Obtained by dissolving carbonate of manganese in aqueous cream of tartar. The salt crystallises with difficulty, is very soluble, and is not precipitated by pure alkalis or alkaline carbonates. (Scheele.) — Peroxide of manganese forms with cream of tartar, at ordinary temperatures, a brown solution, which is decolorised and emits carbonic acid when heated. (Scheele.)

Manganous salts mixed with tartaric acid are not precipitated by alkalis or alkaline carbonates. (H. Rose.)

Tartrate of Arsenious acid? — The solution of arsenious acid in tartaric acid yields prisms by evaporation. (Bergmann.)

Tartrate of Arsenious acid and Ammonia. — Obtained by adding arsenious acid to a boiling aqueous solution of acid tartrate of ammonia as long as it dissolves. Arsenious acid crystallises out first from the filtrate, and afterwards the double salt in beautiful crystals. (Mitscherlich, *Lehrb.*) — The boiling must be continued for a long time, so that a sufficient quantity of arsenious acid may be dissolved. The liquid, when evaporated, yields at first a considerable succession of crusts of acid tartrate of ammonia with but little arsenious acid, but afterwards, when very highly concentrated, large glassy crystals of the double salt, which quickly effloresce, and, at 100° to 105° , give off 4·67 per cent. of water together with a little ammonia. The aqueous solution of 100 pts. of the fresh crystals yields with sulphuretted hydrogen, 48·17 pts. of sulphide of arsenic and 63·12 pts. of acid tartrate of ammonia. (Werther, *J. pr. Chem.* 32, 409.)

	Crystals.		Werther.	
AsO^3	99	...	37·22 37·54
$C^6H^6(NH^4)O^{12}$	167	...	62·78 63·12
$C^6H^6(NH^4)(AsO^3)O^{12} + Aq.$	266	...	100·00 100·00

Therefore as Mitscherlich gives it.

Tartrate of Arsenious acid and Potash and *Tartrate of Arsenious acid and Soda* are obtained in a similar manner but do not crystallise so well. (Mitscherlich.)

Tartrate of Arsenic acid and Potash. — The hot solution of 1 pt. arsenic acid in 6 pts. of water is saturated with finely pulverised cream of tartar; the liquid being well stirred; the filtrate, which still contains free arsenic acid, either left to crystallise by cooling, or better, precipitated by alcohol; and the resulting powder, which is sometimes

amorphous, sometimes crystalline, quickly washed with alcohol, and dried in the air. It is: $\text{KO,AsO}_5,\text{C}^6\text{H}^4\text{O}^{10} + 5\text{Aq}$. — It gives off 5 At. water at 130° , and turns brown at a higher temperature, emitting the odour of burnt sugar and of alkarsin. It dissolves very readily in water; but the solution soon deposits cream of tartar, and yields free arsenic acid. An excess of arsenic acid prevents this separation of cream of tartar, and from such a mixture the undecomposed double salt may always be precipitated by alcohol. (Pelouze, *N. Ann. Chim. Phys.* 6, 63; also *Ann. Pharm.* 44, 100; also *J. pr. Chem.* 28, 18.)

ANTIMONIC TARTRATE. — *a. Neutral.* — By precipitating a solution of antimonious oxide in aqueous tartaric acid with alcohol, a white granular precipitate is obtained, insoluble in water, but dissolving readily in neutral tartrate of potash, with formation of tartar-emetic. The composition of this precipitate is $\text{SbO}_3,\text{C}^4\text{H}^2\text{O}^5,\text{HO}$, [therefore = $2\text{SbO}_3,\text{C}^6\text{H}^4\text{O}^{12} = \text{C}^6\text{H}^4(\text{SbO}_3)_2\text{O}^{12} + 2\text{Aq}$]. At 100° , it gives off 1 At. water [or according to the other formula 2 At., so that $\text{C}^6\text{H}^4(\text{SbO}_3)_2\text{O}^{12}$ remains]. But this residue, when immersed in water, is reconverted into the original salt. The thoroughly dried salt decomposed with sulphuretted hydrogen and alcohol, yields no other acid than tartaric acid, that acid being regenerated by the water formed from the oxygen of the antimonious oxide and the hydrogen of the hydrosulphuric acid [Or: $\text{C}^6\text{H}^2\text{Sb}^2\text{O}^{14} + 6\text{HS} = 2\text{SbS}^2 + \text{C}^6\text{H}^4\text{O}^{12} + 2\text{HO}$]. (Berzelius, *Pogg.* 47, 315, and *Lehrb.*)

b. Acid. — Obtained by precipitating the aqueous solution of the following salt with [perhaps a smaller quantity of?] alcohol. (Peligot.) — This salt is probably identical with that which Soubeiran or Capitaine (*J. Pharm.* 25, 742) obtained by precipitating the solution of antimonious oxide in tartaric acid with alcohol, after evaporating to a syrup, and respecting which they state that the amount of antimony in it is variable, and that, after drying at 100° , it suffers a further loss at 210° .

Dried at 160° .		Peligot.
SbO ₃	153	53·69
8 C	48	16·84
4 H	4	1·40
10 O	80	28·07
SbO ₃ ,C ⁶ H ⁴ O ¹⁰ [?]		285
		100·00

c. Hyperacid. — The solution of antimonious oxide in aqueous tartaric acid evaporated to a syrup, yields after a while, large transparent crystals. (Peligot, *N. Ann. Chim. Phys.* 20, 289; also *J. pr. Chem.* 41, 381.) This solution crystallizes indistinctly (Bergman); deposits a white powder, which after washing with alcohol dissolves in water and reddens litmus (Soubeiran, *J. Pharm.* 10, 535); does not yield any crystals (Dulk). — The crystals obtained by Peligot belong to the right prismatic system. *Fig.* 68 without the *p*-face, but with an *n*-face between *u* and *t*. $u' : u' = 133^\circ 30'$; $u : t = 113^\circ 15'$; $n : t = 137'$; $y : t = 90^\circ$; $y : y$ behind = 76° ; $i : t = 115^\circ$; $y : i = 125^\circ$. (Prevostaye.) — The crystals deliquesce in damp air, and dissolve very readily in water. (Peligot.) — The solution of antimonious oxide in tartaric acid is precipitated by sulphuric, hydrochloric, and nitric acid. (Schnaubert, *Verwandtsch.* 80.) — All antimony salts are protected, by addition of tartaric acid, from precipitation by water or alkalis. (H. Rose.)

SbO ³	153	31·29	31·80
16 C	96	19·63	18·95
16 H	16	3·27	3·50
28 O	224	45·81	46·05

C³H⁴(SbO³)O¹², C³H⁴O¹² + 5Aq. ? 489 100·00 100·00

The crystals give off 23·1 p. c. (12 At.) water at 160°, and therefore leave SbO³, C¹⁶H⁴O¹². (Peligot.) The exact nature of this residue must be decided by further investigations. The formula given by Gerhardt (*N. J. Pharm.* 12, 212) appears too artificial.

Hydrated Antimonic acid dissolves readily in aqueous tartaric acid. (J. A. Buchner, *Repert.* 66, 171.)

Ammonio-antimonic Tartrate. — *Ammoniacal Tartar-emetic.* — An aqueous solution of acid tartrate of ammonia is boiled with antimonic oxide, and the filtrate evaporated, till it forms, on cooling, a stiff jelly, in which regular crystals gradually appear. (L. A. Buchner, *Repert.* 78, 320. On attempting to take these crystals out of the jelly, it again becomes thin and mobile from the effect of the agitation, and deposits a crystalline powder, having the same composition. (Buchner.) Berlin (*Ann. Pharm.* 64, 358), leaves the concentrated solution to evaporate in the air at 15° to 60° till it crystallizes.

The transparent, colourless, shining crystals belong to the right prismatic system, and are isomorphous with ordinary tartar-emetic. (Kobell, Prevostaye.) *Fig. 45.* Let the face below *a* be denoted by *e*; the face below *e* does not occur in these crystals, *p* : *a* = 121° 39'; *u* : *e* = 165° 27' (167° according to Kobell); *p* : *e* = 107° 7'; *p* : *u* = 90°; *a* : *a* at the side = 101° 8' (103° 42' according to Kobell); (*a* : *a* [behind?]) = 108° 57' Kobell); *u* : *u'* = 83° 29'; *a* above : *a* below = 116° 42' (116° 9', Kobell). The faces *x* are subordinate; the faces *a* are alternately absent; and by this hemihedry the crystals become tetrahedral; the *x*-faces also are sometimes half present. (Kobell, Prevostaye.) — When part of the solution of ammoniacal (or ordinary) tartar-emetic has crystallised in this form, the mother-liquor often yields still more efflorescent right rhombic prisms slightly truncated at the lateral edges (whose angles = 127° and 53°), and bevelled in opposite directions at the summits (angle of the bevelling edge = 85° 30'). Pasteur. [Therefore nearly the same as *fig. 72*, together with the *m*-face]. These large and very efflorescent prisms, formed by spontaneous evaporation, give off 15·3 per cent. (5 At.) water at 100°.

The ordinary crystals, when exposed to the air, give off water, and assume the appearance of porcelain, though less quickly than those of common potash-tartar-emetic; at 100°, they give off 5·41 p. c. water, and a little above 100°, they also evolve ammonia. (Buchner.) Heated to 108° in a current of air, they give off water and ammonia. (Dumas & Piria.) They dissolve in water much more readily than those of potash tartar-emetic. (Buchner.)

	<i>Crystals.</i>		<i>Dumas & Piria.</i>	
N	14	4·37
SbO ³	153	47·81
8 C	48	15·00
9 H	9	2·82
12 O	96	30·00
<hr/>				
C ³ H ⁴ (NH ³)(SbO ³)O ¹² + Aq.	320	100·00

				Buchner,
NH ³	17	5·31 5·00
SbO ³	153	47·81 46·60
C ⁸ H ⁴ O ¹¹	141	44·07
HO	9	2·81 5·41

C⁸H⁴(NH⁴)(SbO³)O¹² + Aq... 320 ... 100·00

Potassio-antimonic Tartrate. — *a. Basic?* — *a.* Boiling aqueous tartar-
 emetic dissolves antimonie oxide, and on cooling yields needles which are
 decomposed by water into tartar-*emetic* and a residue of tartrate of
 antimony. (Bucholz.) This statement is contradicted by Soubeiran &
 Capitaine (*J. Pharm.* 25, 745) according to whom, 188·2 pts. (1 At.)
 cream of tartar boiled for 40 hours with 295 pts. (nearly 2 At.) antimonie
 oxide and with water, dissolve only half the oxide, forming with it
 ordinary tartar-*emetic*. — *β.* An aqueous solution of neutral tartrate of
 potash dissolves antimonie oxide (Bergman), which is then not pre-
 cipitated by alkalis. (Thénard.)

b. Neutral. — *Ordinary Tartar-*emetic*, gewöhnlicher Brechweinstein, Spiess-
 glanzweinstein, Tartarus emeticus, Tartarus stibiatus.* — 3 pts. of antimonie oxide
 are digested with 4 pts. of cream of tartar and with water; the solution
 filtered hot; the crystals which are obtained by repeatedly evaporating and
 cooling the filtrate, pulverised and dissolved in 15 times their weight
 of cold water; and the solution again filtered and evaporated to the crys-
 tallising point.

The preparation is made (1) with pure antimonie oxide obtained by
 method 2—6 (iv, 324, 325); — Or (2) with *crocus antimonii* or *vitrum
 antimonii*, containing sulphide of antimony (iv, 359, 360), in quantity
 equal to that of the cream of tartar (the sulphide of antimony then
 remains undissolved); in the latter case, the tartar *emetic* obtained has a
 yellow colour, arising from potassio-ferrie tartrate, and the mother-liquor
 becomes gelatinous from the presence of silica; the solution obtained with
 oxide of antimony containing sulphide yields a yellow mother-liquor
 containing sulphur in the form of kernes [or of hyposulphite of potash?]
 (Fischer, *Kasn. Arch.* 9, 352); — Or (3) with basic sulphate, hydro-
 chlorate, or nitrate of antimonie oxide (the first to be obtained by heating
 2 pts. of antimony with 3 pts. of oil of vitriol, — or more cheaply, though
 contaminated with sulphur, by boiling down to dryness a mixture of
 3 pts. sulphide of antimony, 2 pts. nitre, 2 pts. oil of vitriol, and 24 pts.
 water, and washing out with water, — and then to be digested while still
 moist with 3 pts. of cream of tartar). When these basic antimony salts
 are acted upon by cream of tartar, the mineral acids are separated from
 the antimonie oxide, and remain in the mother-liquor, partly combined
 with the potash of the cream of tartar in the form of acid salts, and
 together with free tartaric acid. As the free acids retard the crystal-
 lisation, the mother-liquor separated from the first crystals must be
 partly neutralised with carbonate of lime, before it is evaporated to
 obtain a second crop of crystals; this free acid, however, holds in
 solution all the iron which frequently occurs in sulphide of antimony,
 and causes the tartar-*emetic* to crystallize out whiter; hence also whiter
 crystals are obtained by the other modes of preparation if a little hydro-
 chloric acid be added to the liquid.

The cream of tartar and antimonie oxide are either treated at first
 with only sufficient water to form a pulpy mass, and this mixture, after

quarter of an hour with a larger quantity of water; the whole of the tartar-
 emetic and the greater part of the antimoniac oxide are dissolved. The
 vessels may be of porcelain, glass, antimony, silver, platinum, or for quick
 preparation, of copper, or cast-iron. — When pure antimoniac oxide and
 pure cream of tartar are used, the mother-liquor yields tartar-
 emetic to the last drop, but when the impure ingredients are used, the impurities
 remain in the last uncrystallisable portion of the mother-liquor. (Phillips.)
 — There often remains a mother-liquor which dries up to a gummy mass,
 and [especially perhaps when basic sulphate, hydrochlorate, or nitrate of
 antimony is used], consists principally of acid potassio-antimoniac tartrate
 (p. 305). (Knapp.) — The resulting crystals of tartar-
 emetic are free from arsenic, even if the antimoniac oxide used in the preparation contained
 arsenic (Serullas, Chevallier, *J. Chim. méd.* 22, 71); but they may be
 contaminated with cream of tartar, tartrate of lime, oxide of iron, silica,
 and the basic potassio-antimoniac tartrate *a, a*; hence the necessity of
 redissolving them in 15 pts. of cold water, filtering and crystallising
 (Bucholz); *comp. Mönch (Crell. Chem. J.* 2, 73.) Demachy (*Crell. Chem.*
J. 4, 184.) Lassone (*Crell. Chem. J.* 5, 166.) — Bergman (*Opusc.* 1, 338.)
 Bucholz (*A. Tr.* 9, 2, 25; *Tascherb.* 1806, 1 and 209; 1811, 126.)
 Soubeiran (*J. Pharm.* 10, 524.) N. E. Henry (*J. Chim. méd.* 1, 521;
 2, 1.) Phillips (*Ann. Phil.* 25, 372.) Herrmann (*Jahrb. pr. Pharm.*
 7, 148.)

a. Dried at 200°. The crystals of tartar-
 emetic give off 2.1 p. c. (1 At.) water at 100°, and at a higher temperature (before decomposition
 begins), 7.38 p. c. (3 At.) in all. (Phillips.) Tartar-
 emetic dried at 100° in a glass tube which is continually turned round over a feeble alcohol-
 flame, can support a heat of 300° without browning, and gives off from
 5.1 to 6.5 per cent. of water. (Liebig, *Ann. Pharm.* 26, 132.) The finely
 pulverised crystals heated in the oil-bath in a current of air, turn brown
 between 235° and 240°, emitting an odour of burnt sugar; but between
 200° and 220°, they give off in 12 hours without any colouring, from 7.6
 to 7.7 p. c. water. (Dumas & Piria.) The crystals heated somewhat above
 100° in a current of dry air, give off 2.63 p. c. (1 At.) water; between
 160° and 180° (and in a longer time even at 130°), 5.26 p. c. (2 At.) in
 all; and at 200° 220°, 7.71 p. c. (3 At.) in all. (Berlin.)

<i>Dried at 200°.</i>				<i>Liebig.</i>
KO	47.2	15.02	
SbO ³	153.0	48.69	
8 C	48.0	15.28	15.54
2 H	2.0	0.64	0.67
8 O	64.0	20.37	
$C^8H^2K(SbO^3)O^{10}$				314.2
				100.00

The salt dried at 200° may be regarded as tartaric anhydride
 ($C^8H^4O^8$, O^8), (or, as Laurent & Gerhardt prefer, as the isomeric
 compound, tartrelic acid), in which 1H is replaced by K and 1H by SbO³,
 = $C^8H^2K(SbO^3)O^8, O^8$, — Gerhardt (*N. J. Pharm.* 12, 214,) supposes
 that, in this compound, an ordinary atom of Sb splits up into 3 At.
 Sba, whence he derives the formula $C^8H^2KSba^3, O^{12}$. — Peligot, (*N. Ann.*
Chim. Phys. 12, and *J. pr. Chem.* 35, 162,) supposes tartaric acid itself
 to be $C^8H^4O^{10}$, and writes $C^8H^2K(SbO^3)O^{10}$, but is thereby obliged to

still contain 2 At. water of crystallisation. — According to the radical theory, Liebig and Dumas & Piria write the formula of the salt, KO , SbO^3 , $\text{C}^3\text{H}^3\text{O}^3$; and Berzelius writes it, KO , $\text{C}^4\text{HO}^4 + \text{SbO}^3$, C^4HO^4 . The latter endeavoured to isolate this peculiar acid, C^4HO^4 , by decomposing the salt suspended in hot absolute alcohol with sulphuretted hydrogen. The decomposition took place slowly, yielding sulphide of antimony and a large quantity of reproduced cream of tartar, while in the alcoholic solution, there remained a very small quantity of the potash-salt of a peculiar acid, which, after evaporating the alcohol, dissolving the residue in water, filtering from sulphide of antimony, and evaporating, remained as an opaque gum, which reddened litmus, (or in crystals by spontaneous evaporation,) burnt without any odour of burnt sugar, and from whose aqueous solution acids did not throw down cream of tartar, [tartralic or tartrelic acid?] (Berzelius, *J. pr. Chem.* 14, 350; *Pogg.* 47, 315; *Lehrb.*) When tartar-emetic, dried between 200° and 220° , is dissolved in water and decomposed by sulphuretted hydrogen, a filtrate is obtained, which, after neutralization with ammonia, behaves with lime-salts like meta-tartrate of ammonia, but after standing for 24 hours, like the tartrate. (Laurent & Gerhardt.)

β. Dried at 100° . The fresh crystals, dried at 100° , retain their form, but turn white and opaque, giving off 2·1 p. c. water (Phillips); 2·39, and at 108° , 2·73 in all (Dumas & Piria); 1·75, and somewhat above 100° , 2·63. (Berlin.)

Dried at 100° .				Liebig.	Dumas & Piria.
KO	47·2	14·21		
SbO ³	153·0	46·06		
8 C	48·0	14·45	14·78
4 H	4·0	1·20	1·24
10 O	80·0	24·03		
<hr/>					
$\text{C}^3\text{H}^4\text{K}(\text{SbO}^3)\text{O}^{12}$	332·2	100·00		

According to Peligot, $\text{C}^3\text{H}^4(\text{SbO}^3)\text{O}^{12}$, or, as likewise established by Dumas & Piria, KO , SbO^3 , $\text{C}^3\text{H}^3\text{O}^3 + 2\text{H}_2\text{O}$; according to Liebig, KO , SbO^3 , $\text{C}^3\text{H}^4\text{O}^{10}$.

γ. Crystallized Tartar-emetic forms transparent, colourless (sometimes partially opaque), shining rhombic octohedrons, isomorphous with ammonio-antimonic tartrate, and tetrahedrons produced by hemihedry. *Fig. 45.* Let the first pair of faces below *a* be denoted by *e*, and the second by *i*; $p : a = 122^\circ$; $a : e = 166^\circ 40'$; $a : i = 165^\circ 40'$; $p : u = 90^\circ$; $a : a$ at the side = $108^\circ 16'$; $a : a$ behind = $104^\circ 15'$ ($103^\circ 3'$, Bernhardt). The faces *e* and *i* are generally striated and indistinct; only one direction of cleavage, parallel to *p*. (Brooke, *Ann. Phil.* 22, 40.) $u : u = 93^\circ 20'$ and $86^\circ 40'$. (Soret, *Taschenb.* 1823, 136; *comp.* Bernhardt, *N. Tr.* 7, 2, 58; and Prevostaye.) — Tartar-emetic has a metallic taste, acts as an emetic, and in larger quantities, as a poison.

	Crystals.	Dumas & Piria.	Thomson.
KO	47·2	13·83
SbO ³	153·0	44·84
8 C	48·0	14·07
5 H	5·0	1·47
11 O	88·0	25·79
<hr/>			
$\text{C}^3\text{H}^4\text{K}(\text{SbO}^3)\text{O}^{12} + \text{Aq.}$	341·2	100·00

Or:

	<i>Crystals.</i>			Phillips.	Wallquist.	Dulk.
KO.....	47.2	13.83	13.64
SbO ³	153.0	44.84	42.99	43.08
C ⁸ H ⁴ O ¹⁰	132.0	38.69
HO.....	9.0	2.64	5.14	5.90

C⁸H⁴K(SbO³)O¹² + Aq..... 341.2 100.00

	<i>Crystals.</i>			Brandes & Wardenburg.	Richard-son.	Göbel.	Thén.
KO.....	47.2	13.83	12.80	9.80	16
SbO ³	153.0	44.84	45.92	42.60	38
C ⁸ H ⁴ O ¹⁰	132.0	38.69	35.25
HO.....	9.0	2.64	4.84	3.75	8

C⁸H⁴K(SbO³)O¹² + Aq. 341.2 100.00

98.81

For Drapier's analyses, see *Ann. génér.* 1819; also *Schw.* 30, 406. — In the analyses by Phillips and by Brandes & Wardenburg (*Ann. Pharm.* 2, 71), the percentages of water are given which the crystals lose at 100°; in the analyses by Wallquist, Dulk, Göbel (*Scäv.* 37, 73) and Thénard, there is no statement as to the temperature at which the water was determined, but to judge from the quantity, it must have been considerably above 100°, so that the salt β would be partially converted into the salt α . Richardson (*Records of Gen. Sc.* 1836) dried his salt at 204°. The rest of his analysis is based upon the fact that 100 pts. of the crystals decomposed in aqueous solution by hydrosulphuric acid, yielded 53.2 pts. of sulphide of antimony and 39.92 cream of tartar. — Wallquist supposes half the antimonious oxide to be combined with half the potash, and accordingly gives the formula: $KO, C^8H^4O^5 + SbO^3, 3C^8H^2O^5 + KO, SbO^3 + 2Aq.$

The crystals gradually become opaque when heated in the air, giving off, according to Brandes & Wardenburg, 0.5 p. c. water, whereas opaque crystals, which generally contain less water, do not suffer any diminution in weight. — They decrepitate in the fire, burn away with an antimonial fume, and leave charcoal mixed with grains of antimony (Bergman), and when ignited in close vessels, leave a highly inflammable pyrophoric mass. (Serullus.)

Iodine added to an aqueous solution of tartar-emetic, forms a precipitate of oxyiodide of antimony, $SbI^3, 5SbO^3$. — From the hot solution of 100 pts. tartar-emetic in 1000 pts. water, 34 pts. of iodine throw down golden-yellow spangles as the liquid cools, and 50 pts. of iodine form an orange-yellow precipitate (which redissolves with brown colour on the addition of more iodine); the colourless, strongly acid filtrate precipitates metallic salts in the manner of hydriodic acid or iodide of potassium. Alcohol added to this filtrate throws down a curdy powder, which dissolves in water, forming an uncrystallizable acid syrup, whilst iodide of potassium remains in solution. Iodine alone does not precipitate neutral acetate of lead or corrosive sublimate; but in presence of tartar-emetic, it throws down iodide of lead or iodide of mercury. (Preuss, *Ann. Pharm.* 29, 214.) — The golden-yellow spangles may likewise be obtained by dropping alcoholic iodine into the saturated solution of tartar-emetic in aqueous tartaric acid, so long as it does not produce any permanent brown colour; or by triturating 2 pts. of tartar-emetic with 1 pt. of iodine and a small quantity of cold water to a pulp, and heating it gently till the iodine dissolves; sometimes a brown-red compound [$SbI^3?$] is formed at the same time. The brown acid liquid filtered from the spangles, leaves, when evaporated, a black residue, which dissolves in water without

solution contains about 1 At. antimony to 2 At. potassium and 2 At. iodine; alcohol precipitates from it a white salt free from iodine, and containing antimony, together with 12.17 p. c. potash, probably, therefore, tartar-emeti. Iodine, therefore, throws down from tartar-emeti only a portion of the antimony, that, namely, which, according to Wallquist's formula, is in combination with the potash. (Stein, *J. pr. Chem.* 30, 48.) [But even if only the portion of antimonic oxide combined with the potash were removed, the liquor could no longer yield a precipitate of tartar-emeti on addition of alcohol. Part of the tartaric acid must necessarily be altered by oxidation during this reaction.]

Of the heavy metals, iron is the only one which precipitates antimony completely from the aqueous solution of tartar-emeti. (Wallquist.) — Sulphuretted hydrogen decomposes it immediately, yielding kermes and tartar-emeti. In very dilute solutions, sulphuretted hydrogen produces only a red colouring, which passes into precipitation on addition of cream of tartar or mineral acids. (Pfaff, Geiger.) A solution of tartar-emeti in 4608 pts. water, assumes only an orange-yellow colour when treated with sulphuretted hydrogen, but deposits kermes on boiling. (Turner.)

Sulphuric, nitric, or hydrochloric acid, added to an aqueous solution of tartar-emeti (not containing free tartaric acid: *Soubeyran*), throws down, not cream of tartar, but a basic sulphate, nitrate, or hydrochlorate of antimonic oxide, soluble in excess of hydrochloric acid or in tartaric acid. (Geiger, *Mag. Pharm.* 7, 258.) According to Turner, the precipitate likewise redissolves in excess of sulphuric acid, but according to Geiger & H. Rose, it does not dissolve. According to Dulk, the precipitate consists of basic tartrate of antimonic oxide with a little of the mineral acid [?]. — The precipitation of the antimony by these three acids is seldom complete; and this circumstance is often looked upon as favourable to Wallquist's formula, according to which half the antimony in the salt is combined with potash, and the other half with tartaric acid. According to this view, mineral acids should precipitate only the atom of antimony which is combined with the potash, and alkalis only that which is in combination with the tartaric acid. But with a due proportion of mineral acid, considerably more than half, often indeed nearly all the antimony is precipitated. From a dilute solution of 100 pts. of tartar-emeti, nitric acid throws down a basic salt containing 41.2 pts., that is to say, nearly the whole of the antimonic oxide; in a saturated solution, nitric acid forms a slighter precipitate, which continually increases when heated or simply left to stand; hence the filtrate yields by evaporation a new precipitate; and the liquid contains, besides a little undecomposed tartar emeti, acid tartrate of potash, which, on heating the liquid, is resolved, for the most part, into nitre and tartaric acid. (Schweizer, *J. pr. Chem.* 33, 470.)

Tartaric added added to tartar-emeti throws down cream of tartar. (Geiger); oxalic acid forms a slight precipitate, insoluble in excess of the acid. (H. Rose.) — Acetic acid does not form any precipitate with tartar-emeti, according to Geiger and Schweinberg (*Mag. Pharm.* 15, 258), but according to N. E. Henry, a precipitate of cream of tartar is formed after 24 hours.

Ammonia, potash, soda, and their compounds with carbonic acid, precipitate the antimonic oxide in white flakes which become minutely crystalline. Ammonia renders the dilute solution very slightly turbid, and throws down from the concentrated solution, fine grains which dissolve

but partially in excess of ammonia (or, according to H. Rose, not at all). Ammonia renders the solution of tartar-emetic turbid in a few minutes (immediately if heated), and throws down white flocculent antimonie oxide, the quantity of which gradually increases; a considerable portion however remains dissolved, unless the ammonia be allowed to act in excess for several days. In this case, 43·35 per cent. (that is to say, the whole, within 1 p. c.) of the antimonie oxide is precipitated from the tartar-emetic; and the filtrate contains, besides a very small quantity of undecomposed tartar-emetic, tartrate of potash and ammonia, which, on evaporation, is partially converted into cream of tartar, with evolution of ammonia. (Schweizer.)—Potash does not precipitate the more dilute solution; but from the more concentrated solution, it throws down an abundance of white flakes completely soluble in excess of the potash.—Carbonate of ammonia has no action on the solution of tartar-emetic; carbonate of potash produces a cloud, by precipitating the oxide, even in a solution containing only 1 pt. of tartar-emetic to 1152 water.—Lime-water does not cloud a solution diluted to that extent, but in a solution containing 1 pt. of tartar-emetic to 576 water, it forms a cloud consisting of tartrate of lime combined with tartrate of antimony. All these precipitates formed by alkalis are soluble in tartaric acid (Turner, *Edinb. Med. and Surg. J. Nr.* 92, 71; also *Kasn. Arch.* 11, 377.)—Carbonate of ammonia and carbonate of soda likewise gradually form precipitates insoluble in excess; but the precipitation by these reagents, as well as by carbonate of potash, is very incomplete. (H. Rose.)—While the solution of tartar-emetic in pure water is not altered, even by boiling, the solution in spring-water, which contains carbonate of lime and carbonate of magnesia, forms at 15° in the course of 12 hours, a precipitate of pure antimonie oxide, and on boiling, a more copious precipitate containing a larger quantity of antimonie oxide, together with the carbonates of lime and magnesia. If the spring-water be boiled, previous to adding the tartar-emetic, till the whole of the carbonates of lime and magnesia are precipitated, the solution will no longer be subject to decomposition. (Guéranger, *J. Chim. méd.* 4, 368 and 412.)

Tartar-emetic added to an aqueous solution of corrosive sublimate forms a precipitate of calomel.—This precipitate is, however, mixed with a small quantity of mercurous tartrate; the solution contains antimonious acid. (Orfila, *J. Chim. méd.* 8, 202.)—When the bodies are dissolved in equal numbers of atoms, and each in 20 pts. of water, the mixture deposits on cooling only the fifth part of the corrosive sublimate in the form of calomel; but on boiling the mixture in a retort, — which does not cause any acid to distil over, — nearly all the mercury is precipitated in the form of calomel; the liquid filtered therefrom deposits about $\frac{2}{3}$ of the tartar-emetic in crystals, on evaporation and cooling; and the mother-liquor dries up to a yellowish white, translucent gum. (Brandes, *Ann. Pharm.* 11, 88.)

Infusion of galls precipitates a somewhat concentrated solution of tartar-emetic in thick yellowish white flakes, and forms a cloud in a solution containing 288 pts. of water, but not in one which contains 576 pts. (Turner.)—If a little nitric acid be added, the precipitation takes place, even with more dilute solutions. (Guéranger, *J. Chim. méd.* 1, 371.)—An excess of tincture of galls redissolves the precipitate. (Orfila.)

Tartar-emetic dissolves in 14·5 pts. of cold and in 1·9 pts. of boiling water. (Bucholz.) It dissolves in 19 pts. at 8·7°, in 12·6 at 21°, in

3 at 87.5°, and in 2.8 pts. at 100°. (Brandes.) The aqueous solution yields a pulverulent precipitate with alcohol.

c. Acid. — *Acid Tartar-emetic.* — The solution of tartar-emetic in boiling aqueous tartaric acid is evaporated to a syrup, and then slowly cooled till it crystallizes, an effect which takes place readily. (Knapp.) — This salt occurs in the mother-liquor of tartar-emetic. When antimoniac sulphate obtained by heating antimony with sulphuric acid is freed from sulphuric acid by treatment with water and carbonate of potash, the oxide dissolved in aqueous cream of tartar, and the ordinary tartar-emetic crystallized as completely as possible from the solution by evaporation and cooling, a very acid mother-liquor is obtained, which, when evaporated to dryness, amounts to $\frac{1}{4}$ to $\frac{1}{2}$ of the crystals of tartar-emetic. The residue in the dry state is a transparent, yellow-brown gum, and forms with water a thick syrup, which is decomposed by alcohol into a precipitate of ordinary tartar-emetic and a solution of tartaric acid — is completely converted into common tartar-emetic by saturation, first with antimoniac oxide, and subsequently with potash — and, on account of accidental impurities, does not yield the crystals of the acid salt above described till after standing for several months, and sometimes not even then. (Knapp.) — [If Phillips's statement (p. 300), that the solution of antimoniac oxide in pure cream of tartar crystallizes to the last drop as ordinary cream of tartar, be admitted as correct — and it is fully borne out by the composition of the salt — we cannot help suspecting that Knapp's antimoniac oxide had not been completely freed from sulphuric acid; that this acid set free the tartaric acid from a portion of the cream of tartar, forming bisulphate of potash; and that the tartaric acid thus liberated, together with a portion of the tartar-emetic, formed the acid salt of the mother-liquor: it is to be regretted that this mother-liquor was not examined by Knapp for sulphuric acid. The bisulphate of potash was probably the accidental impurity which interfered so much with the crystallization]. (*Vid.* also Berzelius, *Jahresber.* 20, 173.)

Transparent, colourless, oblique rhombic prisms, which effloresce in the air, give off 9.22 p. c. (5 At.) water at 100°, assuming at the same time the appearance of porcelain, and at a higher temperature melt to a transparent gum. From their aqueous solution mixed with hydrochloric acid, iron throws down all the antimony; alcohol added to the aqueous solution precipitates ordinary tartar-emetic, retaining the free tartaric acid.

	<i>Dried at 100°.</i>		<i>Knapp.</i>		<i>Pelilot.</i>
KO.....	47.2	9.79	9.50		
SBO ³	153.0	31.73	32.10		31.0
16 C.....	96.0	19.91	20.67		19.1
10 H.....	10.0	2.07	2.10		2.7
22 O.....	176.0	36.50	35.63		
<hr/>					
C ⁸ H ⁴ K(SbO ²)O ¹² + C ⁸ H ⁶ O ¹²	482.2	100.00	100.00		

Therefore 1 At. tartar-emetic dried at 100°, with 1 At. tartaric acid.

d. Compound of 1 At. Tartar-emetic with 3 At. Cream of Tartar. —

1. Obtained by leaving a concentrated boiling solution of 1 At. tartar-emetic with 3 At. cream of tartar to crystallise by cooling. — 2. By dissolving 1 At. neutral tartrate of potash, 1 At. cream of tartar, and 1 At. acid cream of tartar (c) in water. (Crystals of exactly similar character are obtained by using tartrate of potash and ammonia instead of neutral tartrate of potash.) —

precipitating the antimonic oxide from the one half by adding a quantity of carbonate of potash just sufficient for saturation, and mixing the filtrate which contains the neutral tartrate of potash with the other half. [The equation given by Knapp for this reaction does not appear to be correct; inasmuch as he supposes that only 2 At. (not 3 At.) potash are required to precipitate the antimony; the mixture will therefore contain 1 At. potash too much.]—4. By dissolving 9 pts. of tartar emetic and 4 pts. of tartaric acid in water, leaving the free tartar-emetic to crystallise out, then evaporating the mother-liquor to a syrup, and leaving it to cool slowly. It then solidifies to a transparent, turpentine-like mass, which soon becomes turbid from formation of crystalline points; these increase till the whole is converted into a snow-white, crystalline mass, which is freed from the thick mother-liquor by elutriation with water, and washed on the filter with a small quantity of cold water. (Knapp.)

Small nacreous laminae, which do not give off water even when heated in vacuo, dissolve sparingly in water, and are precipitated from the aqueous solution by alcohol. (Knapp.)

				Knapp.
4 KO	188·8	21·05 20·15
SbO ³	153·0	17·06 17·20
32 C	192·0	21·41 22·07
19 H	19·0	2·12 2·30
43 O	344·0	38·36 38·28
$C^8H^4K(SbO^3)_2 + 3C^8H^4KO^3$				
	896·8	100·00 100·00

When carbonate of potash is dropped into the solution of this salt as long as effervescence is produced, and the liquid evaporated, needle-shaped crystals are obtained aggregated in nodules like Wavellite, and very easily soluble in water; from the solution thus obtained, tartaric acid reprecipitates the laminae of the original salt. [Possibly a compound of tartar-emetic with neutral tartrate of potash?]

Ignited *Antimonious acid* does not dissolve in aqueous cream of tartar (Geiger & Reimann, *Mag. Pharm.* 17, 137); it dissolves very slowly and sparingly on boiling; but the hydrate dissolves more readily, and the clear filtrate coagulates on cooling, and leaves a fissured gum when evaporated. (H. Rose, *Pogg.* 47, 339; A. Rose, *Pogg.* 51, 170.)

Hydrated Antimonic acid dissolves in an aqueous solution of 1½ pt. of tartar-emetic (the ignited acid also, but much more slowly) forming a liquid which has a saline sweet taste, is not precipitated by hydrochloric acid, but yields a light orange-yellow precipitate with sulphuretted hydrogen in presence of hydrochloric acid, and leaves by evaporation a yellow gum, permanent in the air and easily soluble in water. (Geiger & Reimann, *Mag. Pharm.* 17, 128). The solution, either of the dry or of the hydrated acid, passes turbid through the filter, and leaves a turbid gum when evaporated. (A. Rose.)—The compound is amorphous, and very soluble. (Mitscherlich, *Ann. Chim. Phys.* 73, 396.)—3 pts. of biantimoniate of potash likewise dissolve in 4 pts. of cream of tartar, forming a rather insipid, sweetish, saline liquid which yields a copious red-brown precipitate with sulphuretted hydrogen in the course of half an hour, and leaves a yellowish gum when evaporated. (Geiger, *N. Tr.* 3, 1, 460.) The solution of biantimoniate of potash in tartaric acid is thickish, passes slowly through the filter, forms with sulphuretted hydrogen a

viscid gum when evaporated. (J. A. Buchner, *Repert.* 66, 171.)

By digesting 1 pt. of *vitrum antimonii* (iv. 360), 1 pt. of *boracic acid*, and 2 pts. of *cream of tartar*, then filtering and evaporating, a gum is obtained. (Bergman.)

Sodio-antimonic Tartrate. — *Soda Tartar emetic.* — The preparation is similar to that of ordinary tartar-etic. Prisms belonging to the right prismatic system. *Fig. 75*, together with a *p*-face, and also a *t*-face at the back between *n* and *n'*; *y*:*y'* behind = 85° 20'; *y*:*m* = 137° 20' nearly. (Prevostaye.) — The crystals heated to 220° in a dry stream of air give off 8.4 p. c. water; they absorb moisture from the air. (Dumas & Piria.)

	<i>Crystals.</i>		<i>Dumas & Piria.</i>	
NaO	31.2	9.59	
SbO ³	153.0	47.05	
8 C	48.0	14.76 14.3
5 H	5.0	1.54 1.6
11 O	88.0	27.06	
<hr/>				
C ⁸ H ⁵ Na(SbO ³)O ¹² + Aq.	325.2	100.00	

Lithio-antimonic Tartrate. — Transparent jelly in which small prisms form after a considerable time. (L. A. Buchner.)

Baryto-antimonic Tartrate. — Tartar-etic. (Wallquist.) Crystalline laminae, which give off 8.21 p. c. water in a stream of dry air at 100°. (Dumas & Piria.)

	<i>Dried at 250°.</i>		<i>Dumas & Piria.</i>	
BaO	76.6	22.29	
SbO ³	153.0	44.53	
8 C	48.0	13.97 13.19
2 H	2.0	0.58 0.66
8 O	64.0	18.63	
<hr/>				
C ⁸ H ³ BaSbO ¹²	343.6	100.00	

	<i>Crystals.</i>		<i>Dumas & Piria.</i>	
BaO	76.6	20.18 19.85
SbO ³	153.0	40.31 11.74
8 C	48.0	12.64 1.72
6 H	6.0	1.58 1.72
12 O	96.0	25.29	
<hr/>				
C ⁸ H ⁴ K(SbO ³)O ¹² + 2Aq.	379.6	100.00	

Dumas & Piria explain the deficiency of carbon by the circumstance that the baryta, in spite of the presence of antimonic oxide, still retains carbonic acid at a red heat; they suppose the crystals to contain $\frac{1}{2}$ At. HO more than the quantity calculated in the preceding table.

Strontio-antimonic Tartrate. — On mixing the hot-saturated solutions of 1 At. tartar-etic and 1 At. nitrate of strontia, a crystalline precipitate is formed, which is washed with hot water, in which it is nearly insoluble, and then dissolved in cold aqueous nitrate of strontia (which takes up more of it than cold water); this solution, when gradually heated to 100°, deposits the salt in small prisms, which scarcely give off $\frac{1}{2}$ p. c. water at 210° in 6 hours. (F. Kessler, *Pogg.* 75, 410.)

Crystals.		Kessler.	
SrO	52	15·43	15·26
SbO ³	153	45·40	45·25
$C^8H^4O^{10}$	132	39·17	39·22
<hr/>			
$C^8H^4Sr(SbO^3)O^{12}$	337	100·00	99·73

Strontio-antimonic Tartrate with Nitrate of Strontia. — 1 pt. of nitrate of strontia is digested for some time at 30° to 35°, with 2 pts. of water and an excess of finely pulverised strontio-antimonic tartrate, the solution filtered at 20°, and left to evaporate in the air. — The large, somewhat efflorescent crystals thus obtained give off the whole of their water, amounting to 18·43 per cent. at 200°, and at a stronger heat burn away suddenly with a glimmering light, and without blackening, leaving a porous mass, which continues to glow for some time in the interior. They are not altered by immersion in cold oil of vitriol, dissolve with noise in warm oil of vitriol, and then give off carbonic oxide, and subsequently nitric oxide gas without any colouring, but afterwards becomes brown and give off sulphurous acid. They dissolve readily in cold water; and the solution when heated deposits crystals of strontio-antimonic tartrate, which do not redissolve completely on cooling, even after a considerable time. (Kessler.)

Crystals.		Kessler.	
2 SrO	104	18·87	19·13
SbO ³	153	27·77	28·02
$C^8H^4O^{10}$	132	23·96	23·92
NO ²	54	9·80	
12 HO	108	19·60	18·43
<hr/>			
$C^8H^4Sr(SbO^3)O^{12}, SrO, NO^2 + Aq$	551	100·00	

Calcio-antimonic Tartrate. — By precipitating a lime-salt with tartar-emetic. The precipitate has the composition of the latter. (Wallquist.)

Antimonio-uranic Tartrate. — When the cold aqueous solutions of tartar-emetic and uranic nitrate are mixed together, the light yellow gelatinous precipitate dissolved in hot water, and the resulting solution slowly cooled, it immediately yields crystals; but if quickly cooled, it yields at first an amorphous precipitate, which however changes after a while to yellow-needles having a silky lustre and united in radiated groups. The same crystals are obtained by mixing the hot solutions of 3 pts. tartar-emetic and 1 pt. uranic nitrate, and leaving the mixture to cool. The air-dried crystals give off in vacuo over oil of vitriol, 11·76 per cent. (7 At. [or 6?]), and at 200° in a dry stream of air, without any alteration of the acid, 18·83 p. c. (11 At. [or 10?]) in all; at 210°, the salt suffers no further loss, but emits a faint odour of burnt sugar; the salt dried in vacuo gives off at 200° in a stream of dry carbonic acid gas, 7·95 p. c. (4 At.), then at 242°, with browning and an odour of caramel, 2 p. c., and at 270°, with deeper brown colour, an additional quantity of water; but there still remains a certain quantity of hydrogen, which escapes in the form of water when the residue is ignited in a glass tube. There remains a mixture of charcoal, uranic oxide, and antimony, which, even when quite cold, takes fire in the air and burns with great splendour. — The salt dissolves in hot water with fine yellow colour, but separates out almost completely on cooling, so

<i>Dried at 200°.</i>				Peligot.
U ³ O ³	144	35·04	
SbO ³	153	37·22	
8 C	48	11·68	11·56
2 H	2	0·49	0·70
8 O	64	15·57	
<hr/>				
C ⁸ H ² (U ³ O ³)(SbO ³)O ¹⁰	411	100·00	

Therefore like common tartar-emetic dried at 200° (p. 300).

<i>Crystals dried in vacuo.</i>				Peligot.
U ³ O ³	144	32·22	32·3
SbO ³	153	34·23	33·7
8 C	48	10·73	11·0
6 H	6	1·34	1·3
12 O	96	21·48	21·7
<hr/>				
C ⁸ H ⁴ (U ³ O ³)(SbO ³)O ¹² + 2Aq.	447	100·00	100·0

<i>Air-dried Crystals.</i>				Peligot.
U ³ O ³	144	28·74	28·30
SbO ³	153	30·54	30·30
8 C	48	9·58	9·64
12 H	12	2·40	2·45
18 O	144	28·74	29·31
<hr/>				
C ⁸ H ⁴ (U ³ O ³)(SbO ³)O ¹² + 2Aq.	501	100·00	100·00

Peligot supposes the air-dried crystals to contain 1 Aq. more.

TELLURIC TARTRATE. — The solution of telluric oxide in the aqueous acid dries up by spontaneous evaporation, to a transparent, colourless mass, which has a radiated crystalline structure, and dissolves readily in water, forming a solution which is not precipitated by alkalis, borax, molybdate of ammonia, tellurate of soda, or infusion of galls. (Berzelius.) Snow-white needles, having a sweet metallic taste and nauseating action. (Kölreuter, *Schw.* 62, 216.)

Potassio-telluric Tartrate. — Telluric oxide, its hydrate, and telluric acid, which is thereby reduced to the oxide, dissolve when digested in aqueous tartar-emetic. The solution deposits a large quantity of cream of tartar when evaporated, and then dries up to a transparent gum. This residue, when treated with cold water, becomes opaque from separation of telluric oxide, but redissolves completely when heated, without depositing anything on cooling. (Berzelius.)

BISMUTHIC TARTRATE. — Precipitated on adding tartaric acid to sulphate, hydrochlorate, or nitrate of bismuth, in the form of a white crystalline meal insoluble in water. (Gren, in his *Lehrbuch.*) — Bismuth-salts are not protected from precipitation by potash by the presence of tartaric acid. (H. Rose.)

¶ On adding a hot concentrated aqueous solution of 4 pts. tartaric to a hot concentrated of 5 pts. bismuthic oxide (BiO³) in nitric acid, the solution remains clear while hot, but, on cooling, deposits neutral bismuthic tartrate in small shining crystals, which collect on the sides of

the vessel, in very solid white crusts. As soon as the separation of these crystals is complete, the clear liquid must be decanted, and the salt washed on a filter for a considerable time, with a cold dilute aqueous solution of tartaric acid mixed with a little nitric acid, then strongly pressed between paper, and dried at a gentle heat. The air-dried salt gives off 9.12 p. c. (5 At.) water at 100°. (R. Schneider, *Pogg.* 88, 55.)

Dried at 100°.			Schneider.	
2BiO ³	474	...	53.38 52.42
24 C	144	...	16.21 16.77
12 H	12	...	1.35 1.39
30 O	240	...	27.03 27.16
2HO	18	...	2.03 2.26
<hr/>				
2BiO ³ , 3C ⁶ H ⁴ O ¹⁰ + Aq.	888	...	100.00 100.00
Air-dried.			Schneider.	
2 BiO ³	474	...	48.46	
3 C ⁶ H ⁴ O ¹⁰	396	...	40.49	
12 HO	108	...	11.05 11.22
<hr/>				
2BiO ³ , 3C ⁶ H ⁴ O ¹⁰ + 6Aq.	978	...	100.00	

When the preceding salt is immersed in hot water, and potash added in small quantities, a white turbidity is first produced, but afterwards, on the addition of more potash, a clear solution which does not become turbid when mixed with more water or with potash. On mixing this solution with a solution of potassio-stannous tartrate prepared in a similar manner (p. 311), there are formed, either at ordinary temperatures or on boiling, according to the degree of concentration, double salts of bismuthous oxide (BiO²), stannic oxide, and tartaric acid, which, in presence of a sufficient quantity of water, dissolve in a slight excess of potash, forming dark brown liquids. From these compounds, the bismuthous oxide is not precipitated by direct treatment with caustic potash. By the addition of certain salts, *e. g.*, carbonate or sulphate of soda, or chloride of sodium, to the slightly alkaline solutions of these double salts, brown compounds of stannic oxide and bismuthous oxide are precipitated, either at ordinary temperatures or on boiling, which appear to contain essentially 1 At. SnO² to 1 At. BiO². If a solution of sesquioxide of tin be used instead of the protoxide, a similar compound is formed containing 2 At. SnO² to 1 At. BiO². From these compounds of stannic and bismuthous oxides, the former oxide is completely separated by potash, only when they have not been precipitated at a boiling heat. (Schneider.) ¶.

Potassio-bismuthic Tartrate. — Cream of tartar is boiled with water and excess of hydrated bismuthic oxide, obtained by digesting *Magisterium Bismuthi* with potash; the clear, somewhat viscid filtrate, which is not clouded by water, but forms a cloud with the stronger mineral acids, evaporated over the water-bath; and the heavy white crystalline powder which settles down, collected. This powder is decomposed by water, and yields an acid filtrate free from bismuth, which is turbid at first, but becomes clear after a while. (A. Schwarzenberg, *Ann. Pharm.* 61, 244.)

Dried at 100°.			Schwarzenberg.	
KO	47.2	...	11.86 12.22
BiO ³	237.0	...	59.52 58.94
8 C	48.0	...	12.05 12.16
2 H	2.0	...	0.50 0.59
8 O	64.0	...	16.07 16.09
<hr/>				
C ⁶ H ² K(BiO ²)O ¹⁰	398.2	...	100.00 100.00

Analogous therefore to tartar-emetic dried at 200° (p. 300.)

tion of hydrogen, and forms a sparingly soluble salt. (Bergman.)— Concentrated solutions of neutral tartrate of potash and sulphate of zinc yield immediately, and dilute solutions, after some hours, a white crystalline meal, which appears to contain 3 At. oxide to 1 At. acid. (Schindler, *Mag. Pharm.* 36, 63.) On mixing the hot concentrated solutions, a yellowish white crystalline meal is obtained; the cold dilute solutions gradually yield small crystals. The salt dissolves but very slowly in water, whether hot or cold, readily however in cold potash or soda. The alkaline solution when boiled, deposits zinc-oxide in combination with the carbonic acid which existed in the caustic potash-ley; absolute alcohol precipitates from it an uncrystallizable syrup soluble in water. Aqueous carbonate of soda digested with tartrate of zinc, gives off carbonic acid, but does not dissolve a trace of zinc. (Werther.) [Probably basic carbonate of zinc and tartrate of soda are formed]— The salt when subjected to dry distillation, leaves a carbonaceous residue, which may be set on fire with a red-hot coal, and burns away with a glimmering light, leaving oxide of zinc. (Böttger.)

Zinc-salts mixed with tartaric acid remain precipitable by potash. (H. Rose.) [Only however when heated.]

Tartrate of Zinc and Potassium.—*a.* When cream of tartar is digested with excess of zinc or its oxide, a gummy mass is obtained, which has a faint taste, deposits a white powder, and dries up to a yellowish translucent gum.—*b.* With a larger proportion of cream of tartar, small yellow crystals are obtained, having a harsh metallic taste. (Lassone. *Crell. N. Entd.* 2, 115.) The compound is not precipitated by pure alkalis or alkaline carbonates, but yields a precipitate with sulphuretted hydrogen. (Thénard.)

TARTRATE OF CADMIUM.—Slender needles, woolly to the touch, and scarcely soluble in water. (Stromeyer.)— John (*Berl. Jahrb.* 1820, 376), distinguishes a *basic* salt insoluble in water; a *neutral* salt, which is very sparingly soluble in water, insoluble in alcohol, and crystallizes in hard granules; and an *acid* salt, which dissolves in water and alcohol, and separates in radiated crystals.— The residue obtained by dry distillation, behaves like that of the zinc-salt. (Böttger.)

STANNOUS TARTRATE.— The concentrated solutions of protochloride of tin and neutral tartrate of potash yield a whitish yellow powder, which does not dissolve in water, even when hot, but dissolves in aqueous potash or soda, and is precipitated by alcohol, in the form of a yellowish white, gummy, uncrystallizable mass. (Werther.)— The residue of the dry distillation behaves like that of the zinc-salt. (Böttger.)— Stannous salts mixed with tartaric acid are not precipitated by caustic alkalis or alkaline carbonates. (H. Rose.) Hence the addition of cream of tartar to tin-mordants which are mixed with an alkali (Berzelius.)

Potassio-stannous Tartrate.— Obtained by boiling oxidised tin with cream of tartar. Easily soluble; not precipitated by alkalis or their carbonates. (Thénard.)— ¶. 1 pt. of crystallized protochloride of tin and 3 pts. of tartaric acid, dissolved in a sufficient quantity of hot water, and carefully mixed with caustic potash till the liquid becomes neutral, form a clear, colourless solution, which may be boiled and mixed with an

indefinite quantity of water, without becoming turbid; the white precipitate which forms in this solution by addition of a little more potash, and especially on boiling, is redissolved by a still further addition of potash. (R. Schneider. *Pogg.* 88, 59.) ¶.

TARTRATE OF LEAD.— Obtained by precipitating nitrate or acetate of lead with tartaric acid. — With tartrate of potash and neutral acetate of lead, a precipitate is formed containing acetic acid, (*vid. inf.*) — Also by precipitating a hot solution of tartrate of lime with neutral acetate of lead, and filtering at a boiling heat. (Casselmann.) — White crystalline powder, of sp. gr. 3·871. (H. Rose, *Pogg.* 33, 48.) The salt precipitated by tartaric acid from neutral acetate of lead, and dried in the air, gives off but a trace of hygroscopic water at 120°. (Berzelius, *Ann. Chim.* 94, 176; *Pogg.* 19, 306.) By dry distillation, it gives off 0·2 p. c. of pyrotartaric acid, besides empyreumatic oil and acetic acid. (Gruner.) When boiled with water and peroxide of lead or manganese, it is decomposed, with formation of formiate of lead. (Persoz, *Compt. rend.* 11, 522.) It dissolves, with evolution of heat, in potash or soda-ley, and alcohol throws down from the solution, a mass which collects in lumps and dries up to a fine crystalline meal. (Werther.) Its solution in ammonia deposits, when boiled, a compound of 4 At. lead-oxide with 1 At. acid. (Erdmann, *Ann. Pharm.* 21, 14.) It dissolves in sal-ammoniac (Brett), and in warm nitrate or succinate of ammonia, imperfectly in the carbonate. (Wittstein.) It is nearly insoluble in water. Dissolves readily in aqueous nitric or tartaric acid. The latter solution does not become turbid on addition of alcohol, and when evaporated, deposits nothing but the neutral salt. (Erdmann.)

	Dried at 100°.		Berzelius. Thomson. Bucholz. Thénard. Casselmann.				
2 PbO	224	62·92	62·74	62·56	63	66	62·3
8 C	48	13·49	13·57				13·5
4 H	4	1·12	1·12				1·5
10 O	80	22·47	22·57				22·7
C ⁸ H ⁶ Pb ² O ¹²	356	100·00	100·00				100·0

By digesting 5 pts. of litharge with 2 pts. of neutral tartrate of potash dissolved in water, tartrate of lead and caustic potash are obtained. (Karsten, *Scher. J.* 5, 594.)

When 2 At. neutral acetate of lead and 1 pt. neutral tartrate of potash, are mixed together in aqueous solution, a precipitate is formed, consisting of a mixture of about 9 pts. of lead-oxide and 2 pts. of sex-basic acetate of lead, while the supernatant liquid is acid, and still contains tartaric acid, so that it is still capable of forming a precipitate with neutral acetate of lead. (Geiger, *Repert.* 9, 176.) — Boile (*Br. Arch.* 20, 1), obtained similar results. The precipitate obtained with various proportions of the materials, and washed with boiling water, contained, besides tartrate of lead, small quantities of sex-basic acetate of lead and cream of tartar; and the filtrate contained, — besides acetate of potash—free-acetic acid which could be separated by distillation, a small quantity of neutral tartrate of potash, and oxide of lead [probably dissolved in the form of tartrate by the acetic acid]. — Werther prepared his tartrate of lead by precipitating the acetate or nitrate of lead with neutral tartrate of potash, and obtained it in the form of a white, dry, soft powder, which contained 56·97 p. c.

impure salt of similar nature.

A lead-salt mixed with tartaric acid, and at the same time with a sufficient quantity of nitric acid to prevent the precipitation of tartrate of lead, is not precipitated by alkalis. (H. Rose.)

Tartrate of Lead and Ammonium. — Tartrate of lead dissolves readily and abundantly in an aqueous solution of neutral tartrate of ammonia; the concentrated solution solidifies, after a while, to a stiff jelly. (Wöhler.)

Tartrate of Lead and Potassium. — Cream of tartar boiled with oxide of lead yields an insoluble salt, which is not decomposed either by alkalis or by sulphates. (Thénard.)

Tartrate of Lead and Chromium. — Blue potassio-chromic tartrate added to acetate of lead, throws down a bluish-green powder. (Berlin.)

Tartrate of Lead and Antimony. — The precipitate obtained in the cold with tartar-emetic and neutral acetate of lead, and dried in the air, gives off 8·84 p. c. (4 At.) water, when heated to 100° in a steam of dry air; and at 200°, at which point decomposition begins, 11·7 p. c. (6 At.) in all. The precipitate obtained with hot solutions has, after drying in the air, the same composition as the precipitate obtained in the cold and dried at 100°; it gives off 4·81 p. c. (2 At.) water between 220° and 230°. (Dumas & Piria.) 2 At. water go off even at 190°, and the residue suspended in alcohol and decomposed by sulphuretted hydrogen, yields nothing but tartaric acid; if, however, this residue be decomposed by a small quantity of oil of vitriol, and exhausted with alcohol, the solution saturated with carbonate of baryta, and the filtrate evaporated, a small quantity of a baryta-salt is obtained = $\text{BaO}, \text{C}^6\text{H}^4\text{O}^4$ [= $\text{C}^6\text{H}^2\text{Ba}^2\text{O}^{10}$, corresponding, therefore, to tartaric anhydride]. (Berzelius, *Pogg.* 47 318.)

<i>The precipitate obtained from hot solutions, dried at 230°.</i>			<i>Dumas & Piria.</i>	
PbO	112	...	29·55	
SbO ³	153	...	40·37	
8 C	48	...	12·66 12·77
2 H	2	...	0·53 0·58
8 O	64	...	16·89	
<hr/>				
$\text{C}^6\text{H}^2\text{Pb}(\text{SbO}^3)\text{O}^{10}$	379	...	100·00	

<i>The same, air-dried.</i>			<i>Dumas & Piria.</i>	
PbO.....	112	...	28·21	
SbO ³	153	...	38·54	
8 C.....	48	...	12·09 12·20
4 H.....	4	...	1·01 1·13
10 O.....	80	...	20·15	
<hr/>				
$\text{C}^6\text{H}^4\text{Pb}(\text{SbO}^3)\text{O}^{12}$	397	...	100·00	

FEROUS TARTRATE. — *a. Anhydrous?* — 1. Obtained by mixing a warm aqueous solution of ferrous sulphate with tartaric acid. (Retzius.) According to Retzius, the salt is deposited as the liquid cools. According to Bolle (*N. Br. Arch.* 37, 33), on the contrary, it is deposited when the solution is heated. In a cold saturated aqueous solution of 4 pts. ferrous sulphate, 3 pts. of tartaric acid dissolve clearly; but each time the liquid

is heated, and especially on boiling, a large quantity of ferrous tartrate is precipitated in the form of a bluish white powder, which disappears almost completely on each application of heat, while ferrous sulphate crystallizes out. The mixture, after dilution with water, must therefore be boiled, the precipitate collected on the filter while hot, and washed with boiling water. By this process, the 4 pts. of ferrous sulphate yield 0.42 pt. of precipitate. When 1 pt. of ferrous chloride is mixed with 2 pts. of neutral tartrate of potash, part of the powder is precipitated, even in the cold, the rest on boiling; in all 1 pt.

According to Retzius, the anhydrous salt forms laminæ; according to Bolle, an apple-green powder containing no water of crystallization, and leaving 40.06 to 40.62 ferric oxide when burned. According to Dulk, it is a white, non-crystalline powder, which contains no water, but dissolves in 11.27 pts. of cold water.

By precipitating ferrous sulphate with neutral tartrate of potash, a pale green powder is obtained, which becomes spotted with red-brown during washing, and dissolves very readily in aqueous alkalis, forming a liquid which oxidises quickly on exposure to the air. (Werther.)

b. Hydrated. — Iron filings or iron wire is immersed in aqueous tartaric acid contained in a flask provided with a gas-delivery tube, the precipitated pulverulent salt separated from the iron by elutriation, and washed with a small quantity of water. (Bucholz, *Ure, N. Quart. J.* 6, 388.) — White powder containing 13 p. c. water (15 p. c. would be 4 At.), soluble in 426 pts. of cold and 402 pts. of boiling water. (Bucholz.) It tastes slightly ferruginous, does not oxidise readily in the air, takes fire at a dull red heat, and burns away like tinder, leaving a residue of ferric oxide. (Ure.) By dry distillation, it gives off carbonic acid and olefiant gases, and leaves a mixture of charcoal and ferrous oxide (without metallic iron, inasmuch as it does not evolve hydrogen from hydrochloric acid), which, when exposed to the air after complete washing, takes fire quickly, and burns away with a glimmering light, leaving ferric oxide of a fine red colour. (Böttger.)

Ferrous sulphate mixed with tartaric acid is not precipitated by alkalis or their carbonates, and forms with ammonia a dark green liquid, which, when exposed to the air, slowly turns yellow from formation of ferric salt. (H. Rose.) On boiling, however, the iron is completely precipitated by potash. (Wackenroder, *N. Br. Arch.* 21, 67.)

FERRIC TARTRATE. — Obtained by dissolving recently precipitated ferric hydrate in aqueous tartaric acid, at a temperature not exceeding 25° . (Werther, Wittstein, *Repert.* 86, 362; 92, 2.) — Ferric hydrate while still moist dissolves easily, but after drying, scarcely at all in the cold acid and very sparingly in the boiling acid, with partial reduction to ferrous oxide (recognizable by the formation of prussian blue with ferricyanide of potassium) and evolution of carbonic acid. (Werther.) — The solution evaporated below 50° , whereby an inconsiderable reduction is produced, leaves an amorphous mass which yields a dingy yellow powder, and consists of $2Fe^2O^3$, $3C^6H^{12}O^{12}$. On boiling the solution, the sesquioxide of iron is partly reduced to protoxide, and a basic salt is precipitated, while free acid remains in solution, together with a small quantity of the sesquioxide. (Wittstein.) The solution is not precipitated by alkalis; but when mixed, first with potash and then with alcohol, it is resolved into a wine-red syrup, and a supernatant liquid of a lighter colour. (Werther.) Sulphuretted hydrogen passed through a solution of

Concentrated solutions of neutral tartrate of potash mixed in proper proportion with ferric sulphate, deposit sulphate of potash; and the blood-red filtrate yields with alcohol containing in solution a large quantity of tartaric acid with a trace of ferric oxide, a viscid precipitate which dries up to a brittle mass, melts at 85° , glimmers away in the fire, with a pale flame and faint odour of caramel, and is insoluble in water, but redissolves in aqueous tartaric acid, forming a blood-red liquid. (Ure.)

Ferroso-ferric Tartrate. — When recently precipitated ferric hydrate is digested with aqueous tartaric acid, 21.2 pts. at most of the dry oxide dissolve in 63.3 pts. of the crystallised acid [1 At. in something less than 2 At.]. On boiling and evaporating this solution, $\frac{1}{4}$ of the ferric oxide is reduced to ferrous oxide without evolution of carbonic acid (at least according to Werther), formic acid, or any other volatile acid, and without formation of oxalic acid; oxygen gas must therefore be evolved [1]. During this boiling and evaporation, a lemon-yellow powder is likewise deposited. If, however, the whole be evaporated to dryness at once, there remain 85 pts. of a mass producing a greenish yellow powder, permanent in the air, and containing, when dried between 60° and 70° , 3.36 p. c. FeO, 21.50 Fe 2 O 3 , 64.75 C 6 H 4 O 10 , and therefore 10.39 Aq. It decomposes quietly in the fire, without melting, and leaves 38 p. c. of ferric oxide. To alcohol and ether it gives up only a little tartaric acid, and is resolved by boiling with water into a lemon-yellow powder, amounting to 58.8 per cent., and a pale yellow liquid, which is aqueous tartaric acid, but still contains in solution a small quantity of the lemon-yellow powder. (Wittstein.)

The lemon-yellow powder does not appear crystalline under the microscope; it is tasteless, and in the undecomposed state does not redden litmus. It contains 4.70 p. c. FeO, 32.25 Fe 2 O 3 , and 62.30 C 6 H 4 O 10 (loss 0.75.) It is decomposed in sunshine, with formation of ferrous salt, and acquires the power of reddening litmus; and when exposed to the sun under water, is completely dissolved, forming a colourless liquid which contains nothing but ferrous salt. It is not altered by ammonia; with potash-ley, it forms a black-brown solution which is completely decomposed at a gentle heat; with warm aqueous carbonate of potash, it forms a dark brown solution which becomes turbid by continued boiling. It dissolves in nitric acid without colour, in hydrochloric acid with yellow colour. The latter solution forms with ammonia a clear brownish yellow mixture; with potash, a clear black-brown mixture, which is completely precipitated on heating; and with carbonate of potash, a dark mixture, which, when boiled, slowly deposits all the iron, the more slowly as it is more concentrated. In cold tartaric acid the powder dissolves slowly, in hot tartaric acid quickly, with greenish yellow colour. Hot acetic acid dissolves only a trace; alcohol and ether, none. (Wittstein, *Repert.* 86, 362.)

Ferrocyanide of potassium added to a solution of neutral ferric tartrate, throws down prussian blue; but if an excess of tartaric acid is present, it forms a clear blue liquid, which when evaporated, leaves a dark blue residue, soluble in water. — Prussian blue recently precipitated from ferric sulphate does not dissolve in tartaric acid; but, if ammonia be then gradually added, it becomes violet, amethyst-red, rose-red, and finally white (ammoniacal prussian blue, vii. 445); it is then turned blue by tartaric acid, and again white by ammonia. The white body remains

white when exposed to the air under water, but becomes blue only drying. If, on the other hand, tartrate of ammonia be immediately added to the blue precipitated mixture of ferric sulphate and ferrocyanide of potassium (and not the acid and ammonia in succession), the prussian blue dissolves with splendid violet colour. (Calloud, *N. J. Pharm.* 10, 182; also *J. pr. Chem.* 39, 227.)—Prussian blue alone likewise dissolves immediately in a cold aqueous solution of neutral tartrate of ammonia. (Monthiers, *N. J. Pharm.* 9, 263; also *J. pr. Chem.* 38, 173.)

Ammonio-ferric Tartrate.—The dark brown solution of recently precipitated ferric hydrate in hot aqueous tartrate of ammonia, leaves, when evaporated over the water-bath, shining, dark brown scales, exhibiting a garnet-red transluence, — or else a granular mass. The residue consists of $NH^3, Fe^2O^3, C^3H^4O^{10} + 4$ to 5 Aq. It dissolves in somewhat more than its own weight of water. The solution is not altered by several hours' boiling, but alcohol precipitates the salt from it. (Procter, *Amer. J. of Pharm.*; abstr. *N. J. Pharm.* 1, 414.)

Potassio-ferrous Tartrate.—By digesting 1 pt. of iron-filings with 4 pts. cream of tartar, and with water out of contact of air. Greenish white needles having a harsh taste, sparingly soluble in water, not precipitated by alkalis or their carbonates, but yielding a precipitate with sulphuretted hydrogen.

Potassio-ferric Tartrate.—Ferric hydrate is digested at 50° or 60° with water and cream of tartar for 24 to 36 hours, the mixture being shaken now and then, and the residue evaporated on plates in the drying chamber at a gentle heat. Shining, black-brown scales, ruby-coloured by transmitted light; the salt, even below 130° , gives off water and carbonic acid, part of the sesquioxide of iron being at the same time reduced to protoxide; and the residue dissolves in water, with separation of a small quantity of black ferruginous matter. The solution of the salt deposits when boiled, nearly colourless tartrate of ferrous oxide [and potash?] (Soubeiran & Capitaine, *J. Pharm.* 25, 738; also *Ann. Pharm.* 34, 204.)

Dried at 100° .		Soubeiran & Capitaine.	
KO	47.2	18.21	18.6
Fe^2O^3	80.0	30.86	30.8
$C^3H^4O^{10}$	132.0	50.93	
$C^3H^4K(Fe^2O^3)O^{12}$	259.2	100.00	

To this salt belong, for the most part, the *Tartarus chalybeatus* or *Mars solubilis*, and the *Globuli martiales* of the pharmacopœas, prepared by heating cream of tartar and water, either with ferric hydrate, or with iron filings in a vessel exposed to the air. These preparations, however, as Wackenroder has shown, always contain a considerable quantity of ferrous salt, inasmuch as, in the first mode of preparation, part of the ferric oxide is reduced by the hot tartaric acid, and in the second, the iron is but imperfectly oxidized by the air. These preparations consist of a very sparingly soluble portion, which, according to the mode of operating, appears to consist of basic ferric tartrate, potassio-ferrous tartrate, or ferrous tartrate, and of an easily soluble portion, which is chiefly potassio-ferric tartrate, but appears always to contain in addition potassio-

s salt), and sometimes also neutral tartrate of potash.

1. *With Ferric Hydrate and Cream of Tartar.* — When the hydrate is boiled for some time with water and cream of tartar, the liquid evaporated to an extract, the extract dissolved in water, the solution filtered from the insoluble portion, and again evaporated, a dark green mass is obtained, which yields a yellow-green powder. It dissolves readily in water. The clear yellow-green solution reddens litmus strongly, and when mixed with hydrochloric acid, forms a copious blue precipitate, both with ferrocyanide and with ferricyanide of potassium. The precipitate produced by the ferrocyanide is about three times as copious as that formed by the ferricyanide. The tartaric acid has therefore reduced a portion of the sesquioxide of iron to protoxide. It forms with ammonia a clear brown mixture, which does not become turbid, even when boiled, but when heated with a small quantity of hydrochloric acid, deposits a rusty-coloured matter, which redissolves in a larger quantity of the acid. The clear dark brown mixture formed with potash remains clear while cold (as observed by Wenzel and H. Rose), but on boiling deposits all the iron in the form of dark brown ferroso-ferric hydrate. With carbonate of soda it assumes a greenish brown colour; with phosphate of soda, dark brownish green, without becoming turbid when boiled; but a small quantity of acetic acid afterwards added, throws down all the iron as a greenish white powder; a small quantity of hydrochloric acid also added after the phosphate of soda, forms, especially when the liquid is heated, a thick precipitate of ferric phosphate; and if acetate of soda be likewise added, the whole of the ferric oxide is precipitated on boiling in the form of phosphate, and the whole of the ferrous oxide remains in solution, also as phosphate. Sulphuretted hydrogen forms a black precipitate with the solution, but does not throw down all the iron. Infusion of galls forms a dark blue precipitate. (Wackenroder, *N. Br. Arch.* 21, 65.) The soluble salt slowly forms with ferrocyanide of potassium a scanty white precipitate, which gradually turns blue (J. A. Buchner, *Repert.* 6, 289), but on addition of a small quantity of acid, it yields immediately a copious blue precipitate. (Fuchs, *Repert.* 9, 214.) With sulphuretted hydrogen and tincture of galls, it gives the ordinary precipitates. (Buchner.)

By boiling about 1 pt. of ferric hydrate with 4 pts. of cream of tartar and with water, then filtering and evaporating to dryness, a dark green or yellowish brown, uncrystallisable, resinous mass is formed, having a sweetish ferruginous taste. — By boiling 188.1 pts. (1 At.) of cream of tartar with a quantity of ferric hydrate containing 82.8 pts. (a little more than 1 At.) of anhydrous ferric oxide, and with water, a soluble and an insoluble compound are obtained, which may be separated by filtration. — The insoluble compound amounts to only 18 pts., contains 68 p. c. ferric oxide, no potash, and may be regarded as basic ferric tartrate. The soluble compound amounts, when evaporated to dryness, to 242 pts.; has the appearance of a brown brittle resin, transparent, with greenish yellow colour in thin sheets; yields a brown greenish yellow powder, which the moisture of the air again hardens to a solid mass; has a pure but mild ferruginous taste; and reddens litmus. The brown-yellow aqueous solution, like all the following examined by Wittstein, is completely precipitated, with blue colour, by ferricyanide of potassium, also by boiling with potash, with separation of dark brown ferroso-ferric hydrate. (Wittstein; see his analysis, a, p. 319.)

digested with 4 pts. of cream of tartar and with water in an open vessel, hydrogen gas is evolved at first, and a white granular mass formed, which is slightly soluble in water, consists chiefly of potassio-ferrous tartrate, and when exposed for some weeks to the action of the air, assisted by constant stirring, is converted into a brown pitchy mass, consisting chiefly of potassio-ferric tartrate, but always containing a little of the ferrous salt. On dissolving this mass in water, the excess of iron filings remains behind, and, according to Wittstein, some iron-black produced therefrom, together with potassio-ferrous tartrate, and any tartrate of lime that may have been contained in the cream of tartar; while the filtered solution leaves on evaporation, a brown mass consisting of a large quantity of potassio-ferric and a small quantity of potassio-ferrous tartrate.

The solution of this mass is dark brown, has a faint taste, slightly sweetish, with an alkaline character, and almost imperceptibly ferruginous. Sulphuric, hydrochloric, nitric, or acetic acid, added in small quantity, precipitates pure ferric hydrate, and the filtrate tastes slightly acid and strongly ferruginous; tartaric acid precipitates cream of tartar from it. (Geiger, *Mag. Pharm.* 7, 262.)

If the mass be redissolved in water and filtered as often as any insoluble matter [potassio-ferrous tartrate?] remains behind, and the filtrate finally evaporated, a dark brownish green mass is obtained, which swells up strongly when ignited, and deliquesces in the air. (Dulk. *Analysis b.*)

When iron filings are digested for a short time with cream of tartar, the resulting solution has a strong acid reaction; after longer digestion the acid reaction is but slight, but the proportion of the protoxide to the sesquioxide remains about the same. The solution exhibits exactly the same reactions as that which is prepared with ferric oxide and cream of tartar (p. 317), especially in being completely precipitated by potash on boiling. (Wackenroder.)

The portion of the resulting mass which is sparingly soluble in water is ferrous tartrate; the easily soluble portion blues reddened litmus, and becomes moist on exposure to the air. (Boutron Charlard, *J. Pharm.* 9, 590.)

Alcohol added to the aqueous solution throws down a viscid mass, and the nearly colourless filtrate contains a very small quantity of iron. (Ure.)

After 1 pt. of iron filings has been digested for a week with 4 pts. of cream of tartar, nearly $\frac{1}{2}$ of the iron is found unaltered. The insoluble portion of the resulting salt is ferrous tartrate mixed with a very small quantity of potassio-ferrous tartrate; if, however, the action of the air has been continued for a longer time, the product gives the analysis c. — The portion soluble in water, which is the larger of the two, exhibits, after evaporation, the appearance of a black, shining, brittle mass, which becomes moist on exposure to the air, and has a mild, saline, sweetish, ferruginous taste; when this mass is dissolved in water, a small portion of the insoluble salt still remains behind. *Analysis d.* (Wittstein.)

In a second similar experiment, $\frac{1}{2}$ of the iron filings remained unattacked, but at the same time $\frac{1}{2}$ of the iron was converted into iron-black. The black watery filtrate left more than 2 pts. of a black shining mass, which, after being three times dissolved in water and filtered from the insoluble portion (the analysis of which is given under e), left a black

of moisture, yielding a greenish brown powder, and having a somewhat ferruginous taste; the analysis of this residue is given under *f*. (Wittstein.)

If iron reduced from the oxide by hydrogen be used, and the mass subsequently digested in water, there remains a greyish white mixture of iron-black and ferrous tartrate free from potash; and the dark greenish brown filtrate, which has a sweetish, ferruginous, and saline taste, and reddens litmus slightly, leaves on evaporation a black residue, which yields a greyish brown powder, deliquesces to a thin paste on exposure to the air, dissolves completely in water, and gives the analysis *g*. (Wittstein.)

	Wittstein.		Dulk.		Wittstein.		Wittstein.	
	At.	a.	At.	b.	At.	c.	At.	d.
KO	4	19.30	4	30.97	6	14.58	7	28.62
FeO	1	4.04			7	12.73	1	2.92
Fe ² O ³	3	24.38	1	12.78	6	24.86	2	10.09
C ⁶ H ⁴ O ¹⁰	4	52.69	3	56.25	7	47.83	5	58.37
		100.41		100.00		100.00		100.00

	Wittstein.		Wittstein.		Wittstein.	
	At.	e.	At.	f.	At.	g.
KO	6	20.61	8	26.02	8	34.06
FeO			1	2.59	1	3.99
Fe ² O ³	6	33.84	3	17.00	1	5.57
C ⁶ H ⁴ O ¹⁰	5	45.55	6	54.00	5	57.25
		100.00		99.61		100.87

[The atomic numbers prefixed to the percentages are but very rough approximations.

According to this, the salt *a* is a mixture of 1 At. C⁶H⁴KFeO¹², and 3 At. C⁶H⁴K(FeO³)O¹²; in salt *b*, Dulk probably overlooked the ferrous oxide; salt *c* is not easy to designate; *d* appears to be a mixture of 1 At. C⁶H⁴KFeO¹², 2 At. C⁶H⁴(Fe²O³)O¹², and 2 At. C⁶H⁴K²O¹²; *e*, which appears to contain a basic salt, is difficult to make out; *f* should be a mixture of 1 At. C⁶H⁴KFeO¹², 1 At. C⁶H⁴K(FeO³)O¹², and 3 At. C⁶H⁴K²O¹²]. — Wittstein gives different calculations, because in each of the compounds analysed, he supposes all the potash, ferrous oxide, ferric oxide and acid, to be united into a single salt.

According to Semmola (*Berzelius Jahresber.* 24, 217), the compound of 1 At. potassio-ferrous tartrate with 1 At. potassio-ferric tartrate is green and difficultly soluble, and when exposed to the air, passes into the black, easily soluble compound containing 2 At. ferric salt.

When iron filings are digested in an open vessel with an aqueous solution of neutral tartrate of potash, an alkaline liquid is obtained, — a proof that the oxidized iron sets potash free. (Boutron Charlard.)

Recently precipitated ferric hydrate dissolves readily, without evolution of gas, in aqueous neutral tartrate of potash, forming a red solution; but after having been dried for some time, it dissolves only after long boiling, and with slight evolution of gas. (Werther.)

If tartrate of potash contains iron in solution, the iron, in presence of carbonate of potash, requires a very large excess of hydrosulphate of potassium to precipitate it completely, but is readily precipitated if the carbonate of potash be decomposed by an acid. (Blumenau, *Ann. Pharm.* 67, 125.)

TARTRATE OF COBALT. — Red, crystallisable. (Gren.) — Cobalt-salts mixed with tartaric acid are not precipitated by alkalis or their carbonates. (H. Rose.)

Tartrate of Cobalt and Potassium. — Large rhomboidal crystals.

TARTRATE OF NICKEL. — When the boiling aqueous acid is saturated with the hydrated oxide or carbonate of nickel, this salt is precipitated in greenish white flakes, having a faint metallic taste (Tupputi); as a siskin-green crystalline powder. (Werther.) By dry distillation, it leaves a black, very soft, non-pyrophoric powder. (Böttger.) It is scarcely soluble in water, either hot or cold (Werther), but dissolves in tartaric acid. (Tupputi.) Nickel-salts in presence of tartaric acid are not precipitated by alkalis or alkaline carbonates. (H. Rose.)

Tartrate of Nickel and Potassium. — Obtained by boiling carbonate of nickel with aqueous cream of tartar. Gummy; not crystallisable; extremely sweet; easily soluble. (Wöhler.)

Tartrate of nickel dissolves readily in warm aqueous potash or soda, and on boiling also in carbonate of soda, with evolution of carbonic acid, forming a liquid which solidifies to a pulp on cooling. The solution in caustic alkalis, which has a fine green colour, yields no crystals by evaporation, but a whitish green gelatinous deposit, which is not deprived of all its potash or soda by washing with cold water, and dissolves but slowly on boiling. The supernatant liquid is turbid, passes milky through the filter, and leaves a gummy mass by spontaneous evaporation. With alcohol, the green solution solidifies to a jelly. (Werther.)

A cold aqueous solution of neutral tartrate of potash or soda dissolves but a small quantity of hydrated oxide of nickel, forming a neutral liquid which does not crystallise. (Werther.)

CUPRIC TARTRATE. — *a. Neutral.* — 1. Obtained by saturating the heated acid with cupric oxide. (Trommsdorff.) The salt separates as soon as the acid is nearly saturated. (Werther.) — 2. By precipitating acetate of copper with tartaric acid, (Trommsdorff) or sulphate, or chloride. (Bergman, *Opusc.* 3, 456.) — 3. By precipitating nitrate or sulphate of copper with neutral tartrate of potash, (V. Rose, Werther,) or with cream of tartar. (Planche, *J. Pharm.* 12, 362.)

Whitish blue powder (V. Rose, Trommsdorff); light green powder, appearing under the microscope to consist of tables (Werther); blue crystals (Bergmann); green crystals (Planche). — The powder gives off all its water at 100° , and becomes greenish white. (Werther.) It then yields by dry distillation, acetic acid, pyrotartaric acid, and an empyreumatic oil of agreeable odour (Gruner), and leaves a dark brown mass, which, when set on fire in the air by a red-hot coal, burns away and leaves oxide of copper (Böttger). The salt, when heated in the air, swells up, blackens, gives out a faint odour, and leaves metallic copper (Planche), which then burns and forms 37.31 p. c. oxide of copper. (Trommsdorff.) — Bright iron immersed in the aqueous solution becomes covered, first with a black, and afterwards with a brown-black film of copper-iron. (Wetzlar, *Schw.* 50, 96.)

It dissolves in 1715 pts. of cold, and 310 pts. of boiling water (Werther); is insoluble in cold water, but dissolves in more than 1000 pts. of boiling water, forming a nearly colourless liquid, which becomes

		<i>Crystalline.</i>		<i>Dumas & Piria.</i>	
2	CuO	80 30·08	29·8
8	C.....	48 18·04	18·2
10	H	10 3·76	3·8
16	O.....	128 48·12	48·2
<hr/>					
	$C^{\circ}H^{\circ}Cu^{\circ}O^{12} + 6Aq.$	266 100·00	100·0
<hr/>					
		<i>Or :</i>		<i>Werther.</i>	
2	CuO	80 30·08	29·67
	$C^{\circ}H^{\circ}O^{10}$	132 49·62		
6	HO.....	54 20·30	20·13
<hr/>					
	$C^{\circ}H^{\circ}Cu^{\circ}O^{12} + 6Aq.$	266 100·00		

Potassio-cupric Tartrate.—Obtained by boiling the oxide (Thénard) or carbonate of copper (Trommsdorff), with aqueous cream of tartar Blue, sweet-tasting crystals (Thénard). The dark blue solution deposits metallic copper when evaporated, and leaves an amorphous residue, 1 pt. of which boiled with 3 pts. of cream of tartar and with water, yields a green solution, from which, by evaporation, green crystals are obtained, together with a precipitate of copper. 10 pts. of neutral tartrate of potash, dissolved in water, likewise take up only 1 pt. of tartrate of copper, and the blue solution deposits metallic copper when evaporated, but nothing crystalline. (Trommsdorff.) Iron immersed in the aqueous solution of this salt is not coppered over, even on boiling; but silver in contact with the iron becomes coated with copper at a boiling heat. (Wetzlar.)

Cupric tartrate forms with potash-ley a dark blue solution, from which alcohol throws down a crystallizable double salt. (Planche.) When mixed with alcohol, it separates into a dark blue oily layer, and a supernatant, thin, pale blue liquid. (Werther.)

Cupric tartrate dissolves in 2·5 pts. of carbonate of potash (dissolved in water), forming a deep blue liquid, which, when evaporated, deposits a red powder of copper, a yellowish powder of hydrated cuprous oxide, and a powder proceeding from decomposition of the acid, and, ultimately, leaves a dark blue, pulverizable, amorphous mass. This mass does not become damp on exposure to the air, and is insoluble in alcohol, but dissolves in warm water, forming a splendid blue liquid, which gives no precipitate with ammonia or potash, a light blue precipitate with baryta-water, lime-water, and neutral acetate of lead, and with sulphuretted hydrogen a brown precipitate of sulphide of copper. (Trommsdorff.)

Cupric salts mixed with tartaric acid form a clear sky-blue mixture with carbonate of potash.

From the solution of cupric tartrate in soda-ley, alcohol throws down thick flakes, which dry up to a light blue powder, and dissolve very readily in water, forming a liquid which, when evaporated, deposits cuprous oxide, becomes thick and gummy, and ultimately leaves a greenish black, amorphous mass. (Werther.)

Cupric tartrate is nearly insoluble in cold dilute carbonate of soda; but in a boiling solution of that salt, it dissolves with violent evolution of carbonic acid, and forms a deep blue, perfectly neutral, liquid. (If the

boiling be too long continued, a small quantity of cuprous oxide is precipitated.) This liquid, evaporated first over the water-bath, then, after filtering from the cuprous oxide, in vacuo, or over sulphuric acid within a receiver containing air, yields small tabular crystals, united in warty masses, of a fine blue colour, dissolving with the same colour in water, and with peculiar facility in warm water. The neutral solution turns green when boiled for some time, but on cooling deposits cuprous oxide and recovers its blue colour; it is not precipitated by alkalis, but the mixture, after standing for some time, deposits cuprous oxide and a black carbonaceous substance. Alcohol precipitates the salt from its aqueous solution in the form of a light blue powder. In the formation of these crystals, 3 At. cupric tartrate appear to decompose with 4 At. soda into 2 At. of the crystals and 1 At. tartrate of soda; but the mother-liquor, which is coloured brown from partial decomposition, does not yield the latter salt. (Werther.)

	Blue tables.		Werther.	
NaO.....	31.2	9.01 9.10
3 CuO.....	120.0	34.66 33.86
$\text{C}^{\text{H}}\text{C}^{\text{O}}^{\text{II}}$	132.0	38.13 38.31
7 HO.....	63.0	18.20 18.65
<hr/>				
2 CuO, $\text{C}^{\text{H}}\text{C}^{\text{O}}^{\text{II}}\text{NaCuO}^{\text{II}} + 7\text{Aq}^?$	346.2	100.00 99.92

MERCUROUS TARTRATE.—1. When 1 pt. of mercurous oxide is heated with 2 pts. of tartaric acid dissolved in water, the temperature being ultimately raised to 75° , the solution deposits white crystalline scales on cooling, but a considerable quantity of mercury remains dissolved. (Harff. *Br. Arch.* 5, 269.) The greater part of the mercurous oxide is, however, resolved into metallic mercury and mercuric oxide. (Burekhardt.)—2. By precipitating a dilute solution of mercurous nitrate with free tartaric acid. (Burekhardt, *N. Br. Arch.* 11, 257.)—3. By triturating together the crystals of mercurous nitrate and neutral tartrate of potash, with addition of water (H. Rose, *Pogg.* 53, 127,) or by mixing the aqueous solutions of the two salts. (V. Rose, Carbonell, & Bravo, *J. Chim. méd.* 7, 161.) The precipitate remains suspended at ordinary temperatures, but is immediately deposited on heating the liquid. (Werther.)—The precipitate, after being washed with cold water, must be dried in the dark.

Soft, white, shining needles or scales, or white crystalline powder, having a metallic taste. The salt contains, according to Burekhardt, 72.45, according to Harff, 74.07 p. c. mercurous oxide. When exposed to light, it turns yellow, grey, and black (at least when it is moist. Harff.) It intumescs strongly in the fire, giving off acetic acid, (but no formic,) and leaving charcoal. When heated with potassium, it decomposes with fire, but without noise. (Burekhardt.) When boiled with water, it does not dissolve, but turns greyish, from reduction of metal, the water at the same time taking up a small quantity of mercuric salt. (H. Rose.) Potash or soda immediately separates mercurous oxide from it. (Werther.)—In boiling concentrated sulphuric acid, it dissolves completely, with dark brown colour, in the dilute acid partially. It dissolves readily in nitric acid, even when dilute; with boiling hydrochloric acid it forms a small quantity of corrosive sublimate. It dissolves readily, especially while still moist, in concentrated acetic acid and in aqueous tartaric acid, but not in water, alcohol, or ether. (Burekhardt.)

aqueous acid, and the resulting white powder separated from the unaltered oxide by levigation. (Burckhardt.)—2. Mercuric acetate (or nitrate, according to Werther,) is precipitated by the free acid or its soda-salt. (Burckhardt.)—When mercuric nitrate is precipitated by an alkaline tartrate, the precipitate is contaminated with a basic nitrate. (Burckhardt.)—White, very light powder, having a metallic taste. (Burckhardt.)—Yellowish white fine grains. (Werther.) At 100°, the salt contains 58.45 p. c. mercuric oxide (Burckhardt), 80.50 p. c. (Harff.) It does not blacken by exposure to light. When heated, it blackens, swells up, and is resolved into carbonic acid, empyreumatic acetic acid, mercury, and charcoal. When heated with potassium, it decomposes with noiseless fire. (Burckhardt.) Caustic potash separates from the salt, a reddish-black mixture of mercuric and mercurous oxides (Werther), yellow mercuric oxide. (Harff.) It is nearly insoluble in cold oil of vitriol, but dissolves with brown colour in boiling oil of vitriol. It dissolves readily in dilute nitric acid, in strong acetic acid, and in tartaric acid, forming liquids which are not precipitated by ammonia, carbonate of ammonia, potash, or soda. It does not dissolve in water, alcohol, or ether, even at a boiling heat. (Burckhardt.) It dissolves very sparingly in pure water, but abundantly, and with precipitation of corrosive sublimate, in water containing sal-ammoniac, together with common salt. (Mialhe.)

Basic Ammonio-mercurous Tartrate.—*a. White.*—The solution of mercurous tartrate is supersaturated with ammonia, and filtered from the scanty grey precipitate; the excess of ammonia which had held the basic salt in solution, driven off from the filtrate by gentle evaporation; this basic salt freed from nitrate and tartrate of ammonia, by washing with a small quantity of cold water, and dried over the water-bath in the dark.—White powder, of saline metallic taste. Blackens quickly when exposed to light. When heated, it gives off carbonic acid, empyreumatic ammoniacal vapours, and mercury, and leaves a trace of charcoal. It is not altered, even by immersion in boiling potash or soda. It dissolves in cold oil of vitriol, in hot nitric and in strong acetic acid. It does not dissolve in water, either hot or cold, but, especially while still moist, in an aqueous solution of pure ammonia, or of nitrate or tartrate of ammonia. (Burckhardt.)

b. Black.—Mercurous tartrate suspended in water, treated with ammonia, and washed, yields when dried a black tasteless powder, which contains 86.27 p. c. mercurous oxide; yields globules of mercury when moistened and rubbed in the hand; gives off a large quantity of ammonia when treated with potash; dissolves in nitric acid with the exception of a white powder; and in acetic acid with separation of mercurial globules; and is insoluble in water, alcohol, and ether. (Harff.)

Ammonio-mercuric Tartrate.—*a. Basic.*—*a.* Mercuric tartrate suspended in water is decomposed by ammonia, then washed and dried in the shade. White powder having a metallic taste. It contains 77.85 p. c. mercuric oxide. When ignited, it gives off ammonia, mercury, and oxygen gas [!], and leaves charcoal. When boiled for some time with water, it turns yellow. With potash it assumes a yellow colour, and gives off ammonia. Oil of vitriol turns it yellow, and partially dissolves it. It dissolves easily in hydrochloric acid, scarcely at all in cold nitric

acid, almost entirely in hot nitric acid, in 1000 pts. of water, in 455 pts. of alcohol, not in ether. (Harff.)

β. Mercuric oxide is boiled with aqueous tartrate of ammonia and excess of tartaric acid; the filtrate precipitated by dilution with water; and the precipitate washed and dried at 100° in the dark. The white metallic-tasting powder blackens on exposure to light. It intumesces when heated, giving off carbonic acid, empyreumatic ammoniacal vapours, afterwards acid vapours and mercury, and leaves a trace of charcoal. With boiling potash it gives off ammonia. Dissolves easily in nitric, acetic, and tartaric acid, but is insoluble in water, alcohol, and ether. (Burekhardt.)

b. Neutral. — Formed by boiling mercurous or mercuric oxide with acid tartrate of ammonia, or by dissolving mercuric tartrate in neutral tartrate of ammonia. Is best prepared by the last mentioned process, the liquid being boiled to saturation and filtered hot. On cooling, the salt crystallizes in small, transparent, colourless, four-sided prisms, having a saline and afterwards harsh metallic taste. These prisms do not blacken when exposed to light; they swell up strongly in the fire, becoming carbonized and giving off ammoniacal vapours, empyreumatic acetic acid, and mercury. With boiling potash, they give off ammonia. They dissolve in cold oil of vitriol. They dissolve readily in water both hot and cold, but are insoluble in alcohol and ether. The aqueous solution yields a red precipitate with potash, a white turbidity with carbonate of potash, nothing with ammonia or carbonate of ammonia. (Burekhardt.)

Potassio-mercurous Tartrate. — 1. Obtained by boiling 1 pt. of mercuric oxide with 6 to 8 pts. of cream of tartar and with water, till the whole is nearly dissolved, then filtering hot, and cooling. (Mounet, Burekhardt.) The crystals thus obtained consist entirely of mercurous salt, whereas if only 3 pts. of cream of tartar are used, the reduction does not take place. (Burekhardt.) — 2. By boiling mercurous oxide or mercurous tartrate with excess of cream of tartar. — White, translucent, very small prisms, having a metallic taste and reddening litmus. The salt blackens quickly when exposed to light. When heated, it intumesces, gives off empyreumatic acetic acid, carbonic acid, and mercury, and leaves a large quantity of charcoal. It is insoluble in cold water, dissolves sparingly in boiling water, readily in nitric, acetic, and hot tartaric acid, from which latter it separates unaltered on cooling. (Burekhardt; *comp.* Carbonell & Bravo, *J. Chim. med.* 7, 161; *J. Pharm.* 19, 620.)

Potassio-mercuric Tartrate. — 1. Prepared by adding mercuric tartrate to a boiling solution of neutral tartrate of potash as long as it dissolves, filtering hot, and cooling to the crystallising point. (Burekhardt.) — 2. By digesting mercuric oxide with water and cream of tartar, and evaporating the filtrate till it crystallises. (Harff.) — Small, white, translucent prisms (shining, according to Harff), which have a metallic taste, and redden litmus. (Burekhardt.) The salt intumesces when heated, giving off empyreumatic acetic acid, carbonic acid, and mercury, and leaving carbonate of potash mixed with charcoal. (Burekhardt.) Its aqueous solution is coloured red by potash, white by carbonate of potash or soda, and is not precipitated by ammonia or carbonate of ammonia. (Burekhardt.) The crystals turn yellowish with potash, white with

ing. They dissolve in hydrochloric acid and in nitric acid. (Harff.) They are nearly insoluble in cold water, dissolve more readily in hot water, also in various acids and in neutral tartrate of potash; not in alcohol or ether. (Burokhardt.) They dissolve in ether. (Harff.)

Tartaric acid forms with oxycyanide of mercury a crystallisable salt, which is resolved by water into a soluble and an insoluble salt. (Johnston, viii, 16.)

TARTRATE OF SILVER. — Precipitated on mixing neutral tartrate of potash (not the free acid) with nitrate of silver. (V. Rose.) With cold dilute solutions of nitrate of silver and Rochelle salt acidulated with a very small quantity of nitric acid, the precipitate is curdy and amorphous; boiling hot dilute solutions turn brown when mixed, and deposit brown laminae of silver. But if a moderately concentrated solution of Rochelle salt be added to a dilute silver-solution of 80°, till the precipitate which at first continually redissolves, begins to become permanent (a small portion of the silver-salt must remain undecomposed), the mixture on cooling yields delicate scales, which, after thorough washing, have a white metallic lustre like polished silver, and at 15° exhibit a sp. gr. of 3.4321. (Liebig & Redtenbacher, *Ann. Pharm.* 38, 132.) — White crystalline powder, having a silky lustre, and free from alkali when thoroughly washed. (Werther.) The salt blackens on exposure to light. (V. Rose.) When gently heated, it gives off pyrotartaric and carbonic acid, without intumescence or spitting, and leaves a shining mass of spongy silver free from alkali. The dry salt is quickly decomposed by dry chlorine gas, with evolution of heat and formation of chloride of silver. (Liebig.) The heat produced by the decomposition gives rise to the evolution of empyreumatic products; chlorine gas passed through water in which tartrate of silver is suspended, produces carbonic acid gas, chloride of silver, and unaltered tartaric acid; part of this acid has therefore been converted into carbonic acid. (Erdmann, *J. pr. Chem.* 25, 504.) When dry ammoniacal gas is passed at a gradually increasing temperature over the salt previously dried at 100°, the salt becomes suddenly brown and black, and when the temperature reaches 70°, gives off dense fumes of pure carbonate of ammonia, and leaves a black residue with partial metallic lustre, from which water extracts a large quantity of tartrate of ammonia, while a black carbide of silver, containing 7.5 p. c. carbon, remains behind. (Erdmann.) The solution of tartrate of silver and aqueous ammonia deposits silver on boiling, partly in the specular form, and afterwards on cooling yields an ammoniacal salt, which dissolves in water less easily than the tartrate, and whose aqueous solution forms with potash-salts, a non-crystalline precipitate, which dissolves in hydrochloric acid less easily than tartrate of lime, and is precipitated from that solution by ammonia, even while the liquid still reddens litmus strongly. Hence another acid appears to be formed. (Werther.) Casselmann did not obtain this reaction. — Cold potash or soda-ley added to tartrate of silver throws down oxide of silver (Werther); but only half the total quantity, because a tartrate of silver and potassium or sodium is formed. (Gay-Lussac & Liebig.) The salt is nearly insoluble in water. (V. Rose, Werther.)

The presence of tartaric acid does not protect silver-salts from precipitation by fixed alkalis. (H. Rose.)

				Liebig.
8 C	48	13.19	
4 H	4	1.10	
2 Ag	216	59.34 59.294
12 O	96	26.37	
<hr/>				
C ⁸ H ⁴ Ag ² O ¹²	364	100.00	

According to Thénard, there exists a tartrate of silver and potassium, which is obtained as a white insoluble powder by digesting silver-oxide with cream of tartar. Liebig however did not succeed in preparing it; for on boiling the silver-oxide with cream of tartar, carbonic acid was evolved, and from the liquid which had become neutral, acetate of silver crystallised on cooling; and by precipitating nitrate of silver with a very large excess of neutral tartrate of potash, he obtained on cooling, silver-shining laminae of tartrate of silver free from potash. [This does not agree with the statement of Gay-Lussac & Liebig above-quoted.]

Argento-chromic Tartrate. — Obtained like the corresponding lead-salt, which it resembles in properties and stoichiometrical constitution. (Berlin.)

Argento-antimonic Tartrate. — Obtained by precipitating nitrate of silver with tartar-emetic. (Wallquist.) The precipitate has the same composition, whether obtained from cold or from hot solutions; the latter, when heated to 150° in a current of dry air, gives off 4.28 p. c., and at 160°, with reddish yellow colouring, 4.4 p. c. (2 At.) water in all. A trace of potash is found in the ignited residue. (Dumas & Piria.)

	<i>Dried at 160°.</i>			<i>Dumas & Piria.</i>
AgO	108	28.80 28.05
SbO ³	153	40.80	
8 C	48	12.80 12.43
2 H	2	0.53	
8 O	64	17.07	
<hr/>				
C ⁸ H ² Ag(SbO ³)O ¹⁰	375	100.00	

	<i>Air-dried.</i>			<i>Dum. & Piria.</i>	<i>Wallquist.</i>
AgO	108	27.48		27.31
SbO ³	153	39.93		36.94
8 C	48	12.22 12.18	
4 H	4	1.02 1.08	
10 O	80	20.35		
<hr/>					
C ⁸ H ² Ag(SbO ³)O ¹²	393	100.00		

TARTRATE OF PALLADIUM. — The neutral tartrates of the alkalis form a light yellow precipitate with nitrate of palladium. (Berselius.)

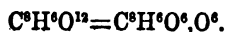
Tartaric acid dissolves readily in *Wood-spirit* and in *Alcohol*. The latter solution, according to Pelouze, does not redden litmus.

Concentrated solutions of tartaric acid and *Urea* form, after a while, a crystalline precipitate. (Gm.)

The solution of *Glycol* in the aqueous acid mixed with absolute alcohol, deposits an oil, which is not altered by repeated agitation with alcohol, and dries up to a gum on exposure to the air. (Horsford.)

Tartaric acid combines with organic alkalis, forming crystallisable salts. Tartrate of asparagine forms very beautiful crystals. (Pasteur.)

Metatartaric Acid.



BRACONNOT. (1831.) *Ann. Chim. Phys.* 48, 299; also *Schw.* 64, 338; also *Pogg.* 26, 322.

ERDMANN. *Ann. Pharm.* 21, 9.

LAURENT & GERHARDT. *Compt. Chim.* 1849, 1 & 97; also *Ann. Pharm.* 70, 348; also *J. pr. Chem.* 46, 360; abstr. *Compt. rend.* 27, 318.

Amorphous Tartaric Acid, Metatarterssäure, amorphe Weinsäure, Acide metatartrique.

Formation and Preparation. Tartaric acid, pulverised and dried at 100°, is heated in the oil-bath to 170°—180°, till it just begins to melt, and then immediately removed from the fire. (Laurent & Gerhardt.)—If the melting be too long continued, the product becomes mixed with tartralic acid. If it is not continued long enough, only 0.20 p. c. water is given off; at a few degrees above the melting point, more water escapes. But the evolution of a little water is not essential to the conversion of tartaric into metatartaric acid. When 60 pts. of tartaric acid are melted for an hour in a flask with 2 or 3 pts. of water renewed as it evaporates, so that the flask always contains more than 60 pts., a viscid mass is obtained, which is no longer tartaric, but a mixture of metatartaric and tartralic acids; for its solution in a very small quantity of water, mixed with a little ammonia, solidifies to acid metatartrate of ammonia; its solution neutralised with ammonia, forms, with a concentrated solution of acetate of lime, but only after a few minutes, a precipitate, which consists of metatartrate of lime, and does not exhibit any crystals of tartrate of lime when examined by the microscope; and the liquid filtered from the precipitate, yields, when alcohol is added to it drop by drop, a semi-viscid precipitate of tartrate of lime, easily soluble in water; lastly, the fused mass neutralised with chalk, with addition of water, yields a neutral filtrate, which, when boiled, becomes very acid (in consequence of tartrate of lime remaining in solution), and deposits crystals of metatartrate of lime. (Laurent & Gerhardt.)—Braconnot exposes tartaric acid for a second to a strong heat, till it melts and swells up.—Erdmann melts tartaric acid at 120° [does it melt at that temperature?], till it forms, with intumescence and loss of water, a transparent colourless syrup, which, when placed upon a cold surface, no longer solidifies to a turbid crystalline mass (from admixture of tartaric acid), but to a clear glass. This acid, obtained by Erdmann, appears to have contained tartralic and tartralic acids. (Laurent & Gerhardt.)

Properties. Transparent, vitreous or gummy mass. (Erdmann, Laur. & Gerh.) When softened by heat, it may be drawn out into capillary threads. (Braconnot.) According to Pasteur, its solution exerts upon polarised light the same rotatory action to the right as tartaric acid. Tartaric acid poured immediately after fusion into a quadrangular glass box and solidified, likewise turns the plane of polarisation strongly towards the right, so long as it is hot; at ordinary temperatures, however, it deflects but feebly to the right, and at 0° to the left. (Biot & Laurent, *Compt. rend.* 29, 681.)

Metatartaric acid is isomeric with tartaric acid. (Erdmann, Laurent & Gerhardt.)

Decompositions. The acid, when exposed to a continued gentle heat, is partially reconverted into crystalline tartaric acid. (Laurent & Gerhardt.) When exposed to the air, it deliquesces to a syrup, which changes to crystalline tartaric acid. Its concentrated aqueous solution evaporated over oil of vitriol within a bell-jar containing air, deposits crystals of tartaric acid, the formation of which is accelerated by the presence of a little sulphuric acid. (Erdmann.) Its solution neutralised with potash, deposits, on addition of alcohol, a transparent oil, which gradually crystallises to neutral tartrate of potash. Ammonia acts in a similar manner. (Laurent & Gerhardt.)

Combinations. The acid dissolves readily in water, and is very deliquescent. (Braconnot, Erdmann, Laurent & Gerhardt.)

The *Metatartrates* differ in form from the tartrates, and dissolve more readily in water. (Laurent & Gerhardt.)

Metatartrate of Ammonia — a. Neutral. — On neutralising the acid with ammonia, a salt is produced, which behaves, sometimes like metatartrate, sometimes like tartrate. (Laurent & Gerhardt.)

b. Acid. — Formed by adding to the concentrated solution of the acid, a quantity of ammonia not sufficient to neutralise it, and washing the crystalline precipitate which appears after a few seconds, first with water containing a little alcohol, and then with alcohol. — Shining rhombic and six-sided laminæ, often aggregated in such a manner as to form re-entering angles. From its solution in lukewarm water, the salt may be recrystallised without alteration, but on boiling it changes into acid tartrate of ammonia. It dissolves in water much more readily than the latter, and the solution does not precipitate lime-salts. (Laurent & Gerhardt.)

				Laurent & Gerhardt.
8 C.....	48	28·74 29·0
N.....	14	8·38 8·0
9 H	9	5·39 5·4
12 O.....	96	57·49 57·6
<hr/>				
C ⁶ H ⁶ (NH ⁴)O ¹²	167	100·00 100·0

Metatartrate of Potash. — The neutral salt cannot be prepared. (Laurent & Gerhardt.) It is amorphous and gummy, and becomes moist on exposure to the air. (Braconnot.) — *Acid.* — Metatartaric acid added in excess to solution of potash, throws down a fine, non-granular powder, which is as sparingly soluble as cream of tartar. (Braconnot.) Crystals exhibiting the same appearance and reactions as those of the ammoniacal salt; they contain 20·3 p. c. potash, and are therefore = C⁶H⁶KO¹². (Laurent & Gerhardt.)

Metatartrate of Soda. — *Neutral.* — Uncrystallisable, gummy, deliquescent. (Braconnot.)

Metatartrate of Soda and Potash. — Crystallisable, like Rochelle salt. (Braconnot.)

excess of baryta-water, but not with baryta-salts. The ammonia-salt precipitates baryta-salts, but the precipitate does not appear till after some time, if the solutions are dilute. (Erdmann.) — The salt is obtained by precipitating a baryta-salt with neutral metatartrate of ammonia. Globules aggregated in masses. The salt dried at 160° contains 44.8 p. c. barium and 2 At. water, and is therefore = $C^6H^4Ba^2O^{12} + 2 Aq.$ It dissolves in water much more readily than tartrate of baryta. (Laurent & Gerhardt.) It is easily soluble in excess of the acid. (Erdmann.)

Metatartrate of Lime — The hot aqueous acid saturated with carbonate of lime, gradually becomes turbid as it cools, and deposits a viscid, transparent, tasteless mass, which may be drawn out into threads, dries up to a transparent gum permanent in the air, and when heated with water or dilute acetic acid, again acquires the consistence of turpentine without sensibly dissolving. Its solution in warm metatartaric acid leaves a transparent, brittle, rather acid salt, which, when kept for some time under water, is converted into granular tartrate of lime. (Braconnot.) The aqueous acid gives a precipitate with excess of lime-water, but not with lime-salts. The ammonia-salt precipitates lime-salts, but after a time only if the solutions are dilute. (Erdmann.) — Metatartrate of lime is obtained by precipitating a lime-salt with neutral metatartrate of ammonia in concentrated solutions. In dilute solutions the precipitate takes some time to form; the acid ammonia-salt gives no precipitate. — The precipitate, which is flocculent at first, soon becomes granular, and then appears under the microscope, to consist, partly of granules, partly of prisms, having one end rounded and the other perpendicularly or obliquely truncated. The salt dried at 230° , = $C^8H^4Ca^2O^{12}$; after drying at 160° , it contains 19.35 p. c. calcium, and is therefore = $C^8H^4Ca^2O^{12} + 2Aq.$; and the air-dried crystallised salt contains 15.35 p. c. calcium, gives off 27.10 p. c. water at 240° , and is therefore = $C^8H^4Ca^2O^{12} + 8Aq.$, the same therefore as air-dried tartrate of lime. (Laurent & Gerhardt.) — The once-crystallised salt dissolves in a large quantity of cold water, and but slowly in boiling water, being thereby converted into tartrate. The cold aqueous solution forms, with ammonia, a large quantity of flakes (soluble in excess), which become crystalline. Cold water to which a small quantity of hydrochloric or nitric acid is added, dissolves the salt abundantly, and when neutralised with ammonia, deposits it after a while unaltered. But the hydrochloric acid solution of the salt dried at 220° , yields by precipitation with ammonia, rectangular octohedrons of tartrate of lime. (Laurent & Gerhardt.) When metatartaric acid, somewhat supersaturated with ammonia is mixed with chloride of calcium and then with a quantity of water sufficient to redissolve the precipitate, the whole of the salt crystallises out, after a few hours, as tartrate of lime. (Erdmann.)

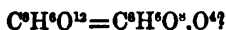
Metatartrate of Magnesia. — The solution of magnesia in the acid, leaves a varnish when evaporated. (Braconnot.)

Metatartrate of Lead. — Even the free acid forms with nitrate or acetate of lead, a white precipitate containing 60.13 to 60.48 p. c. lead-oxide. The precipitate obtained on adding the acid not quite neutralised with ammonia to nitrate of lead, is insoluble in cold, and very sparingly soluble in boiling water, from which it is deposited in flakes on cooling. It

dissolves easily in metatartaric and other acids, also in ammonia. (Erdmann.)

With sulphate of copper, metatartrate of ammonia forms no precipitate at first, but the mixture, after a while, deposits tartrate of copper. (Erdmann.)

Isotartaric Acid.



EDM. FREMY. (1838.) *Ann. Chim. Phys.* 68, 353; also *Ann. Pharm.* 29, 142; also *J. pr. Chem.* 16, 322. Further: *N. Ann. Chem., Phys.* 31, 329; *Ann. Pharm.* 78, 297; abstr. *Pharm. Centr.* 1851, 937; *Jahresber.* 1851, 407.

LAURENT & GERHARDT. *Compt. chim.* 1849, 6 & 105; also *Ann. Pharm.* 70, 354; also *J. pr. Chem.* 46, 365. — GERHARDT. *Compt. chim.* 1851, 182.

Tartrilsäure (Liebig); formerly called *Tartralic Acid* by Fremy; *Acide isotartrique*. (Laurent & Gerhardt.)

Formation. By melting tartaric acid at a temperature above the point at which it is converted into metatartaric acid. — The tartaric acid then gives off water. (Fremy.) This loss is not essential, and isotartaric acid is formed, together with metatartaric acid, even when 60 pts. of tartaric acid are fused with 2 or 3 pts. of water, and the water continually renewed, so that the mass constantly weighs more than 60 pts. (p. 327). When the tartaric acid was fused without water, till the loss of water amounted to 3.04 p. c., there remained a mixture of isotartaric and metatartaric acids, and when the fusion was continued till the loss amounted to 7.2 per cent. there remained a mixture of isotartaric (or tartralic,) and tartrellic acids, perfectly soluble in water, and, therefore, free from anhydrous tartaric acid. (Laurent & Gerhardt.) — ¶ According to Biot, (*N. Ann. Chim. Phys.* 28, 215, 351,) tartaric acid, in all the phases through which it passes before arriving at its final anhydrous state, exerts, when the solid mass is dissolved in cold water, *instantly* the same amount of rotatory action on polarised light as the crystallised acid in its unaltered state. The absolute rotatory power, as well as the law of dispersion, (p. 271,) appear to be the same for the modified as for the crystallised acid. Biot regards these facts as confirmatory of Laurent and Gerhardt's view, that tartaric acid, when heated, does not undergo any *chemical* change, till it passes to the condition of the anhydrous acid. ¶. — 2. A mixture of tartaric acid and sugar deliquesces in the air to a no longer crystallisable syrup, in which the greater part of the tartaric acid is converted into tartralic [isotartaric?] acid. For after saturating the filtrate with carbonate of lime, and filtering again to separate tartrate of lime, alcohol added to the filtrate throws down tartrate [isotartrate] of lime, the aqueous solution of which deposits tartrate of lime on boiling. (A. Vogel, *Jun. Report.* 92, 325.)

Preparation. 1. A few grammes of tartaric acid are heated for some time in a porcelain basin to 200°, stirring all the time, during which treatment the acid should not turn yellow, and should give off water, but no acid vapours. The residual mass (which however is only a mixture,) contains

tartrelic acid, is dissolved in water, and neutralized with carbonate of lime, the filtrate decomposed by sulphuric acid, and the filtered solution of the acid evaporated. (Fremy.) — ¶. In the *Traité de Chimie générale* of Pelouze & Fremy, 2me Ed. 1855, tom. 2, pp. 225, 226, it is stated that tartaric acid heated to 200°, yields, not tartralic or isotartaric acid, but tartrelic acid; that isotartaric acid, the acid whose salts have the formula $C^8H^8MO^{12}$ or $MO, C^8H^8O^{11}$ is obtained, as well as metatartaric acid, by heating tartaric acid to 170°; and that tartralic acid, $1\frac{1}{2}HO, C^8H^8O^{10}$ is formed by heating tartaric acid to 190°. ¶. — When tartaric acid is heated for some time to its boiling point, but not high enough to make it froth, there remains a mixture of metatartaric, isotartaric, and tartrelic acids, which, when dissolved in water, and saturated with chalk, yields tartretale of lime in the form of a precipitate of pitchy consistence, and a filtrate which does not redden litmus; but from this filtrate, alcohol throws down isotartrate of lime mixed with metatartrate, by the analysis of which mixture, Fremy obtained an incorrect analysis of tartrale [isotartrate] of lime. The metatartaric acid in this lime-salt may be recognized by the character that, when dissolved in water after drying, it leaves crystalline metatartrate of lime: for when the acid separated therefrom is mixed with a small quantity of ammonia, it forms, after a few hours, crystals of acid metatartrate of ammonia. (Laurent & Gerhardt.)

2. To obtain the lime-salt in a state of perfect purity, tartaric acid is heated till it froths; dissolved in cold water; neutralized or slightly supersaturated with ammonia; mixed with concentrated acetate of lime; and alcohol dropt into the clear mixture, while the liquid is stirred with a glass rod: the viscid precipitate then collects together, and settles down to the bottom in the form of a nearly colourless oil. — If the alcohol be too rapidly added, the salt is precipitated in flakes, which do not unite, and must therefore be washed on a filter, during which process they suffer partial decomposition; it is also necessary not to precipitate the whole of the salt by the alcohol. — The oil, after the watery liquid has been decanted, is well kneaded with fresh alcohol, and boiled for a few seconds, whereupon it suddenly hardens as if it had become crystalline, although no crystalline structure can be perceived in it by the microscope, then comminuted with the rod, rinsed three times with alcohol, and dried between paper. (Laurent & Gerhardt.)

Properties. Not crystallisable; tastes somewhat less sour than tartaric acid. (Fremy.)

The acid is highly deliquescent. (Fremy.)

The *Isotartrates* [the tartrates of Fremy's earlier investigations,] have in the neutral state the formula $C^8H^8MO^{12}$. (Laurent & Gerhardt.) Perhaps therefore = $C^8H^8MO^8, O^4$. — In the dry state, they are unalterable, but in the state of aqueous solution, they pass, with especial rapidity when heated, into the state of acid tartrates (Fremy), metatartrates. (Laurent & Gerhardt.)

Isotartrate of Ammonia. — When tartrelic acid is added at ordinary temperatures to alcoholic ammonia, which must remain somewhat in excess, isotartrate of ammonia is precipitated in the form of an oil, which may be washed with alcohol. This oil is deliquescent. When

heated, it gradually solidifies without evolution of ammonia, from formation of acid metatartrate of ammonia, with which it is metameric. Fremy. (Laurent & Gerhardt.)

Isotartrate of Potash. — Obtained in a similar manner. Not crystallizable; deliquescent; contains 20.3 p. c. potassium, and is therefore = C⁶H⁴KO¹². Partially converted, by gentle heat, into acid metatartrate of potash. (Laurent & Gerhardt.)

Isotartrate of Baryta. — Aqueous isotartaric acid is saturated with carbonate of baryta, and the salt precipitated from the filtrate by alcohol. It dissolves sparingly in water, and contains 43.5 p. c. baryta. (Fremy.) According to what is above stated, this salt likewise contains metatartrate of baryta. (Laurent & Gerhardt.)

Isotartrate of Lime. — (For the preparation *vid. supra.*) The salt dissolves very readily in cold water, even that which has been dried at 150°, and contains but a trace of metatartrate of lime; the neutral solution turns sour when boiled, neutral metatartrate of lime separating out, and free metatartronic acid remaining in solution :



Alcohol precipitates the salt from its aqueous solution in thick flakes, which, when collected on a filter, dry slowly in the air, and yield an acid viscid mass by partial conversion into metatartrate and free acid. (Laurent & Gerhardt.) — The salt which was obtained by Fremy, and, according to Laurent & Gerhardt, was contaminated with metatartrate, dissolves sparingly in water, and is precipitated therefrom by alcohol. The aqueous solution is neutral, turns acid in a few hours at ordinary temperatures, and quickly on boiling, depositing granular crystals of tartrate of lime. (Fremy.)

			Laur. & Gerh. at 160°.		Fremy.
8 C	48	28.40		
5 H.....	5	2.96		
Ca	20	11.84	11.2
12 O	96	56.80		16.36
<hr/>					
C ⁶ H ⁴ CaO ¹²	169	100.00		

[Fremy deduced from his analysis, the formula C⁶H⁴O¹⁰, 1½ Ca.O (*vid. inf.*)

Isotartrate of Lead. — Obtained by precipitating nitrate of lead with the free acid, washing the precipitate quickly on a filter with cold water, and drying it quickly between paper, afterwards in vacuo. (Fremy.) — If the precipitation be performed with the potash or ammonia salts, the precipitate always retains a certain portion of the alkali-salt. (Fremy.) — The moist precipitate is completely converted into tartrate of lead, even by 24 hours' contact with water. (Fremy.) — The pure lime-salt forms with neutral acetate of lead a white precipitate insoluble in water. (Laurent & Gerhardt.)

			Fremy.	
PbO	54.55		to	52.61
C.....	16.74		..	17.40
H	1.14		..	1.43
O	27.27		..	28.56
<hr/>				
	100.00		100.00

acetate or sulphate of copper, yields, on addition of alcohol, a pale green, somewhat crystalline precipitate, which becomes glutinous when spread out on blotting paper, and, after drying at 150°, contains 17.9 p. c. copper, therefore = $C^6H^4CuO^{12}$. (Laurent & Gerhardt.)

Isotartrate of Silver.—The lime-salt forms with nitrate of silver a white precipitate soluble in a large quantity of water. (Laurent & Gerhardt.)

The acid dissolves in *Alcohol*. (Fremy.)

¶. **TARTRALIC ACID.**— $C^8H^4O^{10}, 1\frac{1}{2}HO$ or $2C^8H^4O^{10}, 8HO$.—Obtained, according to Fremy's latest statement (*Traité de Chimie générale, par J. Pelouze et E. Fremy, Par. 1855, iv. 226*), by heating tartaric acid to 190°.

Fremy had formerly stated (*Ann. Pharm. 78, 304*) that this acid is formed at 170°; but he now agrees with Laurent & Gerhardt in asserting that the product formed at that temperature is the monobasic acid, isotartaric acid.

The acid is deliquescent and uncrystallisable.

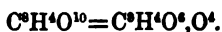
		Fremy.	
8 C	48.0	33.0	33.3
5½ H	5.5	3.7	3.4
11½ O	92.0	63.3	63.3
$C^8H^4O^{10}, 1\frac{1}{2}HO$	145.5	100.0	100.0

The general formula of the *tartrates* is $C^8H^4O^{10}, 1\frac{1}{2}MO$ or $2C^8H^4O^{10}, 3MO$. When treated with excess of base, they are converted into tartrates. By boiling with water, they are resolved into tartrates and free tartaric acid. The tartrates of baryta, strontia, and lime are soluble in water.

Tartrate of Lime,—obtained by boiling tartaric acid, either till it is only partially converted into tartralic acid, or till the formation of tartralic acid has commenced, dissolving the product in cold water, saturating with carbonate of lime, precipitating the filtrate with alcohol, and drying the precipitate, first in *vacuo*, and afterwards at 200°,—yields by analysis 23.7 p. c. lime, the formula $C^8H^4O^{10}, 1\frac{1}{2}CaO$ requiring 24.1 p. c. (Fremy, *Ann. Pharm. 78, 314*.)

Tartrate of Lead,—prepared by dissolving the lime-salt in cold water, decomposing with oxalic acid, precipitating the tartralic acid with neutral acetate of lead, and washing the precipitate with cold water,—or by treating tartrate of ammonia with excess of ammonia to convert it into tartrate, and precipitating with neutral acetate of lead,—yielded by analysis 55.2 and 55.9 p. c. PbO , while the formula $C^8H^4O^{10}, 1\frac{1}{2}PbO$ requires 56.0 p. c. (Fremy.) ¶.

Tartrelic Acid.



E. FREMY. (1838.) *Ann. Chim. Phys.* 68, 367; also *Ann. Pharm.* 29, 152; also *J. pr. Chem.* 16, 331.—Further: *N. Ann. Chim. Phys.* 31, 329; *Ann. Pharm.* 78, 315.

LAURENT & GERHARDT. *Compt. Chim.* 1849, 9, & 101; also *Ann. Pharm.* 70, 356; also *J. pr. Chem.* 46, 368.

Tartrelsäure, Isotartrinsäure, Acide tartrelique, Acide isolartridique, Acide tartarique anhydre soluble.

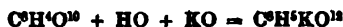
Formation. By keeping tartaric, or tartralic, or isotartaric acid in a state of continued fusion at 180°, [or 200° according to the latest statements (p. 331).]—After the tartaric acid has lost by fusion $\frac{1}{2}$ At. water, it is converted into tartralic acid = C⁶H¹¹O², and when by continued fusion it has lost $\frac{1}{2}$ At. more of water, it becomes tartrelic acid = C⁶H⁹O¹¹. (Fremy.)—Tartaric acid must give off 2 At. water in the formation of tartrelic acid; for the latter is isomeric with tartaric anhydride (C⁶H⁴O¹⁰), and when heated for a longer time to 180°, passes, without further loss of water, into that substance. (Laurent & Gerhardt.)

Preparation. By heating tartaric acid to 180° [200°] till all the tartaric acid is converted into tartrelic, but not long enough or strong enough to produce tartaric anhydride. (Fremy.)—By heating tartaric acid over the open fire quickly and with agitation, till, in about six minutes, it thickens and swells up into a spongy mass. (Laurent & Gerhardt.)

Properties. Slightly coloured, easily crystallisable, strongly acid, (Fremy.)—[Deliquescent, and uncrystallisable. (Fremy, *Traité de Chimie, P. and F.* 1855, iv, 226.)]

Calculation according to Laurent & G.			Calculation according to Fremy.			Fremy.
8 C 48 36·36	8 C 48 34·04 34·56
4 H 4 3·03	5 H 5 3·55 3·72
10 O 80 60·61	11 O 88 62·41 61·72
C ⁶ H ⁴ O ¹⁰ 132 100·00	C ⁶ H ⁹ O ¹¹ 141 100·00 100·00

Decomposition.—The acid dissolved in water is converted, slowly at ordinary temperatures, quickly on boiling, first into tartralic [or isotartaric], then into tartaric acid. (Fremy.) When made to unite with potash, it immediately forms isotartrate of potash. (Laurent & Gerhardt.)



Combinations. With *Water.* The acid is deliquescent, but much less so than tartralic acid. (Fremy.)

The *Tartrelates* or *Isotartrides* contain at most but 1 At. base = C⁶H³MO¹⁰. To obtain them, it is best to decompose an acetate with the free acid, because, when that acid is brought in contact with a free alkali, an isotartrate is produced.—In contact with water, the tartrelates are converted, first into tartralates, and then, with elimination of acid, into tartrates. (Fremy.)—Tartrelic acid is distinguished from tartralic acid by the syrupy precipitates which it forms with the acetates of baryta, strontia, and lime, whereas tartralic acid does not precipitate those salts. (Fremy.)

The tartrelates of *Ammonia*, *Potash*, and *Soda* are precipitated from their aqueous solutions by alcohol. Dry ammoniacal gas passed into a

tartrelate of ammonia. (Fremy.) The potash-salt = $C^6H^3KO^{10}$. (Laurent & Gerhardt.)

Tartrelate of Baryta. — The aqueous acid added to acetate of baryta throws down this salt in the form of a syrup. (Fremy.) It does not precipitate nitrate of baryta. The syrup is insoluble in water. (Laurent & Gerhardt.)

				Laur. & G. at 150°.	Fremy.
8 C	48.0	...	24.05		
3 H	3.0	...	1.50		
Ba.....	68.6	...	34.37	33.6
10 O	80.0	...	40.08		33.57
<hr/>					
$C^8H^2BaO^{10}$	199.6	...	100.00		

Tartrelate of Strontia. — Prepared in a similar manner. Contains 24.7 per cent. of strontium, and is therefore = $C^6H^3SrO^{10}$. (Laurent & Gerhardt.)

Tartrelate of Lime. — The aqueous acid added to acetate of lime, throws down this salt in the form of a syrup. (Fremy.) As an excess of tartrelic acid exerts a decomposing action on the salt, the concentrated aqueous acid must be added to the concentrated solution of acetate or hydrochlorate of lime, with constant stirring, and only in such quantity that a part of the latter may remain undecomposed; and the precipitated syrup, after the watery liquid has been poured off, must be quickly washed with alcohol, whereby it is hardened. The salt is so sparingly soluble in water, that acetate of lime diluted to such an extent that it is no longer clouded by neutral tartrate of ammonia, still shows turbidity when mixed with tartrelic acid. (Laurent & Gerhardt.)

	Calculation, according to Laurent & Gerhardt.			Laur. & Gerh. at 160°.
8 C.....	48	...	31.79	
3 H	3	...	1.98	
Ca	20	...	13.25
10 O	80	...	52.98	12.95
<hr/>				
$C^8H^3CaO^{10}$	151	...	100.00	

	Calculation according to Fremy.			Fremy. at 120°.		at 140°.
8 C	48	...	30.0	30.3
4 H	4	...	2.5	2.3
Ca	20	...	12.5	12.1
11 O	88	...	55.0	55.3
<hr/>						
$C^8H^4CaO^{10}$	160	...	100.0	100.0

	Dried in vacuo.			Fremy.
8 C.....	48	...	28.4
5 H.....	5	...	2.9
Ca	20	...	11.8
12 O.....	96	...	56.9
<hr/>				
$C^8H^4CaO^{10} + Aq.$	169	...	100.0

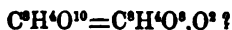
Tartrelate of Lead. — a. When the dry acid is heated with excess of oxide of lead, a quantity of water is given off, about sufficient to produce $C^8H^2Pb^3O^{10}$. For, 100 pts. of tartaric acid heated to intumescence, then triturated with 100 pts. lead-oxide and a small quantity of alcohol, and deiccated in a stream of dry air at 150° , give off 16.7 p. c. water. This tumefied acid, when heated alone, gives off an additional 1 to 2 per cent. of water; consequently, the water produced from the lead-oxide amounts to only 15.7 to 14.7 per cent. If $C^8H^2Pb^3O^{10}$ be hereby produced, then, according to calculation, 100 pts. of tartrelic acid should give off 13.65 pts. of water. 132 (tartrelic acid); 18 (2 At. Aq) = 100 : 13.65. (Laurent & Gerhardt.)

b. The aqueous acid is poured into an aqueous solution of neutral acetate of lead, which should remain in excess, and the white precipitate quickly washed with alcohol, because otherwise metatartrate or tartrate of lead, will be formed, in which the quantity of lead is larger. (Laurent & Gerhardt.)

			Laur. & G. at 150° .	Fremy.
8 C	49	20.43	19.48
3 H	3	1.28	1.82
Pb	101	44.25	43.56
10 O	80	34.04	35.14
$C^8H^2Pb^3O^{10}$	235	100.00	100.00

Tartrelic acid is soluble in *alcohol*. (Fremy.)

Anhydrous Tartaric Acid.



E. FREMY. (1838.) *Ann. Chim. Phys.* 68, 372; also *Ann. Pharm.* 29, 156; also *J. pr. Chem.* 16, 335.

Tartaric Anhydride, wasserfreie Weinsäure, Acide tartarique anhydre insoluble.

Formation. By heating tartaric acid to 180° , [200° ?] till it becomes infusible. (Fremy.) — When tartaric acid is heated over the open fire and quickly stirred till (in about six minutes) it begins to swell up, and the mass then pulverised and again heated for some minutes to 140° — 170° , it is found to be still perfectly soluble in water, and is therefore still tartrelic acid; but after being heated for 10 minutes to 180° , till acid vapours begin to escape, the powder is found to have diminished in weight by 0.32 p. c., and to be aggregated in lumps, tasteless, and perfectly insoluble in water. The trifling loss, arising chiefly from the evolution of acid vapours, shows that tartrelic acid and the anhydride have the same composition per cent., and that heat converts the former into the latter, not by elimination of water, but by transposition of atoms. (Laurent & Gerhardt, *Compt. Chim.* 1849, 101.) [At first, $C^8H^4O^8, O^2$; afterwards $C^8H^4O^8, O^2$; so that 20 pass into the nucleus, and the monobasic acid is transformed into an aldehyde?].

Preparation. 15 or 20 grammes of pulverised tartaric acid is heated in a basin over an open charcoal fire, so that in the course of 4 or 5

heated for a few seconds in the oil-bath to 150°. By rapid heating, the anhydride is obtained more nearly colourless, and the subsequent heating in the oil-bath causes it no longer to swell up when immersed in water, but remain pulverulent. The pulverised residue is washed with water till the wash-liquid no longer reddens litmus, in order to free it from admixed tartrelic acid, then well pressed between paper, and dried in vacuo at ordinary temperatures. If it were dried by heat, the water which still adheres to it would reproduce tartaric acid. (Fremy.) — Crystallised tartaric acid may be completely transformed into the anhydride by heating it for several hours in a stove to 190°. (*Traité de Chimie par Pelouze et Fremy, 1855, iv, 227.*)

Properties. White powder, or yellowish if it has been heated too long; of very slightly acid taste. (Fremy.)

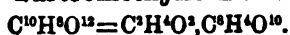
					<i>Fremy.</i>
8 C.....	48	36.36	37.08
4 H	4	3.03	3.23
10 O.....	80	60.61	59.69
C ⁸ H ⁴ O ¹⁰	132	100.00	100.00

Decompositions. The anhydride is converted, in a few hours when immersed in cold water, and quickly in boiling water, into tartrelic, tartalic, and tartaric acid successively; it dissolves quickly in aqueous potash, but is not precipitated therefrom by acids, because it exists in the solution as one of the three acids just mentioned. (Fremy.)

Combinations. The anhydride is at first insoluble in cold water. (Fremy.)

It absorbs *Ammoniacal gas*, with evolution of heat. (Fremy.) When ammoniacal gas is passed over the anhydride moistened with alcohol, a thin syrup forms below the alcohol, and may be washed with alcohol, dissolved in water, and precipitated therefrom by alcohol. The aqueous solution does not precipitate chloride of calcium; but on addition of alcohol and application of heat, a glutinous precipitate is formed, which, when quickly washed with cold water, dissolved in warm water, and reprecipitated by alcohol, contains 16.91 p. c. lime, and 1.9 nitrogen, numbers from which it is not possible to calculate a formula. If the aqueous solution of the syrup be precipitated by bichloride of platinum, the liquid filtered from the chloroplatinate of ammonium gradually deposits, when boiled, a new precipitate of the chloroplatinate. (Laurent, *N. Ann. Chim. Phys.* 23, 116; also *Compt. rend.* 20, 513.)

The anhydride is insoluble in alcohol and in ether; but after being washed with alcohol, it retains a small quantity of that body in combination, which cannot be expelled by heat without decomposition. (Fremy.)

*Conjugated Compounds of Tartaric Acid.***Tartromethylic Acid.**

DUMAS & PELIGOT. (1835.) *Ann. Chim. Phys.* 61, 200.

GUÉRIN-VARRY. *Ann. Chim. Phys.* 62, 77; also *Ann. Pharm.* 22, 248; also *J. pr. Chem.* 9, 376.

DUMAS & PIRIA. *N. Ann. Chim. Phys.* 5, 373; also *Ann. Pharm.* 44, 83.

Methyltartersäure, Methyleweinsäure, Weinmethyleensäure, Acide tartrométhyl-lique.

Formation. Tartaric acid dissolves more readily in wood-spirit than in alcohol, and converts it with greater facility into the conjugated acid. (Guérin.)

Preparation. 1 pt. of tartaric acid is dissolved in 1 pt. of absolute or hydrated wood-spirit at a boiling heat, the solution evaporated to a syrup at a temperature below 100°, the syrup left to evaporate freely, and the resulting crystals dried in vacuo. (Guérin.)

Properties. Colourless right prisms, heavier than water, fusible, inodorous, of acid, not sweet taste. (Guérin.)

	<i>Crystals.</i>		Guérin.	Dumas & Piria.
10 C	60	36.58	36.94	36.6
8 H	8	4.88	4.88	5.2
12 O	96	58.54	58.18	58.2
$\text{C}^{10}\text{H}^8\text{O}^{12}$	164	100.00	100.00	100.0

Decompositions. 1. The acid melts when subjected to dry distillation giving off water, wood-spirit, acetate of methyl, and a heavy liquid which, however, does not contain oxalate of methyl. — 2. It burns with a flame like that of wood-spirit. — 3. When boiled for some time with water, it is resolved into wood-spirit, which evaporates, and a residue of tartaric acid — not so quickly, however, as tartrovinic acid, — and crystallizes from its aqueous solution by spontaneous evaporation in its original state. (Guérin.)

Combinations. The acid scarcely becomes moist when exposed to the air, but dissolves very readily in cold water, and in all proportions in boiling water. (Guérin.) The *Tartromethylates* or *Methylotartrates* = $\text{C}^{10}\text{H}^7\text{MO}^{12} = \text{C}^8\text{H}^3\text{MO}^2, \text{C}^8\text{H}^4\text{O}^{10}$.

Tartromethylate of Potash. — Neutral. — Obtained by precipitating the baryta-salt with a slight excess of sulphate of potash, evaporating the filtrate to a syrup, dissolving in alcohol, and leaving the filtrate to evaporate. Colourless, tasteless, right rectangular prisms, which give off 4.2 p. c. water in vacuo over oil of vitriol. At 150°, they soften and turn yellowish, and at 200° give off water, carbonic acid gas, olefiant gas, and a fluid mixture of water, wood-spirit, acetic acid, acetic ether, and a syrupy substance. They dissolve much more readily in hot than in

cold water, are insoluble in absolute alcohol, and in 95 per cent. spirit. (Guérin.)

		<i>Crystals.</i>		Guérin.		Dumas & Piria.	
KO	47.2	23.35	22.23	
10 C	60.0	29.67	28.79 30.35
7 H	7.0	3.46	3.76 3.90
11 O	88.0	43.82	45.22	
$C^{10}H^7KO^{12}$		202.2	100.00	100.00	

Guérin supposes the crystals to contain 1 Aq. more.

Acid ? — An excess of the acid forms with potash a milky liquid, which becomes clear on the addition of a large quantity of water. (Guérin.)

Tartromethylate of Soda. — An excess of the acid forms with soda (not with sulphate of soda), an abundant granular precipitate, which dissolves in a large quantity of water. (Guérin.)

Tartromethylate of Baryta. — The acid forms with baryta-water, a precipitate which dissolves on addition of a slight excess of acid. To obtain the neutral salt, the above-mentioned heated solution of tartaric acid in wood spirit, is saturated with carbonate of baryta, and the filtrate left to crystallise by spontaneous evaporation. Colourless, shining right prisms, bevelled with two faces, and having a bitter taste. Between 150° and 160°, they yield a syrupy distillate, having an odour of garlic, and containing water, wood-spirit, acetate of methyl, and a substance which crystallises on evaporation, and is soluble in water. They decompose by boiling with water, more readily than the potash-salt. They are more soluble in hot than in cold water, insoluble in absolute alcohol, and in 95 p. c. spirit. (Guérin.) Dumas & Peligot, by mixing a solution of tartaric acid in wood-spirit, with a solution of baryta in wood-spirit, obtained the salt in the form of a gelatinous precipitate, which was washed with absolute wood-spirit, since when, washed with water, it was converted into granular tartrate of baryta.

				Dumas & Peligot.	
BaO	76.6	31.83 30.8
10 C	60.0	24.94 23.9
8 H	8.0	3.33 3.0
12 O	96.0	39.90 42.3
$C^{10}H^7BaO^{12} + Aq$		240.6	100.00 100.0

The acid forms with *Strontia-water* or *Lime-water*, a precipitate which dissolves in a slight excess of the acid; the lime-salt also in a large quantity of water. (Guérin.)

It dissolves *Zinc* and *Iron*, with evolution of hydrogen. (Guérin.)

Tartromethylate of Lead. — The acid forms, with an aqueous solution of neutral acetate of lead, a flocculent precipitate, which, in presence of excess of the acid, changes to a powder consisting of flat prisms. (Guérin.)

Tartromethylate of Silver. — From a concentrated silver-solution the acid throws down flakes, which are insoluble in excess of the acid, but sparingly soluble in water. (Guérin.)

Tartromethylic acid dissolves readily in *Wood-spirit* and *Alcohol*, but sparingly in *Ether*. (Guérin.)

Tartrovinic Acid.



TROMMSDORFF. *A. Tr.* 24, 1, 11.

GUÉRIN VARRY. *Ann. Chim. Phys.* 62, 57; also *Ann. Pharm.* 22, 237;
also *J. pr. Chem.* 9, 361.

Weintartrersäure, Aetherweinsäure, Acide tartarovinique. First observed by Morian (*A. Tr.* 23, 2, 43,) in 1814, afterwards recognised as to its composition by Trommsdorff, and more accurately investigated by Guérin.

Formation. 1. By mixing tartaric acid, crystallised or dissolved in a small quantity of water, with strong alcohol. The saturated solution of tartaric acid in absolute alcohol forms tartrovinic acid, when set aside for 23 days even at ordinary temperatures, but much more if continuously heated. Spirit of 90 per cent. likewise produces this acid. (Trommsdorff.)

Preparation. 1. Pulverised tartaric acid is dissolved in an equal weight of boiling absolute alcohol; the solution kept for six hours at 60° to 70°; the resulting yellowish syrup diluted with water and saturated with carbonate of baryta; the solution filtered from the small quantity of tartrate of baryta formed at the same time, concentrated at 40° to 50°, again filtered to separate the fresh quantity of tartrate of baryta thereby formed, and left to evaporate; the resulting crystals of tartrovinic acid dissolved in water and decomposed by the exact quantity of sulphuric acid required; and the filtrate evaporated in vacuo over oil of vitriol till it crystallises. (Guérin.) When baryta-water is used instead of the carbonate, a larger quantity of tartrate of baryta is precipitated. (Guérin.) — 2. A solution of tartaric acid in an equal weight of boiling absolute alcohol, is left to evaporate to $\frac{1}{3}$ in a retort between 60° and 70°; and the syrup, which no longer contains any free tartaric acid, diluted with a small quantity of water, and left to evaporate till it crystallises. (Guérin.)

Properties. Long, colourless, oblique rhombic prisms, heavier than water; they soften at 30°, and at 90° melt to a syrup, which up to 140°, when decomposition begins, becomes continually thinner. Inodorous; and has a sweet and agreeably sour taste. (Guérin.) Morian and Trommsdorff, by evaporating tartaric acid mixed with excess of alcohol, obtained a residue which coagulated to a soft curdy mass, or by further evaporation, a residue of the consistence of turpentine.

<i>Crystals.</i>		Guérin.	
12 C	72	40.45	40.90
10 H	10	5.62	5.71
12 O	96	53.93	53.39
$\text{C}^{13}\text{H}^{10}\text{O}^{13}$	178	100.00	100.00

Decompositions. 1. The acid heated in a retort begins to give off fumes, and appears to boil at 165°; it then emits carbonic acid, carburetted hydrogen, water, alcohol, acetic acid, and acetic ether; the residue left after heating to 180° contains an acid resembling meta-

over, together with a liquid resembling acetone; and there remains charcoal, together with pyrotartaric acid and an oil. (Guérin.)—2. The acid set on fire in the air, burns with a flame like that of alcohol, and the odour of burnt tartaric acid. (Guérin.)—3. Distilled three times with water (Trommsdorff), or boiled for ten hours with 40 pts. of water (Guérin), it gives off all its alcohol and leaves ordinary tartaric acid.—When diluted with water and exposed to the air, it becomes somewhat mouldy, but deposits crystals of tartrovinic acid. (Guérin.) The acid diluted with a small quantity of water, and exposed to the air in a flat dish, deposits ordinary tartaric acid. (Morian.)—4. Gently heated with nitric acid, it emits red vapours, together with carbonic and acetic acid, and leaves oxalic acid. (Guérin.)—5. It dissolves without effervescence in oil of vitriol, and afterwards gives off on evaporation, carbonic acid, sulphurous acid, sulphuretted hydrogen, acetic acid, and traces of oil of wine. (Guérin.)

Combinations. The acid is highly deliquescent and dissolves very readily in *Water*. (Guérin.)

The *Tartrovinates* in the dry state = $C^{12}H^9MO^{12} = C^4H^3MO^4, C^3H^4O^{10}$. They generally crystallise well, are inodorous, and unctuous to the touch. When set on fire, they burn with an alcoholic flame, and yield by dry distillation, carbonic acid, olefiant gas, water, alcohol, acetic acid, acetic ether, and a small quantity of empyreumatic oil, leaving charcoal, and, in the case of the alkali-salts, if the heat has not been too strong, a pyrotartrate. Heated with alkalis to $160^\circ - 170^\circ$, they give off alcohol, acetic ether [?], and a very bitter oil; when boiled for a long time with water, they are converted into acid tartrates, the alcohol evaporating. They almost all dissolve readily in water, sparingly in strong, more readily in weak alcohol. (Guérin.)

Tartrovinate of Ammonia.—The acid exactly neutralised with carbonate of ammonia yields by spontaneous evaporation, silky needles, which appear to be rhombic prisms. (Guérin.)

Tartrovinate of Potash.—*a. Basic*—Eight-sided prisms acuminate with several faces, and having an alkaline reaction.

b. Neutral.—Obtained by precipitating the baryta-salt with sulphate of potash, evaporating the filtrate to a syrup, dissolving the syrup in alcohol, filtering from the sulphate of potash, and leaving the liquid to evaporate. Colourless prisms belonging to the right prismatic system. *Fig. 66*, without the *t*-face and the two small faces above *t*; $y : u = 101^\circ 5'$; $y : m = 112^\circ 39'$; $y : y = 134^\circ 41'$; $u : u' = 59^\circ 52'$; $u : m = 119^\circ 56'$; cleave easily parallel to *m*; in very small crystals, every alternate pair of the *y*- and *u*-faces disappears. (Prevostaye, *N. Ann. Chim. Phys.* 3, 139; *comp.* Bernhardt, *N. Tr.* 7, 2, 60.)—The crystals soften at 200° , and melt at 205° ; their taste is very slightly bitter. They give off 4 p. c. water in vacuo, and leave when burnt, 38.45 p. c. carbonate of potash. Their aqueous solution moderately heated in the air gives off alcohol, and deposits cream of tartar, the quantity of which increases by continued boiling. They are insoluble in wood-spirit and in cold alcohol of 95 p. c. but dissolve very sparingly in boiling absolute alcohol. (Guérin.)

	Crystallized.		Guérin.		Dumas & Piria.
KO	47.2	20.96	20.78		
12 C	72.0	31.97	32.20		33.9
10 H	10.0	4.44	4.44		4.5
12 O	96.0	42.63	42.58		
<hr/>					
C ² H ⁴ KO ¹² + Aq	225.2	100.00	100.00		

Dumas & Piria (*N. Ann. Chim. Phys.* 5, 375), in accordance with their analysis, suppose the crystals to contain no water; but they probably do contain it.

Tartrovinat of Soda.—Prepared like the potash-salt. Colourless, rhombic, rectangular laminae. (Guérin.)

Tartrovinat of Baryta.—The acid dropt into baryta-water, forms a precipitate of *basic* salt easily soluble in nitric acid, which, as soon as the mixture becomes neutral, disappears with the exception of a slight turbidity; but with a larger quantity of acid, a fresh precipitate is formed, less soluble in nitric acid. *Preparation* (p. 340). Colourless, slightly bitter, oblique rhombic prisms and nacreous tables. (Guérin.) Rhombic prisms of 126° to 127°, bevelled with two faces resting on two lateral faces at angles of 105° to 106°. (Prevostaye.) The crystals give off 7.15 p. c. water in vacuo; they soften at 190° and melt at 200°, giving off an odour of alcohol and ether. They dissolve in 2.63 pts. of water at 23°, in 0.78 pt. of boiling water, are insoluble in wood-spirit and absolute alcohol, but dissolve sparingly in spirit of 95 per cent. (Guérin.)

	Crystals.		Guérin.	
BaO	76.6	29.06	28.78	
12 C	72.0	27.32	27.56	
11 H	11.0	4.17	4.22	
13 O	104.0	39.45	39.44	
<hr/>				
C ¹² H ¹¹ BaO ¹³ + 2Aq.....	263.6	100.00	100.00	

Guérin supposes the crystals to contain 1 Aq. less.

Strontia-water is not precipitated by the acid in any proportion (Guérin.)

Tartrovinat of Lime.—The acid added to an excess of lime-water throws down a *basic* salt.—The *neutral* salt is obtained in the same manner as the corresponding baryta-salt. Colourless rectangular prisms and laminae. The crystals contain 5 At. water, undergo the aqueous fusion at 100°, the igneous at 210°, and decompose at 215°. (Guérin.)—Trommsdorff, by evaporating the aqueous solution of the lime-salt, obtained a turpentine-like mass, which, when digested with dilute sulphuric acid, gave off a spirituous odour, and yielded a filtrate whence ordinary tartaric acid was deposited in crystals.

Tartrovinat of Zinc.—Zinc dissolves in the aqueous acid with evolution of hydrogen, and the solution yields colourless rectangular prisms, unctuous to the touch. (Guérin.)

Tartrovinat of Lead.—The acid forms with aqueous neutral acetate of lead, small colourless prisms, which have a pearly lustre when dry, are insoluble in aqueous tartrovinic acid, but dissolve in nitric acid. (Guérin.)

(Guérin.)

Tartruvinate of Copper. — The solution of cupric oxide in the heated aqueous acid yields blue, silky, efflorescent needles containing 6 At. water. (Guérin.)

Tartruvinate of Silver. — 1. The free acid forms with nitrate of silver, a precipitate which does not dissolve in excess of acid. — 2. By mixing the concentrated solution of the potash or baryta-salt with excess of silver-solution, a needle-shaped precipitate is obtained, which must be washed in the dark with cold water and dried below 50°, after which it suffers no further loss in a dry vacuum. The white needles when exposed to light, assume a rose-red, afterwards a darker-red, and lastly a brown colour. They decompose at 100°, whether alone or under water. They are slightly soluble in water. (Guérin.)

	72	25.26		Guérin.
12 C					
9 H	9	3.16		
Ag	108	37.89	37.65
12 O	96	33.69		
$C^{12}H^9AgO^{12}$	285	100.00		

Tartruvinic acid dissolves very readily in *alcohol*, but not in *ether*. (Guérin.)

Tartrate of Ethyl.



DEMONDESIR. *Compt. rend.* 33, 227; *Ann. Pharm.* 80, 301.

Vinic or Ethylic Tartrate, Tartaric ether.

¶ Formed by passing hydrochloric acid into an alcoholic solution of tartaric acid, neutralizing the acid liquid with a carbonate, and agitating several times with ether, which dissolves out the tartrate of ethyl, and leaves it behind when evaporated. Tartaric ether thus obtained is a liquid which acts upon polarized light. It supports a high temperature without decomposing, but when heated to a certain point, yields considerable quantities of pyrotartaric acid; it is completely decomposed by dry distillation. When treated with ammonia, it yields tartramic ether or tartramide, according to the time for which the action is continued. It mixes in all proportions with water. (Demondesir.) ¶

Scheele (*Opusc.* 2, 142) did not succeed in any way in preparing a compound of this nature.

Thénard (*Mém. d'Arcueil*, 2, 13), by heating 7 pts. of alcohol with 6 pts. of tartaric acid and 2 pts. of oil of vitriol till ether began to form; then diluting with water; neutralising exactly with carbonate of potash; evaporating to dryness; exhausting the residue with cold alcohol; and evaporating the filtrate; obtained a brown, inodorous, somewhat bitter, neutral syrup, which, when heated, gave off thick vapours smelling of garlic, and left a non-alkaline charcoal, together with a large quantity of sulphate of potash [probably proceeding from sulphovinate of potash], which residue was resolved by distillation with aqueous potash into alcohol and tartrate of potash, and dissolved very readily in water and alcohol.

Tartrate of Methyl, $C^{12}H^{10}O^{12} = 2C^2H^3O, C^8H^4O^{10}$, is prepared in a similar manner to tartrate of ethyl. (Demondesir.)

Υ. Tartramic Acid C⁶NH⁷O¹⁰.

LAURENT. *Compt. Chim.* 1845, 153.

DEMONDESIR. *Compt. rend.* 33, 227.

Formation. 1. By the action of ammonia on anhydrous tartaric acid. (Laurent).—2. By the action of ammonia on tartaric ether. When tartaric ether is treated with alcoholic ammonia, tartrate of ethyl, or tartramethane is produced; and this compound carefully treated with alkalis, yields tartramic acid. (Demondesir).—There are two varieties of this acid, corresponding to, and obtained from, the two opposite varieties of tartaric acid (p. 365). They crystallise in rhombic prisms of the same form, but with opposite hemihedral faces. (Pasteur.)

Calculation.

8 C.....	48	32·21
N	14	9·39
7 H	7	4·69
10 O	80	53·71
<hr/>			
C ⁶ NH ⁷ O ¹⁰	149	100·00

Acid tartrate of ammonia minus 2 At. water : C⁶NH⁷O¹⁰ = C⁶H⁶(NH⁴)O¹² - 2HO.

By the continued action of ammonia, tartramic acid is converted into tartramide.

Tartrate of Ammonia is obtained by passing a current of ammoniacal gas over anhydrous tartaric acid moistened with alcohol. Two strata of liquid are then formed, the upper of which is alcohol, while the lower contains tartrate of ammonia.—This salt is liquid at ordinary temperatures; when heated, it gives off water, and is converted into a slightly crystalline solid mass. It dissolves in all proportions in water, but is insoluble in alcohol, which precipitates it from its aqueous solution in the liquid form. (Laurent, *comp.* p. 337.)

Tartrate of Lime.—The aqueous solution of tartrate of ammonia does not precipitate chloride of calcium; but on pouring alcohol into a mixture of the two salts, a copious precipitate is formed, which agglutinates by boiling. The aqueous solution of this salt is gradually resolved by boiling into ammonia and acid tartrate of lime. It does not precipitate bichloride of platinum. (Laurent.)

Tartrate of Ethyl or Tartramethane. C¹²NH¹¹O¹⁰ = C⁶NH⁶(C⁶H⁶)O¹⁰ is obtained by the action of an alcoholic solution of ammonia on tartaric ether, care being taken that the action does not go too far. (Demondesir.)

Υ. Tartramide. C⁶N²H⁶O⁶.

DEMONDESIR. *Compt. rend.* 33, 229.

PASTEUR. *Compt. rend.* 35, 176; *N. Ann. Chim. Phys.* 38, 437.

Obtained by the prolonged action of ammonia on tartaric ether. (Demondesir.) It is a crystallisable body which acts upon polarised light. The crystals which form in a solution containing a small quantity of ammonia, exhibit hemihedral faces, but those which separate from solution in pure water are rarely hemihedral. (Pasteur.)

8 C	48	32.43
2 N	28	18.91
8 H	8	5.40
8 O	64	43.26
<hr/>			
C ⁶ N ² H ⁸ O ⁸	148	100.00

Neutral tartrate of ammonia *minus* 4 At. water : C⁶N²H⁸O⁸ = C⁶H⁴(NH²)²O¹²—4HO.

Tartramide exhibits two varieties, one of which turns the plane of polarization to the right, the other to the left. Both varieties combine with active malamide, (p. 249,) forming compounds which have the same composition, but differ in crystalline form and in solubility, that which contains the lævotartramide being much the more soluble of the two. (Pasteur.)

¶. Nitrotartaric Acid.

DESSAIGNES. *Compt. rend.* 34, 731. *Ann. Pharm.* 82, 362.

Finely pulverized tartaric acid dissolves rapidly in 4½ times its weight of monohydrated nitric acid; and on mixing the solution with an equal volume of oil of vitriol, the mixture coagulates into a firm white gelatinous mass of nitrotartaric acid, which, when left for a day or two between two plates of porous earthenware under a bell-jar, to remove the greater part of the oil of vitriol, yields a light, white, silky mass, giving off copious white fumes on exposure to the air. It is purified by dissolving it in tepid water, and immediately cooling the solution to 0°, whereupon the liquid solidifies in a mass of silky interlaced crystals, which, when pressed in a funnel, give out a large quantity of mother-liquor, and diminish considerably in volume; the purification is completed by pressing the crystals between filtering paper.

The acid is very instable. The crude product first obtained, when exposed to a moist atmosphere, gives off copious white fumes of nitric acid, and is ultimately reconverted into tartaric acid. On saturating the acid with ammonia, and heating the solution, after addition of hydro-sulphate of ammonia, it decomposes with effervescence, deposits a considerable quantity of sulphur, and the filtered solution yields by concentration crystals of neutral tartrate of ammonia. (Dessaignes.)

Appendix to Nitrotartaric Acid.

Tartronic Acid. C⁶H⁴O¹⁰.

DESSAIGNES. *vid.* Memoir above cited.

Formation and Preparation. By the spontaneous decomposition of nitrotartaric acid, either in the state of aqueous solution, or in combination with potash or lead-oxide. — An aqueous solution of nitrotartaric acid decomposes at a few degrees above 0°, continuing for several days to give off carbonic acid and nitric oxide; and if, when this decomposition is at an end, the liquid be heated to 40° or 50°, carbonic acid escapes with effervescence, and the nitrotartaric acid is transformed into oxalic. But if the temperature be prevented from rising above 30°, very little gas is evolved, and the liquid ultimately deposits crystals of tartronic acid.

Properties. Bulky prisms which sometimes remain transparent on exposure to the air, sometimes become opaque, and assume a fibrous texture. The latter crystals give off no water at 100°.

<i>Crystals dried in vacuo.</i>		<i>Dessaignes.</i>	
6 C.....	36 30·00	30·00	30·41
4 H.....	4 3·33	3·38	3·64
10 O.....	80 66·67	66·62	65·95
<hr/>			
C ⁶ H ⁴ O ¹⁰	120 100·00	100·00	100·00

The crystals melt at 175°, giving off gas and a mere trace of water, and leave an amorphous, very slightly coloured residue, nearly insoluble in water. By rapid distillation over a lamp, they yield another acid, crystalline, volatile, and easily soluble.

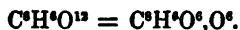
The aqueous solution of tartronic acid is not altered by boiling. It does not precipitate acetate of potash, chloride of barium, chloride of calcium, sulphate of magnesia, ferric chloride, or cupric sulphate, even in presence of excess of ammonia; but it forms precipitates with nitrate of lead, nitrate of silver, mercurous nitrate, and mercuric chloride; also with the acetates of baryta, lime, and cupric oxide; the lime-precipitate is soluble in sal-ammoniac.

With *Ammonia*, tartronic acid forms a *neutral* and an *acid* salt, whence it appears to be bibasic, and homologous with malic acid, C⁶H⁶O¹⁰.—The neutral salt forms precipitates with chloride of barium, chloride of calcium, and bichloride of platinum.—The acid salt crystallises in beautiful prisms.

Silver-salt. Obtained by precipitating nitrate of silver with the aqueous acid.

<i>Dried in vacuo.</i>		<i>Dessaignes.</i>	
6 C.....	36 10·77	10·74	
2 H.....	2 0·60	0·70	
2 Ag.....	216 64·67	64·53	
10 O.....	80 23·96	24·03	
<hr/>			
C ⁶ H ² Ag ² O ¹⁰	334 100·00	100·00	¶

Racemic Acid.



JOHN in his *Handwörterbuch der Chemie*, 4, 125.

GAY-LUSSAC. *J. Chim. méd.* 2, 335; also *Schw.* 48, 38.

WALCHNER. *Schw.* 49, 239, and epistolary communication.

BERZELIUS. *Pogg.* 19, 305; 36, 1.

FRESENIUS. *Ann. Pharm.* 41, 1; 53, 230.

WERTHER. *J. pr. Chem.* 32, 385.

PASTEUR. *N. Ann. Chim. Phys.* 24, 442.—*Compt. rend.* 28, 477; 29, 297.—Further: *Compt. rend.* 36, 19.

BIOT's Report upon PASTEUR. *Compt. rend.* 29, 433.

Artificial Formation of Racemic acid: PASTEUR, *Compt. rend.* 37, 162; *Instit.* 1853, 257; *Arch. Ph. Nat.* 24, 83; *Pogg. Ann.* 9, 504; *J. pr. Chem.* 60, 134; *Ann. Pharm.* 88, 211; *Pharm. Centr.* 1853, 613; *Chem. Soc. Qu. J.* 6, 277; *Chem. Gaz.* 1853, 401.

Paratartronic acid, Upic acid, Traubensäure, Vogesensäure, Paratartronsäure, Acide racémique, Acide paratartrique, Acidum uticum.—Obtained and recognized as a peculiar acid by Kestner, the proprietor of a large che-

tartaric acid, only in the years 1822—1824, but in large quantity. It remains undecided, whether the tartar then employed contained the racemic acid ready formed, or whether this acid was produced from the isomeric body, tartaric acid, by the mode of preparation then employed. It appears, however, from a communication made to the author by Kestner, that the tartaric acid was at that time separated from the lime by a considerable excess of sulphuric acid, and that the aqueous acid, after being decolorized by chlorine, was, in part, exposed for a considerable time to a freezing temperature, the racemic acid then crystallising out, whereas the present practice is to evaporate the acid to the crystallising point immediately. Since Kestner, in the years just mentioned, likewise worked up Italian tartar, and White, a manufacturer of tartaric acid in Glasgow, also (about 25 years ago), obtained racemic acid by the use of tartar from Naples and Sicily, and from Oporto, it is rather to be supposed that climate has some influence on the formation of racemic acid in the grape. (*Compt. rend.* 29, 526, and 557.) — ¶. Kestner has since (in 1850), obtained small quantities of racemic acid, together with tartaric acid, in working French and Tuscan tartar. (*Compt. rend.* 36, 17.) It appears also from Pasteur's observations of numerous tartaric acid manufactories in Germany, that racemic acid exists in tartar from the most various localities, though in variable quantity, and diminishing in the refining of the tartar. In Fikentscher's manufactory at Zwickau, in particular, the occurrence of racemic acid in small quantity has long been observed. These observations show, that racemic acid is not so rare and isolated a product as was formerly supposed, although it has never again been obtained in so large a quantity as on the occasion of its first discovery. Pasteur has lately shown, that racemic acid may be prepared at pleasure from tartaric acid by an artificial process (*vid. inf.*).

Formation. By the action of heat on tartrate of cinchonine and on tartaric ether. When tartrate of cinchonine is heated, the base first undergoes alteration, being transformed into cinchoninic and then into chinoidine (*vid. Cinchonine*); and afterwards the alteration extends to the acid, which, in the course of 5 or 6 hours, is partially converted into racemic acid. The resinous product is exhausted with boiling water, and the filtrate, when cool, mixed with excess of chloride of calcium, whereupon it yields an immediate precipitate of racemate of lime. The acid separated from the lime-salt thus obtained, exhibits all the properties of natural racemic acid. — Racemic acid is also obtained by heating tartaric ether; whence it appears that the conversion of tartaric into racemic acid does not require the presence of an optically active substance (such as cinchonine), but that the union of the tartaric acid with another body, merely enables it to sustain a stronger heat without decomposition. — Antitartaric or lævotartaric acid (p. 365), likewise yields racemic acid under the same circumstances as ordinary (dextro-) tartaric acid. As racemic acid is a compound of these two opposite varieties of tartaric acid (*vid. p. 365*), it appears that the formation of racemic from tartaric acid by heat, really consists in the conversion of a portion of the dextrotartaric into lævotartaric acid, or *vice versâ*. (Pasteur.) ¶.

By drying at 100° to 150°, crystallised racemic acid is converted into the anhydrous acid.

Properties. White effloresced mass, inodorous, having a stronger acid taste than tartaric acid, and reddening litmus strongly. The aqueous

solutions of racemic acid and its salts do not act upon polarised light. (Biot.)

<i>Effloresced Acid.</i>			
8 C	48	32
6 H	6	4
12 O	96	64
<hr/>			
C ⁸ H ⁴ O ¹²	150	100

The radical theory assumes a hypothetical anhydrous acid = C⁸H²O⁶ = \bar{U} .

Decompositions. 1. After the crystallised acid has given off all its water of crystallisation at 150°, it remains unaltered up to 200°, but at a higher temperature, melts, and is converted, with effervescence, first into paratartralic, then into paratartronic acid, and lastly, into paratartronic anhydride. (Fremy, *Ann. Chim. Phys.* 68, 378.) The formation of paratartronic acid is preceded, without loss of water, by that of an acid which corresponds to metatartronic acid, and whose ammonia-salt may be distinguished by the microscope from that of racemic acid. (Laurent & Gerhardt, *Compt. Chim.* 1829, 11 and 504.) — According to Löwig (*Pogg.* 42, 588), racemic acid may, by careful heating, be converted into tartaric acid. — The effloresced acid, when subjected to *dry distillation*, melts, turns grey, swells up, and yields exactly the same products as tartaric acid. (Berzelius, Pelouze.) When heated alone, it swells up at 185° to 190°, and afterwards, between 195° and 200°, gives off a large quantity of a gas, of which only 90 p. c. is absorbed by potash; if the acid is mixed with spongy platinum, the copious evolution of gas takes place, even between 185° and 190°, and the portion not absorbed by potash amounts to only 3 or 4 per cent.; if the acid is mixed with pumice-stone, the evolution of gas takes place even at 175°, and the gas is entirely absorbed by potash, with the exception of a mere trace. (Reiset & Millon, *N. Ann. Chim. Phys.* 8, 785.)

3. The acid decomposes with *bichromate of potash* and water in the same manner as tartaric acid (p. 270), but with less violence. (Winckler.) Similarly, Pöttger. (*Beitr.* 2, 126.) — 4. It takes fire when triturated with 8 pts. of *peroxide of lead*. (Böttger, *Beitr.* 2, 38.) — 5. Heated with *sulphuric acid* and *peroxide of manganese*, it yields a very large quantity of carbonic acid, together with acetic acid. (Walchner.) — 6. It reduces the oxide of *gold* or *silver* dissolved in an acid. (Walchner.) — 7. Its dilute aqueous solution becomes mouldy by keeping. (Walchner.)

Combinations. With Water. — *a. Crystallised Racemic acid.* — The acid crystallises from its aqueous solution in transparent, colourless, oblique rhombic prisms, belonging to the doubly oblique prismatic system. *Fig.* 125°, to which may also be added the faces *b* (between *y* and *q*); *a* (between *y*, *q*, *v*, and *u*); and *w* (between *t* and *u*); *y* : *v* = 107° 28'; *y* : *b* = 153° 54'; *b* : *q* = 147° 58'; *y* : *u* = 51° 27'; *a* : *z* = 123° 32'; *v* : *u* = 69° 15'; *v* : *z* = 129° 51'; *z* : *w* = 152° 54'; *w* : *u* = 146° 30' (Prevostaye, *N. Ann. Chim. Phys.* 3, 129; *comp.* Bernhardt, *Repert.* 49, 395; Guérin Varry, *Ann. Chim. Phys.* 62, 71; Waackroder, *J. pr. Chem.* 23, 207; Delffs, *Jahrb. prakt. Pharm.* 8, 378; Rammelsberg, *Pogg.* 96, 29.) — The crystals are permanent in the air, becoming partially opaque only in warm air (Walchner), and give off all their water in a current of dry air at 100°. (Berzelius.)

	<i>Crystallised.</i>		Berzelius.	Fresenius.
C ⁸ H ⁴ O ¹²	150	89·29
2 HO	18	10·71
<hr/>				
C ⁸ H ⁴ O ¹² + 2Aq	168	100·00
			100·00
			100·00

or cold water. (Walchner.)

Racemic acid appears to have a still stronger affinity for bases than tartaric acid. But the alcoholic solution of the acid does not decompose any carbonate if water be absent (Pelouze); because racemates are not soluble in alcohol. (Braconnot.) The formula of the *Racemates* is the same as that of the tartrates. The crystals of racemates never exhibit those hemihedral forms which characterise the tartrates, and their solutions do not exert any rotatory action on polarised light. (Pasteur.)

RACEMATE OF AMMONIA. — *a. Neutral.* — Obtained by neutralising the acid with ammonia, and evaporating, best over lime within a bell-jar. Transparent, colourless, four-sided prisms. (Fresenius.) Right prismatic system, *Fig. 66*, but without the *m*-face and the two small faces below *a*, *a*; on the other hand, they have the face *n* right and left of *t*, and a triangular face below *y*. $y : y = 118^\circ$; $y : a = 169^\circ$; $u : u' = 80^\circ 30'$; $u : t = 130^\circ 15'$; $u : n = 160^\circ 50'$. (Prevostaye.) — The crystals become turbid in the air from loss of ammonia, very quickly at 100° ; the aqueous solution also gives off ammonia when left to evaporate; acetic acid added to the aqueous solution throws down the salt *b*. — Easily soluble in water, nearly insoluble in alcohol. (Fresenius.)

	<i>Crystallised.</i>		Fresenius.	
8 C	48	26.09	26.76	
2 N	28	15.22	15.47	
12 H	12	6.52	6.54	
12 O	96	52.17	51.23	
<hr/>				
$C^8H^4(NH^4)O^{12}$	184	100.00	100.00	

b. Acid. — When 1 pt. of the acid is neutralised with ammonia, and 1 pt. more afterwards added in the cold, the acid salt is precipitated in the form of a crystalline powder; if the process be performed at a higher temperature, and the liquid then rapidly cooled, the acid salt separates in needles and four-sided lamina; but by slow cooling, it crystallises in prisms belonging to the singly oblique prismatic system. The crystals become tabular by predominance of the oblique terminal face. The salt is permanent in the air, even at 100° ; reddens litmus; dissolves in 100 pts. of water at 20° ; much more abundantly in hot water; easily in mineral acids; but is insoluble in alcohol. (Fresenius.)

	<i>Crystals.</i>		Fresenius.	
8 C	48	28.74	29.14	
N	14	8.38	8.43	
9 H	9	5.39	5.39	
12 O	96	57.49	57.04	
<hr/>				
$C^8H^4(NH^4)O^{12}$	167	100.00	100.00	

RACEMATE OF POTASH. — *a. Neutral.* — The aqueous acid saturated with carbonate of potash, yields, by rapid evaporation, a saline crust; by slow evaporation, large, hard, transparent, colourless, four-sided prisms permanent in the air, and having a cooling saline taste. (Fresenius.) *Fig. 70*, often with *m*-faces, and with the edges between *p* on the one side and *u*, *t*, and *m* on the other, truncated; $t : u = 128^\circ 30'$ (Pasteur, *N. Ann. Chim. Phys.* 24, 453; 28, 93.) — The crystals give off all their water at 100° with efflorescence but sustain a heat of 200° without

further decomposition; they dissolve in 0.97 pts. of water at 25°, but are nearly insoluble in alcohol. From the concentrated aqueous solution racemic acid and the stronger mineral acids throw down the acid salt. (Fresenius.)

Crystals.		Fresenius.
2 KO	94.4	35.97
C ⁶ H ⁴ O ¹⁰	132.0	50.31
4 HO	36.0	13.72
<hr/>		
C ⁶ H ⁴ K ² O ¹² + 4Aq ...	262.4	100.00

b. Acid. — Racemic forms a granular precipitate in a saturated solution of chloride of potassium. (Geiger, *Mag. Pharm.* 20, 349.) Prepared like the acid ammonia-salt, either as a crystalline powder, or, by cooling of the hot liquid, in four-sided tables. The crystals have a sour taste; are permanent in the air, even at 100°; dissolve in 180 pts. of water at 19°; in 139 pts. at 25°; in 14.3 pts. of boiling water; easily in mineral acids, but are insoluble in alcohol. (Fresenius.)

Crystals.		Fresenius.
KO.....	47.2	25.08
C ⁶ H ⁴ O ¹¹	141.0	74.92
<hr/>		
C ⁶ H ⁴ KO ¹²	188.2	100.00

Racemate of Boracic acid and Potash. — By dissolving 1 At. boracic acid and 2 At. acid racemate of potash in water, and evaporating at 100°; a white, almost crystalline, friable, acid mass is obtained, which does not become moist by exposure to the air, but dissolves readily in water. (Fresenius.)

Racemate of Potash and Ammonia. — The aqueous solution of the acid potash-salt, supersaturated with ammonia and evaporated over lime in vacuo, yields at the bottom of the vessel, a few regular crystals, consisting almost entirely of ammonia-salt, and on the sides, effloresced saline crusts, which contain more than 3 At. potash to 1 At. ammonia, and are rather to be regarded as a mixture. (Fresenius.) — According to Pasteur, racemate of potash and ammonia crystallises with difficulty in striated rectangular prisms, whose lateral edges are truncated with *u*-faces, often to the obliteration of *t* and *m*; *t* : *u*' = 130° 45'.

RACEMATE OF SODA. — *a. Neutral.* — Crystallises very readily in transparent, colourless, four and six-sided prisms (Walchner), belonging to the right prismatic system (Fresenius; Pasteur, *N. Ann. Chim. Phys.* 28, 93); permanent in the air even at 100° (Walchner, Fresenius); soluble in 2.63 pts. of water at 25°, insoluble in alcohol: the dilute solution, when exposed to the air, becomes mouldy, and forms carbonate of soda. (Walchner.)

Crystals.		Fresenius.
2 NaO	62.4	32.10
C ⁶ H ⁴ O ¹⁰	132.0	67.90
<hr/>		
C ⁶ H ⁴ Na ² O ¹²	194.4	100.00

b. Acid. — The salt *a* and racemic acid in equal numbers of atoms are dissolved in a small quantity of boiling water; the salt *b* precipitated from the solution by alcohol in the form of a crystalline powder; and subsequently crystallised from hot water. Small, transparent, colourless, highly lustrous prisms, belonging to the oblique prismatic system, with

manent in the air at ordinary temperatures, but effloresce at 100°, with loss of 9.41 p. c. (2 At.) water; dissolve in 11.3 pts. of water at 19°, and in a much smaller quantity of boiling water; but are insoluble in alcohol. (Fresenius.)

	Crystals.		Fresenius.	
NaO	31.2	...	16.40 16.28
C ⁶ H ⁴ O ¹¹	141.0	...	74.13
2 HO	18.0	...	9.47 9.41
<hr/>				
C ⁶ H ⁴ NaO ¹³ + 2Aq.	190.2	...	100.00

Racemate of Soda and Ammonia. — The aqueous solution of the acid soda-salt, supersaturated with ammonia and evaporated over lime under a bell-jar, yields large, hard, transparent, colourless, four-sided tables, belonging to the doubly oblique prismatic system. (Fresenius.) The crystals agree exactly in form, angles, double refraction, specific gravity (= 1.58), and composition, with those of the tartrate of soda and ammonia; but their solution exerts no rotatory action on polarised light (Mitscherlich, *Compt. rend.* 19, 719.) The crystals effloresce in the air, especially in hot air, giving off water and ammonia. They dissolve readily in water, and then give off ammonia on boiling. (Fresenius.) The crystals consist half of tartrate of soda and ammonia and half of antitartrate; but every time that the entire mass of crystals is dissolved, the racemate is reproduced. (Pasteur, p. 365.)

	Crystals.		Fresenius.	
NH ⁴ O	26.0	...	12.55
NaO	31.2	...	15.06 15.08
C ⁶ H ⁴ O ¹⁰	132.0	...	63.70 62.66
2 HO	18.0	...	8.69
<hr/>				
C ⁶ H ⁴ Na(NH ⁴)O ¹³ + 2Aq.	207.2	...	100.00

The crystals examined by Mitscherlich contained 8 Aq.

Racemate of Soda and Potash. — First obtained by Mitscherlich (*Pogg.* 57, 484), whereas, in the hands of Berzelius, Fresenius, and the author, the preparation formerly did not succeed, the simple salts crystallising out separately. — 1. One half of the aqueous acid is neutralised with potash, the other half with soda, and the mixture left to evaporate spontaneously in summer. — 2. A boiling aqueous solution of the acid potash-salt is neutralised with carbonate of soda, then evaporated and cooled, or left to evaporate spontaneously. Large, transparent, colourless, hard rhomboïdal prisms and tables, belonging to the doubly oblique prismatic system. They effloresce only at a summer temperature and on the surface. Their powder mixed with sand gives off all its water in two hours at 100°; between 90° and 100°, they melt to a clear viscid liquid, which at 100° gives off only 22.41 p. c. water in seven hours; and between 150 and 200°, boils briskly, becomes gradually turbid, and then solidifies in a white compact mass, which, if the heat has not risen above 190°, consists of dry unaltered salt. But at 200°, it begins to turn brown, then swells up with an odour of burnt sugar, and leaves charcoal mixed with the carbonates of the alkalis. — The crystals dissolve in 1.32 pt. water at 6°, in every proportion of hot water, and separate therefrom unaltered. (Fresenius, *Ann. Pharm.* 53, 230.) — This double racemate also exists only in the state of aqueous solution. When crystallised, it yields crystals of tartrate

	<i>Crystals.</i>	<i>Fresenius.</i>
KO	47·2	16·72
NaO	31·2	11·04
C ⁶ H ⁴ O ¹⁰	132·0	46·74
8 HO	72·0	25·50
C ⁶ H ⁴ KNaO ¹² + 8Aq. 282·4 100·00		

Racemate of Boracic acid, Soda, and Potash. — When 1 pt. of crystallised borax is digested with 3 pts. of acid racemate of potash and with water, and the filtrate evaporated, there is obtained at 100° a white mass, which becomes moist when exposed to the air, and exactly resembles the *Boraxweinstein* of the German pharmacopœas.

A similar, but more deliquescent mass is obtained with acid racemate of soda. (Fresenius.)

RACEMATE OF BARYTA. — 1. The acid forms, with baryta-water, white flakes soluble in excess of the acid (Walchner); but the clear solution becomes turbid in a few seconds, and deposits nearly all the salt in the neutral state, and in the form of a crystalline powder; the small quantity which remains in solution may be precipitated by alcohol. (Fresenius.) — 2. From a solution of acetate of baryta, racemic acid throws down neutral racemate of baryta; (a), from a hot solution, it precipitates the anhydrous salt as a white, slightly crystalline powder; and (b), from a cold solution, the hydrated salt, in the form of a heavy white precipitate consisting of fine needles. (Fresenius.) — 3. Neutral racemate of soda added to chloride of barium, throws down white flakes, which in a minute pass completely into the crystalline state. (Wittstein, *Repert.* 57, 22.) In case of great dilution, it does not precipitate nitrate of baryta. (Walchner.)

Hydrated racemate of baryta gives off at 200° the whole of its water, amounting to 13·8 per cent. (Fresenius.) The salt, when ignited in a close vessel, leaves a pyrophoric residue. (Böttger.) It is nearly insoluble in cold water, but dissolves in 200 pts. of boiling water, readily in hydrochloric and nitric acid, not in acetic acid, and is precipitated from the hydrochloric acid solution by ammonia, not immediately, but after a few seconds. (Fresenius.) It does not dissolve in aqueous hydrochlorate nitrate, or succinate of ammonia, even with the aid of heat (Walchner); or in potash-ley. (Fresenius.)

	<i>2, a.</i>	<i>Fresenius.</i>
2 BaO	153·2	53·72
C ⁶ H ⁴ O ¹⁰	132·0	46·28
C ⁶ H ⁴ Ba ² O ¹²		
	285·2	100·00
	<i>2, b.</i>	<i>Fresenius.</i>
2 BaO	153·2	46·39
C ⁶ H ⁴ O ¹⁰	132·0	39·98
5 HO	45·0	13·63
C ⁶ H ⁴ Ba ² O ¹² + 5Aq. 330·2 100·00		

Racemate of baryta dissolves in the aqueous acid but without producing a definite acid salt: for the solution, as it cools, deposits the greater part of the baryta in the form of neutral salt, and the rest when evaporated, while free acid crystallises out. (Fresenius.)

Racemate of Baryta and Potash and *Racemate of Baryta and Soda* are not obtainable.

water, thick flakes which do not become crystalline in 12 hours. (Wittstein.)—2. With nitrate of strontia, it forms the same precipitate, nearly insoluble in excess of the acid. (Walchner.) From acetate of strontia, it throws down a white, shining, crystalline powder. (Fresenius.)—3. Neutral racemate of potash forms with chloride of strontium, a white, crystalline, granular precipitate. (Wittstein.)—The crystalline powder obtained by (2) gives off 22·87 p.c. water at 200°, without further decomposition. It is nearly insoluble in cold water, very sparingly soluble in boiling water, from which it separates almost completely on cooling, so that the filtrate is scarcely clouded by sulphuric acid. It dissolves readily in hydrochloric acid, whence it is immediately precipitated by ammonia. It is insoluble in acetic acid. With racemic acid it behaves just like the baryta-salt. (Fresenius.) With hot aqueous hydrochlorate, nitrate, or succinate of ammonia, it forms a clear solution, which becomes turbid as it cools. (Wittstein.)

	<i>Crystalline powder (2).</i>	<i>Fresenius.</i>
2 SrO	104	33·77
C ⁸ H ⁴ O ¹⁰	132	42·86
8 HO	92	23·37
C ⁸ H ⁴ Sr ² O ¹² + 8Aq.		
	308	100·00

RACEMATE OF LIME.—1. The free acid precipitates lime-water in thick plates (Gay-Lussac), which [after a while] consist of extremely fine needles (Walchner); the flakes dissolve in a larger quantity of the acid, provided the addition be made quickly and before the precipitate has become crystalline and consequently insoluble, but the clear liquid then becomes quickly clouded by formation of a crystalline precipitate. (Gmelin.)—Lime-water added to an excess of the acid, precipitates after a few seconds a [crystalline] neutral salt. (Fresenius.)—2. The free acid added to aqueous gypsum forms delicate needles in a quarter of an hour (Walchner, Geiger); the turbidity begins in an hour, and in 24 hours nearly all the lime is precipitated. (Berzelius.) With hydrochlorate and nitrate of lime, it forms a precipitate more quickly than with gypsum, but more slowly as the solutions are more dilute. (Gay-Lussac, Walchner.) From a concentrated solution of acetate of lime, it throws down a snow-white, crystalline powder; from a more dilute solution, small shining needles. (Fresenius.)—3. Neutral racemate of ammonia or soda quickly precipitates even a dilute solution of gypsum and other lime-salts (Fresenius, Herzog), the precipitate consisting of an amorphous powder or of delicate laminæ. (Pasteur.)

The needles obtained by (2) give off all their water = 27·75 p. c. at 200°, without further decomposition. (Fresenius.) The salt heated with ammonia and fragments of nitrate of silver precipitates the silver in a speculum like tartrate of lime. (Casselmann, *vid.* p 288.)—The salt is so sparingly soluble in cold water, that the solution is not clouded by oxalic acid, but only by oxalate of ammonia; in boiling water it is somewhat more soluble. (Fresenius.) It dissolves in hydrochloric acid and is precipitated therefrom by ammonia (distinction from tartrate of lime) (Gay-Lussac); the opaque, semicrystalline precipitate is produced immediately or (in case of great dilution, according to Fresenius) after a few seconds; when the hydrochloric acid solution is evaporated in the cold, crystals of racemic acid are formed; but when the solution is

evaporated by heat, the greater part of the hydrochloric acid goes off, and racemate of lime remains. (Berzelius.) The salt does not dissolve in acetic acid, nor [after becoming crystalline] in racemic acid. (Fresenius.) It dissolves sparingly in warm aqueous sulphate, hydrochlorate, or succinate of ammonia, whereupon needles are produced on cooling. (Wittstein.) Its solubility in sal-ammoniac is however quite insignificant. (H. Rose.) It dissolves readily in cold and tolerably strong potash-ley free from carbonic acid, the solution becoming turbid when heated, pasty when boiled, and clear again on cooling, and when heated to the boiling point after dilution with water, depositing all the [basic?] racemate of lime in flakes. (Fresenius.)

	<i>Air-dried Crystals.</i>		Berzelius.	Fresenius.
2 CaO	56	21·54 21·59
$C^8H^{10}O^{10}$	132	50·77	
8 HO	72	27·69 27·75
<hr/>				
$C^8H^4Ca^2O^{12} + 8Aq.$	260	100·00	

Neither *Racemate of Lime and Potash* nor *Racemate of Lime and Soda* can be prepared.

RACEMATE OF MAGNESIA.—The aqueous solution of neutral racemate of soda does not precipitate sulphate of magnesia. (Walchner.)—The aqueous acid is boiled with excess of carbonate of magnesia, and the filtrate left to crystallise slowly by cooling.—Small right rhombic prisms, or when obtained by sudden cooling or evaporation, a white powder.—The crystals effloresce in dry air, give off 27·24 p. c. (8 At.) water at 100°, and in all 32·9 p. c. (10 At.) at 200°, without further decomposition. They dissolve in 120 pts. of water at 19°, and in a smaller quantity of boiling water; easily in the stronger mineral acids, not in acetic acid. From the concentrated solution in hydrochloric acid, ammonia throws down immediately, and from the dilute solution after a while, a precipitate of *polybasic racemate of magnesia*. The hot aqueous solution of the salt in an equal quantity of racemic acid, again yields by cooling and evaporation, crystals of the neutral salt, which may also be precipitated therefrom by alcohol. Its solution in potash-ley becomes pasty when heated, but clear again on cooling. (Fresenius.)—Magnesia-salts are not protected by racemic acid from precipitation by ammonia or carbonate of soda. (Fresenius.)

	<i>Crystals.</i>		Fresenius.
2 MgO.....	40	15·27
$C^8H^4O^{10}$	132	50·38
10 HO	90	34·35
<hr/>			
$C^8H^4Mg^2O^{12} + 10Aq.$	262	100·00

When acid racemate of ammonia, potash, or soda, is boiled to neutralisation with carbonate of magnesia, a filtrate is obtained, which, after standing for several days, deposits crystals of racemate of magnesia, but if continuously evaporated at 100°, leaves a syrup, which, on cooling, solidifies after some time to an amorphous saline mass, which dissolves but slowly even in boiling water, and from which the alkali-salt is but very incompletely extracted by water. (Fresenius.)

CEROUS RACEMATE.—The free acid precipitates cerous acetate but not the hydrochlorate; alkaline racemates precipitate also the latter.

(Berlinger.)

CHROMIC RACEMATE.—The very acid violet solution of hydrated chromic oxide in the boiling aqueous acid, leaves a violet crystalline mass when evaporated. Its aqueous solution acquires a fine green colour when mixed with carbonate of potash; is completely precipitated by lime-water; and yields with alcohol a violet precipitate, which becomes nearly black when dry, and is insoluble in water, but soluble in racemic acid. (Fresenius.)

When the aqueous acid is boiled with bichromate of potash, carbonic acid is violently evolved, and a blackish grey liquid with violet iridescence is formed, which, when evaporated, leaves a blackish, amorphous, easily friable mass. The solution of this mass in water acquires a fine green colour when mixed with potash, and is completely precipitated by lime-water. (Fresenius.)

MANGANOUS RACEMATE.—1. The solution of manganous carbonate in the acid diluted with 40 pts. of water, yields after a while transparent, flesh-coloured prisms and crystalline grains, very sparingly soluble in water. (John.)—2. An aqueous mixture of manganous acetate and racemic acid yields by evaporation small yellowish-white crystals, which are permanent in the air even at 100°, and dissolve very sparingly in cold, somewhat more readily in boiling water, readily in hydrochloric acid. (Fresenius.)

	Crystals.		Fresenius.	
2 MnO.....	72	...	32.43 31.52
C ² H ⁴ O ¹⁰	132	...	59.46	
2 HO	18	...	8.11	
<hr/>				
C ² H ⁴ Mn ² O ¹² + 2Aq.	222	...	100.00	

Racemate of Arsenious acid and Ammonia.—Discovered and stoichiometrically determined by Mitscherlich, as well as the two following salts.—Arsenious acid is digested with aqueous acid racemate of ammonia, or better 2 At. arsenious acid and 1 At. racemic acid are gradually added in alternate small portions to 1 At. neutral racemate of ammonia, so that the arsenious acid is always in excess up to the end of the operation, after which the filtrate is evaporated, and cooled to the crystallising point. The solution takes place slowly, and requires constant boiling; for acid racemate of ammonia is soon deposited, and a large quantity of arsenious acid remains undissolved, even after boiling for hours.—Large, quickly efflorescing crystals. Between 90° and 100°, they give off altogether 4.1 p. c. water and ammonia. They dissolve in 10.62 pts. of water at 15°, and are, for the most part, resolved by evaporation into crystallising acid racemate of ammonia and arsenious acid, which remains in solution. (Werther.)

	Crystals.		Werther.	
NH ⁴ O	26	...	9.77 9.99
AsO ³	99	...	37.21 37.72
C ² H ⁴ O ¹⁰	132	...	49.63 50.70
HO.....	9	...	3.39 3.04
<hr/>				
C ² H ⁴ (NH ⁴)(AsO ²)O ¹² + Aq.	266	...	100.00 101.45

Racemate of Arsenious acid and Potash.—2 At. arsenious and 1 At. racemic are added very gradually, and in alternate small portions to

1. At neutral racemate of potash, which is dissolved in a large quantity of water, and maintained for several hours in constant ebullition, the arsenious acid being kept in excess even to the last, to prevent the separation of too great a quantity of acid racemate of ammonia, which would have to be redissolved by addition of water and boiling. The liquid concentrated, but not too much, by boiling, and filtered hot, deposits, on cooling, first small prisms of acid racemate of potash, then large rhombic crystals of the double salt, which are separated, either by picking them out or by treating the whole with a small quantity of warm water, filtering from the acid potash-salt, which remains for the most part undissolved, and evaporating to the crystallising point, during which operation, however, a portion of the acid potash-salt is always reproduced. — Large colourless rhombic crystals, having a pearly lustre. They effloresce gradually, give off 4.23 p. c. water at 100°, and the whole between 155° and 170°, and then sustain a heat of 250° without further decomposition; at 255°, the residue assumes a brownish colour, and gives off water, together with vapours, having an alliaceous and empyreumatic odour. The crystals dissolve in 7.96 pts. of water at 15°, and when this solution is evaporated, are resolved almost entirely into acid racemate of potash, and arsenious acid which remains dissolved, even when the liquid is highly concentrated. (Werther.)

	Crystals.		Werther.	
KO	47.2	15.46
AsO ³	99.0	32.44
C ² H ⁴ O ¹⁰	132.0	43.25
3 HO	27.0	8.85
<hr/>				
C ² H ⁴ K(AsO ³)O ¹³ + 3Aq.	305.2	100.00

Racemate of Arsenious acid and Soda. — When 1 pt. of racemic acid is neutralised with soda, then arsenious acid and 1 pt. more of racemic acid added, in alternate small portions, to the boiling liquid, and the solution repeatedly evaporated and cooled, a large quantity of the crystallised double salt is obtained. The preparation is much easier than that of either of the two preceding salts. — Large crystals permanent in the air, and having a brilliant pearly lustre. They give off 10.65 p. c. (about 4 At.) water at 100°, and the rest at 130°. Decomposition begins at 275°. The salt dehydrated at 130°, becomes heated by contact with cold water, and dissolves completely. The crystals dissolve in 14.59 pts. of water at 19°, and the solution, when evaporated, yields nearly all the salt undecomposed, but in crystals, having a higher vitreous lustre. (Werther.)

	Crystals.		Werther.	
NaO.....	31.2	10.16
AsO ³	99.0	32.23
C ² H ⁴ O ¹⁰	132.0	42.97
5 HO	45.0	14.64
<hr/>				
C ² H ⁴ Na(AsO ³)O ¹³ + 5Aq.	307.2	100.00

Potassio-antimonic Racemate. — Obtained by saturating acid racemate of potash with antimonic oxide. Sometimes rhombic crystals are obtained, acuminated with four faces; sometimes delicate needles, which become opaque when exposed to the sun. (Berzelius.) *Fig. 62*, without the *p*-face, *a* : *a* = 142° 55'; *a* : *a* behind = 140°; *a* : *u* = 118° 2'; *u* : *u* = 94° 40'. (Prevostaye.) — The air-dried crystals contain 13.46

water of crystallisation at 100°; the salt dried at 100° gives off 5.50 p. c. water at 260°, without becoming coloured, exactly therefore like tartar-
 emetic. (Liebig, *Ann. Pharm.* 26, 134.)

RACEMATE OF ZINC.—1. The aqueous acid dissolves zinc readily with evolution of hydrogen, and deposits the resulting salt, partly immediately, partly on evaporation, in white needles, whose aqueous solution is very apt to turn mouldy. (Walchner.)—2. The free acid precipitates from acetate of zinc a jelly, which dries up to a white viscid mass. This mass is nearly insoluble in water, but dissolves more readily in racemic, and still more in hydrochloric acid. (Werther.)

STANNOUS RACEMATE.—The aqueous acid dissolves tin very slowly, and yields by evaporation, colourless six and eight-sided prisms, soluble in water. (Walchner.)

RACEMATE OF LEAD.—168 pts. of the crystallised acid, mixed with a treble quantity of lead-oxide and with water, and dried over the water-bath, give off 32.76 p. c. water, and somewhat above 100°, 36.07 p. c. (4 At.) in all. (Berzelius.)—1. The free acid precipitates from neutral acetate of lead a snow white crystalline powder (Fresenius); if the racemic acid is in excess, the vessel becomes covered with a crystalline crust; if the boiling acid is mixed with only just sufficient acetate of lead to render the precipitate permanent, and then filtered boiling, it yields on cooling a few small needles. (Fresenius.)—2. Neutral racemate of soda yields a flocculent precipitate, consisting of slender needles. (Walchner.) The salt after drying has a density of only 2.530 at 19°, much smaller therefore than that of tartrate of lead. (H. Rose, *Pogg.* 33, 48.) The precipitated salt contains no water. (Berzelius.) After ignition in a close vessel, it leaves a greyish-black, coherent mass, which, after cooling, takes fire in the air, globules of lead then appearing on the surface, and quickly burning to oxide. (Böttger.)—The salt dissolves in racemic acid (Walchner), and more readily than tartrate of lead in tartaric acid; and the solution of the salt in the hot acid yields, on cooling, small crystalline grains, which when heated crumble to a fine powder, with slight decrepitation and loss of water. (Berzelius.)

	(1.) <i>Crystalline crust dried at 100°.</i>			Berzelius.
2 PbO	224	62.92 62.75
C ² H ⁴ O ¹⁰	132	37.08 37.25
<hr/>				
C ⁸ H ⁴ Pb ² O ¹²	356	100.00 100.00

FERROUS RACEMATE.—1. The aqueous acid acts upon iron with evolution of hydrogen, forming soft white needles, which dissolve but very sparingly in water, and when exposed to the air, gradually change into the yellow ferric salt. (Walchner.)—2. Ferrous sulphate added to an aqueous mixture of acetate of potash and racemic acid, produces a white precipitate, which soon turns greenish and brown, if the air has access to it, but dries up in vacuo to a yellowish white powder. This powder dissolves sparingly in water, readily in mineral acids, racemic acid, ammonia, and potash; the acid solutions are not precipitated by alkalis, nor the alkaline solutions by acids.

ferric hydrate, and filtered from a basic salt, yields a red-brown liquid, which, when evaporated, still deposits a portion of basic salt, and dries up to a brown, hard, friable mass. This mass is completely precipitated from the aqueous solution by alcohol; the solution is also precipitated by ferrocyanide of potassium but not by alkalis. (Fresenius.)—The brownish yellow solution of ferric hydrate in [excess of ?] the aqueous acid, gradually loses its colour by conversion into ferrous salt, both in the air and in closed vessels. (Walchner.)

Ammonio-ferric Racemate.—The above solution of ferric hydrate in the aqueous acid, forms with ammonia a clear mixture, which, when evaporated, deposits granules very easily soluble in water, and containing a large quantity of ammonia. (Walchner.)

Potassio-ferric Racemate.—The aqueous solution of the acid potash-salt digested with ferric hydrate, yields a red-brown filtrate which deposits a basic salt on evaporation.—*a.* This basic salt is a light yellow powder, which chars and swells up in the fire, leaving an alkaline ash; it is almost insoluble in water, but dissolves in cold potash-ley, forming a dark green liquid which yields a copious brownish green precipitate when heated.—*b.* The liquid filtered from the yellow powder remains clear when further evaporated, and leaves a brownish-black, crystallo-granular, deliquescent mass; and on dissolving this mass in water, an additional quantity of basic salt is separated, and a brownish yellow, slightly alkaline liquid produced, which is not precipitated by potash, and but slowly and incompletely by yellow or red prussiate of potash. (Fresenius.)

RACEMATE OF COBALT.—1. Recently precipitated protoxide of cobalt forms, with racemic acid, a strongly acid red solution, which, when evaporated, deposits dingy, pale red, crystalline crusts, free acid crystallising out at the same time.—2. A mixture of acetate of cobalt and racemic acid left to evaporate in a warm place, yields the same crusts. (Fresenius.)—Pale red crystalline grains. (Winkelblech.)—The salt dissolves very slowly in water, whether cold or boiling, more readily in racemic acid, whence it is not precipitated by alkalis; still more readily in hydrochloric acid and in potash-ley. The red hydrochloric acid solution forms, with caustic ammonia, potash, or their carbonates, a precipitate which dissolves in excess of the alkali, the liquid, however, soon becoming turbid, and a dingy blue precipitate being formed. The beautiful violet solution of the salt in caustic potash is not altered by boiling, but forms spontaneously after a while, and more quickly on addition of water, a dingy blue precipitate, losing its colour at the same time. (Fresenius.)

Racemate of Cobalt and Potassium.—The beautiful red neutral solution of the recently precipitated protoxide in warm aqueous racemate of potash, becomes turbid by evaporation, and deposits a pale red crystalline crust, from which the potash cannot be completely extracted by washing. The crust dissolves sparingly in water, easily in racemic acid, or in potash. (Fresenius.)

RACEMATE OF NICKEL.—The aqueous solution of acetate of nickel mixed with racemic acid and evaporated, forms four-sided needles of a

beautiful green colour. These crystals effloresce very slowly in dry air at ordinary temperatures, quickly at 100°. They dissolve very sparingly in water, even at a boiling heat, more readily in racemic acid, still more readily in hydrochloric acid, whereupon a small quantity of carbonate of potash produces a precipitate which redissolves in a larger quantity. With potash-ley the salt forms a green solution which becomes turbid when heated and does not recover its transparency on cooling. (Fresenius.) In a hot solution of carbonate of soda, it dissolves abundantly and with evolution of carbonic acid, forming a liquid which solidifies in a jelly on cooling. (Werther.)

	<i>Needles.</i>		Fresenius.
2 NiO	75 25·25 25·47
C ² H ⁴ O ¹⁰	132 44·45	
10 HO	90 30·30	
<hr/>			
C ² H ⁴ Ni ² O ¹² + 10Aq.	297 100·00	

Racemate of Nickel and Ammonium. — The aqueous solution of acid racemate of ammonia yields, by digestion with excess of carbonate of nickel, and filtration, a green liquid; and on evaporating this liquid, green flakes are deposited, from which the ammonia cannot be completely extracted by washing. (Fresenius.)

CUPROUS RACEMATE. — The aqueous acid exposed to the air in contact with copper, deposits, after several days, a greenish blue cupric salt, and if then evaporated, yields white oblique rhombic prisms which dissolve pretty readily in water, and form a yellow precipitate with potash. (Walchner.)

CUPRIC RACEMATE. — 1. The free acid added to a solution of cupric sulphate throws down at first only a few grains, but gradually the whole of the copper. (John.) If the solutions are mixed hot and concentrated, bluish green tables are formed after a while. (Werther.) — 2. A dilute solution of cupric acetate mixed with free racemic acid, forms light blue four-sided needles. (Fresenius.) — 3. Neutral alkaline racemates precipitate cupric salts (Walchner), forming a siskin-green crystalline powder. (Werther.) — The needles (2) are permanent in the air; effloresce at 100°; dissolve very sparingly in cold, somewhat more freely in boiling water, readily in hydrochloric acid. The solution acquires a fine blue colour when mixed with potash, but is not decolorised thereby even on boiling. (Fresenius.) — The green powder (3) is not much more soluble in water than cupric tartrate; it dissolves readily in caustic potash or soda, but in the carbonates only when heated. (Werther.)

	<i>Needles (2) dried over oil of vitriol.</i>		Fresenius.
2 CuO	80 32·26 31·75
C ² H ⁴ O ¹⁰	132 53·22	
4 HO	36 14·52	
<hr/>			
C ² H ⁴ Cu ² O ¹² + 4Aq.	248 100·00	

Potassio-cupric Racemate. — The sky-blue neutral solution obtained by saturating a warm aqueous solution of acid racemate of potash with cupric carbonate, deposits, when evaporated over oil of vitriol, blue crusts destitute of crystalline structure; they are but sparingly soluble in water, even at the boiling heat, and cannot be freed from potash by washing. (Fresenius.)

Basic Sodio-cupric Racemate. — a. When soda-ley is saturated with cupric racemate (3) stirred up with water, and absolute alcohol carefully added so as to form a layer on the top, light blue tables are formed at the bottom of the vessel, and deep-blue needles at the contact-surface of the two liquids. The tables may be recrystallised by dissolving them in hot water and pouring a layer of alcohol on the surface of the liquid. They dissolve sparingly in cold, more readily in hot water. The solution may be boiled for a long time without decomposition; it is not decomposed by soda in the cold even after the lapse of several weeks; but when boiled with soda, it deposits cuprous oxide. (Werther.)

		Werther.	
		tables.	needles.
2 NaO	62.4	18.01	17.92
2 CuO	80.0	23.09	22.98
C ³ H ³ O ¹⁰	132.0	38.11	37.81
8 HO	72.0	20.79	21.54
<hr/>		<hr/>	
2CuO, C ³ H ³ Na ² O ¹² + 8Aq.	346.4	100.00	100.25

b. Werther once obtained by the same mode of preparation with alcohol, dark blue rectangular octohedrons, which gave off 19.93 p. c. water at 100°.

c. The dark blue solution obtained, with evolution of carbonic acid, by boiling cupric racemate with aqueous carbonate of soda, yields both on addition of alcohol, and by evaporation, a light blue powder which gives off 3.88 p. c. water at 100°, and dissolves slowly in cold, but readily in hot water, forming a neutral liquid which neither crystallises nor decomposes when evaporated. (Werther.)

		Werther.	
		Octohedrons b.	Light blue powder c.
NaO	24.36	10.78	
CuO	11.05	34.24	
C ³ H ³ O ¹⁰			
HO	19.93	3.88	

MERCUROUS RACEMATE. The acid forms with mercurous nitrate a white precipitate which blackens on exposure to light. (Walchner.) The snow-white, heavy powder acquires a greyish brown colour when exposed to the sun for a few minutes: it is insoluble in water and in racemic acid, but dissolves readily in nitric acid, forming a liquid which is precipitated light grey by ammonia, olive-green by carbonate of potash in the cold, and black on boiling. (Fresenius.)

RACEMATE OF SILVER. — On adding a hot and moderately strong solution of acid racemate of ammonia to nitrate of silver heated to 80°—85°, till the precipitate begins to become permanent, the liquid yields on cooling, dazzling white crystalline scales, having a lustre like that of polished silver, a sp. gr. of 3.7752 at 15°, and less soluble in water than the tartrate. (Liebig & Redtenbacher, *Ann. Pharm.* 38, 133.)

		Liebig & Redtenbacher.		Liebig (<i>Ann. Pharm.</i> 26, 133.)
		Dried.		
2 Ag.	216	59.34	59.29	59.14
C ³ H ³ O ¹²	148	40.66		
<hr/>		<hr/>		<hr/>
C ³ H ³ Ag ² O ¹²	364	100.00		

Paratartralic Acid.

E. FREMY. *Ann. Chim. Phys.* 68,378; also *Ann. Pharm.* 39, 161; also *J. pr. Chem.* 16, 339.

Pulverised racemic acid is heated in a porcelain dish to a temperature somewhat above 200° till it melts, removed from the fire while yet perfectly fluid and colourless; dissolved in water; the solution saturated with carbonate of baryta, and filtered from racemate of baryta; and the filtrate decomposed by the proper quantity of sulphuric acid.

The acid is colourless; is reconverted by water into racemic acid; deliquesces in the air; is, in the hyp. anhydrous state, = C⁸H⁴O¹⁰, and saturates 1½ At. base. It forms with all the alkalis, soluble salts, which are reconverted by water into racemates. The baryta-salt contains 43·2 p. c. baryta, the lime-salt 21·1 p. c. lime.

The lead-salt contains:

	Fremy.
PbO	50·07
C	18·00
H	1·53
O	30·40
	100·00

Paratartrelic Acid.

FREMY. *Ibid.*

Produced from paratartralic acid by continued fusion; prepared like tartrelic acid. Exactly like the latter, and converted into racemic acid under the same circumstances as tartrelic acid into tartaric. May likewise be regarded, in the hypothetical anhydrous state, as C⁸H⁴O¹⁰, but saturates only 1 At. base. The baryta-salt contains 36·04 p. c. and the lime-salt 17·4 p. c. of alkali. (Fremy.)

	<i>Lead-salt.</i>		Fremy.
PbO	43·20	to	48·43
C	22·99	,,	19·26
H	1·91	,,	1·59
O	31·90	,,	30·72
	100·00	,,	100·00

Anhydrous Racemic Acid.

FREMY. *Ibid.*

Racemic Anhydride, Traubenanhydrid, wasserfreie Traubensäure, Acide paratartrique anhydre.

By heating racemic acid till it froths and solidifies.

Resembles tartaric anhydride; likewise forms a jelly with water, and has a slightly sour taste.

In contact with water, it is gradually converted into paratartrelic, paratartralic, and racemic acid successively. (Fremy.)

				Fremy.
8 C	48	...	36·36 37·14
4 H	4	...	3·03 3·09
10 O	80	...	60·61 59·77
C²H²O²				132
			100·00 100·00

Racemomethylic Acid.



GUÉRIN-VAËRY. (1836.) *Ann. Chim. Phys.* 62, 77; also *Ann. Pharm.* 22, 252; also *J. pr. Chem.* 9, 376.

Methyltraubensäure, Methylentraubensäure, Paramethylenweinsäure, Acide paratartraméthyllique.

Formation and Preparation, as for tartromethylic acid (p. 338).

Properties. Right rectangular prisms, passing, by truncation of the lateral edges, into rhombic prisms. Inodorous, having a sour, not sweet taste.

				Crystallised.	Guérin.	Dumas & Piria.
10 C	60	...	34·68 35·08 35·15	
9 H	9	...	5·20 5·41 5·10	
13 O	104	...	60·12 59·51 59·75	
C¹⁰H²O¹² + Aq.				173	100·00	100·00
			100·00 100·00 100·00	

Decompositions. The acid, when subjected to dry distillation, or when burnt, exhibits the same phenomena as tartromethylic acid. By boiling with water, it is resolved into wood-spirit and racemic acid, but not so readily as racemovinic acid; and its aqueous solution, when left to evaporate freely, yields the crystals in their original state.

Combinations. The acid dissolves very easily in cold, and in all proportions in boiling *Water*.

Racemomethylate of Potash. — Obtained like the tartromethylate. Right prisms, colourless and inodorous. In vacuo over oil of vitriol they give off 4·25 p. c. water. They soften at 100°, melt at 150°, and yield at 200° the same products as tartromethylate of potash. By continued boiling with water, they are resolved into wood-spirit and acid racemate of potash. They dissolve in hot water more readily than in cold, but are insoluble in wood-spirit and in 95 p. c. alcohol.

				Crystals.	Guérin.
KO	47·2	...	22·35 22·25	
10 C	60·0	...	28·41 28·37	
8 H	8·0	...	3·79 3·89	
12 O	96·0	...	45·45 45·49	
C¹⁰H⁷KO¹² + Aq.				211·2	100·00
			100·00 100·00	

An excess of the acid forms, with aqueous *Potash*, an amorphous pulverulent precipitate, soluble in a larger quantity of water.

Similarly, an excess of acid produces, with *Soda-ley*, a granular precipitate, soluble in a large quantity of water.

precipitate soluble in excess of acid. The neutral salt is obtained like the tartromethylate. Colourless, bitter, oblique rhomboïdal prisms. Angles of the lateral edges = 119° and 61°; inclination of the base to the two lateral edges = 113° and 87°. [There is a figure wrong here.] The crystals effloresce in the air, giving off 3 At. water out of the 4 At. which they contain, and leaving a residue which gives off 38 p. c. more water in a dry vacuum. They soften at 60°; give off vapours at 100°, which condense in beautiful crystalline laminæ, not consisting of methylic oxalate; these laminæ melt at 105°, boil at 120°, and are converted at 130° into a transparent colourless liquid, which turns yellow at 175°, and at 205° yields a distillate, consisting of water, wood-spirit, methylic acetate, and a crystalline substance apparently identical with the above. The effloresced salt yields this crystalline sublimate only at 130°, and does not emit strong fumes till it is heated to 140°. The salt dissolves in hot water more readily than in cold, is insoluble in wood-spirit, and in 95 p. c. alcohol.

	<i>Effloresced.</i>			<i>Guérin.</i>	
BaO	76·6	31·83	31·47
10 C	60·0	24·94	24·50
8 H	8·0	3·33	3·38
12 O	96·0	39·90	40·65
<hr/>					
$C^{10}H^7BaO^{12} + Aq.$	240·6	100·00	100·00

The aqueous acid forms, with *strontia-water*, a precipitate which is not soluble in excess of acid, but dissolves in a large quantity of water; and with *lime-water*, delicate needles, insoluble in excess of acid.

It dissolves *zinc* and *iron* with evolution of hydrogen.

From neutral or basic acetate of *lead*, and from a concentrated solution of nitrate of *silver*, it throws down flakes insoluble in excess of acid.

Racemomethylic acid dissolves readily in *wood-spirit* and in *alcohol*, sparingly in *ether*. (Guérin.)

Racemovinic Acid.



GUÉRIN-VARRY. (1836.) *Ann. Chim. Phys.* 62, 70; also *Ann. Pharm.* 22, 245; also *J. pr. Chem.* 9, 372.

Weintraubensäure, Aethertraubensäure, Acide paratartrovinique.

Formation and Preparation. In general, similar to that of tartrovinic acid. As, however, racemic acid is less soluble in alcohol than tartaric acid, it is necessary to use 4 pts. of absolute alcohol to 1 pt. of racemic acid. The liquid must also be gently boiled in the retort, with cohobation, till the solution evaporated to a syrup no longer yields any deposit on cooling. It is then to be diluted with water, and saturated with carbonate of baryta; the filtrate evaporated in an open vessel at 50° to 60°; and the crystallised baryta-salt decomposed by sulphuric acid, just as in the preparation of tartrovinic acid.

Properties. Colourless oblique rhombic prisms, whose base is less obliquely inclined to the lateral edges than that of the crystals of

tartrovinic acid. Inodorous, with a sour taste, and sweeter even than tartrovinic acid.

	Crystals.		Guérin.
12 C	72	38·50	38·66
11 H	11	5·88	5·92
13 O	104	55·62	55·42
<hr/>			
C ¹² H ¹⁰ O ⁴ + Aq.	187	100·00	100·00

Decompositions. The acid burns with a flame like that of tartrovinic acid; its decompositions by dry distillation, by treatment with nitric or sulphuric acid, and by boiling with 40 pts. of water, are likewise the same as those of tartrovinic acid.

Combinations. The acid dissolves very easily in water, and is highly deliquescent.

The *Racemovينات*, or *Paratartrovينات*, resemble the tartrovينات in most respects, but form less beautiful crystals; and these crystals contain a larger quantity of water of crystallisation, which, however, is given off in a dry vacuum, so that the residual salts agree in composition with the dry tartrovينات.

Racemovinate of Potash. — Obtained in the same manner as the tartrovininate. Colourless, four-sided and apparently square prisms, truncated at the terminal edges (*compare* Prevostaye, *N. Ann. Chim. Phys.* 3, 140). The crystals have the taste of tartrovininate of potash. Give off 7·65 p. c. water in a dry vacuum.

	Crystals.		Guérin.
KO	47·2	20·15	19·95
C ¹² H ⁹ C ¹¹	169·0	72·16	
2 HO	18·0	7·69	7·65
<hr/>			
C ¹² H ⁹ KO ¹² + 2Aq.	234·2	100·00	

The acid added in excess to an aqueous solution of potash precipitates a fine powder.

Racemovinate of Soda. — The acid forms, with aqueous soda, even when the latter is in excess, a precipitate which is insoluble in cold water, and increases on adding the acid in excess.

Racemovinate of Baryta. — *Preparation, vid. sup.* — Small white needles united in nodules; they give off 6·95 p. c. water in a dry vacuum, dissolve in hot water much more readily than in cold, are insoluble in absolute wood-spirit, and in 95 per cent. alcohol.

	Crystals.		Guérin.
BaO	76·6	29·06	28·74
12 C	72·0	27·32	27·62
11 H	11·0	4·17	4·24
13 O	104·0	39·45	39·40
<hr/>			
C ¹² H ⁹ BaO ¹² + 2Aq.	263·6	100·00	100·00

Strontia-water forms, with the acid, a precipitate which dissolves in excess of that acid; *lime*-water, a precipitate, insoluble in racemovinic but soluble in nitric acid.

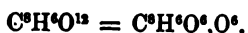
The dilute acid dissolves *zinc* and *iron*, with evolution of hydrogen. It forms a white precipitate with neutral acetate of *lead*.

precipitate consisting of delicate white needles.—2. The concentrated solution of the potash or baryta-salt, added to solution of nitrate of silver, likewise throws down needles, which, after being washed in the dark with cold water, and dried below 50°, give off nothing in vacuo over oil of vitriol; turn red and afterwards brown when exposed to light; decompose at 100°, even under water; and are sparingly soluble in water.

				Guérin.
12 C	72	...	25·26 26·93
9 H	9	...	3·16 3·31
Ag	108	...	37·89 37·70
12 O	96	...	33·69 32·06
<hr/>				
C ¹² H ⁹ AgO ¹²	285	...	100·00 100·00

Racemovinic acid dissolves very readily in *alcohol*, but is insoluble in *ether*. (Guérin.)

Antitartaric Acid.



PASTEUR. *N. Ann. Chim. Phys.* 24, 442; 28, 56. — *Compt. rend.* 28, 477; 29, 297. — BIOT'S Report upon PASTEUR: *Compt. rend.* 29, 433; *N. Ann. Chim. Phys.* 28, 99.

Lavoracemic acid, Lavotartaric acid.

Racemic acid may be regarded as the indifferent compound of tartaric acid with an equal quantity of another acid, viz. *Antitartaric acid*, which agrees exactly with tartaric acid in most of its properties, but with regard to crystalline form, thermo-electricity, and action upon polarised light, exhibits diametrically opposite characters, these characters completely neutralising one another when the two acids are combined in the form of racemic acid.

Racemic acid, and most of its salts, crystallise from their aqueous solutions unaltered; but on evaporating and cooling a solution of racemate of soda and ammonia, or of racemate of soda and potash, we obtain, instead of a double racemate, equal weights of two kinds of crystals, which have the same form, the one being, in fact, the exact reflected image of the other, but exhibit certain hemihedral faces, which in one kind of crystal (identical with that of tartrate of soda and ammonia, or of soda and potash), are situated to the right, and in the other kind, which may be called antitartrate of soda and ammonia or potash, to the left, when the crystal is held in the same position before the face. Each of these two kinds of crystals dissolved by itself in water produces rotation to the right or to the left, and when added to dilute solutions of lime-salts, throws down tartrate or antitartrate of lime, but only after some time; but the united solution of the entire mass of crystals, as also the mother-liquor, exhibits no rotatory power, behaves like racemate of potash, and when added to lime-salts, immediately throws down an amorphous powder, or delicate laminae. The two kinds of crystals are elected out by examining the position of their hemihedral faces, and

purified, each for itself, by recrystallisation, the mother-liquor retaining the small quantity of racemate, which, as it is impossible to effect a complete separation of the two kinds of crystals by mechanical selection, has been reproduced from the two opposite salts when redissolved in water.

When the crystals thus purified, whose hemihedral faces lie to the right, are dissolved in water, the solution precipitated by nitrate of lead, and the washed precipitate decomposed by dilute sulphuric acid, *Dextroracemic acid* is obtained, which, from all experiments made with it, appears to agree in every respect with tartaric acid. — By applying the same treatment to those crystals whose hemihedral faces are situated to the left, we obtain *Antitartaric* or *Lavoracemic acid*.

The separation of the two acids may likewise be effected by means of the compounds of racemic acid with cinchonidine and chinicine. From a solution of cinchonidine in racemic acid, antitartrate of cinchonidine crystallises out, first at a certain degree of concentration; from a solution of racemate of chinicine, the tartrate crystallises first.

Properties. The crystals of antitartaric acid agree exactly in appearance, form, magnitude of angles, specific gravity (1.75), composition, solubility in water, &c., with tartaric acid, with exception of the three following physical properties.

1. *Crystalline Form*: When a crystal of tartaric or antitartaric acid (*Fig.* 109) is held towards the observer in such a position that the *i*-face shall be opposite to the eye, and below *i* shall be the *f*-face (concealed in the figure), above *i* the *e*- and *t*-faces, and right and left of *i* the *a*-faces, then, in the crystal of tartaric acid, there will be found two other faces, leading to an irregular tetrahedron, the upper between *a*, *i*, *e*, and *t*, the lower between *a*, *i*, and *f*, which two faces are wanting to the left of *i*; in the crystals of antitartaric acid, on the contrary, these two faces occur on the left, but are wanting on the right. Sometimes the faces which are usually deficient are found in the crystals of both acids; but less developed.

2. *Thermo-electricity*: During the cooling of a heated crystal of tartaric acid, positive electricity appears on the right-hand side; but antitartaric acid, under the same circumstances, exhibits positive electricity on the left side.

3. *Circular Polarisation*: Antitartaric acid dissolved in water at a given temperature and a given degree of concentration, turns the plane of polarisation to the left, to the same amount as tartaric acid turns it to the right. Boracic acid increases this rotatory power of antitartaric acid to the left exactly in the same degree as that of tartaric acid to the right. (Biot, p. 27.)

Racemic acid, on the contrary, and all its salts form homohedral crystals which do not exhibit either thermo-electricity or rotatory power.

Crystallised antitartaric acid contains 31.90 p. c. C, 4.02 H, and 64.08 O.

When equal parts of antitartaric and tartaric acid (the latter either the ordinary acid or that prepared from racemic acid) are mixed in concentrated solution, great heat is evolved, and racemic acid produced, the crystallisation of which causes the mixture to solidify.

in specific gravity, double refraction, composition, solubility, &c., but they likewise, though with similar crystalline forms and equal angles, exhibit opposite hemihedry, thermo-electricity and rotation. For the peculiar relation of the lime-salt dissolved in hydrochloric acid towards polarised light, see that salt. Equal parts of the antitartrate and tartrate of the same base dissolved in water combine immediately and form a racemate.

Neutral Antitartrate of Ammonia generally forms the same crystals with the same angles as the tartrate, only with opposite hemihedry. *Fig. 89*, with easy cleavage parallel to *i*. In tartrate of ammonia, there occur to the right of *m*, first two hemihedral faces, then the two *a*-faces; whereas to the left of *m*, the two *a*-faces present themselves immediately; in antitartrate of ammonia, the arrangement of the faces is the reverse. — The crystals of the latter contain 26.3 p. c. C and 6.6 H, and are therefore, like the tartrate, = $C^2H^4(NH^4)_2O^{12}$. Its aqueous solution produces a rotation to the left as strong as that produced by tartrate of ammonia to the right. — A solution strongly supersaturated with ammonia, sometimes deposits irregular tetrahedrons, which, when taken out of the mother-liquor, become opaque in the interior. [Respecting the indices of refraction, &c. of this and the two following salts, *vid. Sénarmont, N. Ann. Chim. Phys.* 33, 391; *Pogg.* 86, 35; *abstr. Compt. rend.* 33, 447; *Jahresber.* 1851, 161.]

Antitartrate of Soda and Ammonia. — *Preparation* (*comp.* p. 365). — 1 pt. of racemic acid is neutralised with carbonate of soda and 1 pt. with ammonia, the mixture concentrated, and then either left to evaporate freely or cooled, whereupon it yields the two kinds of crystals in exactly equal quantities, whether the quantity of mother-liquor which remains be large or small. The resulting crystals, which resemble those of Rochelle salt (*Fig. 80*), exhibit two additional faces, one below the other; *y* and *yy*, between *p* and *m*. Moreover, in the crystals of tartrate of soda and ammonia, there occurs a truncation-face between *p* and *u* on the right side (as well as diametrically opposite), and in those of antitartronic acid on the left (sometimes the oppositely situated faces are likewise present, but less developed). It is by this character that the difference of the two crystals is recognised, and their separation effected, after they have been freed from the mother-liquor by pressure between paper. As it is not possible to effect a very complete separation of crystals which have grown together, they must be dissolved in the heated mother-liquor, the ammonia being replaced as it evaporates, whence, after a few days, they are deposited separately, provided the solution is not too concentrated. The picking out of the crystals is best performed in the morning, because, as the temperature rises, the hemihedral faces are rendered less distinct by partial solution of the crystals. The selected crystals are purified by recrystallisation from water, racemate of soda and ammonia then remaining in the mother-liquor, and separating into the two kinds of crystals on further evaporation. The specific gravity of the crystals (like those of tartrate of soda and ammonia) is 1.576. They dissolve (exactly like the tartrate) in 3.74 pts. of water at 0°.

Antitartrate of Soda and Potash. — May be prepared in the same manner, or by saturating antitartronic acid half with soda and half with potash. Isomorphous with the preceding salt, and also, with exception of the oppositely placed hemihedral faces, with Rochelle salt. The first mode of preparation sometimes yields individual homohedral crystals,

some of which are found (by the reaction with lime-salts) to be racemates (or mixtures of tartrate and antitartrate) while others behave like one or the other of these salts.

Antitartrate of Lime. — Antitartrate of ammonia, or one of the above-mentioned double salts, mixed with a dilute solution of a lime-salt, deposits, after a while, small, hard, brittle, shining rhombic prisms, having certain perfectly homohedral truncations by which they may be converted into octohedrons. They contain 14·8 p. c. C, 4·69 H, therefore 8 At. water of crystallisation. They agree exactly, in form, solubility, &c., with the crystals of tartrate of lime, which are likewise perfectly homohedral. When mixed with the latter, they immediately form racemate of lime. Their solution in hydrochloric acid turns the plane of polarisation of a luminous ray to the *right*, whilst that of tartrate of lime in hydrochloric acid turns it to the *left*. A dilute solution of a lime-salt precipitated with antitartrate of ammonia often yields at first tufts of needles having a silky lustre, and likewise containing 8 At. water of crystallisation; but these when left to stand till the next day, are converted into separate octohedrons.

A mixed solution of antitartrate and tartrate of soda and ammonia mixed with a dilute solution of a lime salt, instantly forms a precipitate of racemate of lime.

Ammonio-antimonio Antitartrate. — The solution yields at first tetrahedrons perfectly similar to those of the corresponding tartrate (p. 298), then, by evaporation of the mother-liquor, right rhombic prisms containing 14·05 p. c. C, and 3·49 H, therefore 4 At. water of crystallisation, which is more than the tetrahedrons contain; the rhombic crystals are truncated on two oppositely situated edges between *p* and *u*, whereas the right rhombic prisms of the corresponding tartrate possess the oppositely placed truncation-faces.

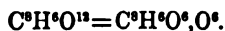
Potassio-antimonio Antitartrate. — Transparent, colourless, shining crystals, having exactly the appearance of tartar-emic, but likewise with an opposition in the alternate development of the *a*-faces. For the figure see Pasteur's memoir. The specific gravity of the crystals is 2·477 (while that of the crystals of tartar-emic is 2·557); they contain 14·45 p. c. C and 1·47 H, and their aqueous solution turns the plane of polarisation of a luminous ray to the left, as much as an equally strong solution of tartar-emic turns it to the right. (Pasteur.)

¶ The exact similarity of tartaric and antitartaric acid, exhibited in the compounds just described, exists only so long as these acids are combined with optically inactive substances. Their compounds with optically active bodies exhibit, on the other hand, neither similar composition nor equal solubility; neither are they similarly affected by rise of temperature. In many instances, indeed, the one acid is capable of forming compounds which cannot be obtained with the other. Thus, acid tartrate of ammonia combines in equal numbers of atoms with optically active acid malate of ammonia (p. 213); but acid antitartrate of ammonia does not form any such compound. — The compound of antitartramide with optically active malamide is much more soluble than the corresponding compound of tartramide, and differs from it in crystalline form (p. 345). — Asparagine forms a beautifully crystalline compound with tartaric acid, but with antitartaric acid only a syrupy, non-crystallising liquid. — Similar differences are observed in the compounds of the

contains 11.6 water, gives off its water and becomes coloured at 100°, and dissolves readily in absolute alcohol; whereas the neutral antitartrate contains only 2 At. water, and though it likewise gives off its water at 100°, and from that point upwards exhibits the same composition as the tartrate, can nevertheless support a temperature of 140° without becoming coloured; it is also but sparingly soluble in absolute alcohol.—The tartrates and antitartrates of brucine also differ in crystalline form, solubility, &c.—The corresponding salts of strychnine contain equal quantities of water of crystallisation, but differ in the force with which they retain their water, also in form and in solubility.

The rotatory powers of the two opposite acids are altered in an equal degree by combination with an optically inactive substance, such as potash; but combination with an active substance, such as cinchonine, increases the rotatory power of the one acid while it diminishes that of the other, and if its own optical power be sufficiently great, may even reverse it. (Pasteur.)

¶. Inactive Tartaric Acid.



PASTEUR. *Compt. rend.* 37, 162; *Ann. Pharm.* 88, 212; *Chem. Soc Qu. J.* 6, 277.

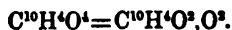
Obtained from ordinary tartaric or antitartritic acid by the same process as artificial racemic acid, viz., by heating the tartrate or antitartrate of cinchonine. When the racemic acid thereby produced has been precipitated as a lime-salt, the liquid, if immediately filtered, deposits, after 24 hours, crystals of inactive tartrate of lime, from which the acid may be obtained by the action of sulphuric acid. The formation of the inactive tartaric acid takes place at the expense of the racemic acid previously formed; for, when racemate of cinchonine is kept for some hours at 170°, a large proportion of the racemic acid is converted into inactive tartaric acid.

Inactive tartaric acid is identical in composition with ordinary tartaric acid, and resembles it in all its properties, excepting that it has no action upon polarised light. It is distinguished from racemic acid by not being divisible into two oppositely active acids. It is crystallisable, and forms salts quite equal in beauty to the tartrates and racemates. (Pasteur.) ¶.

COMPOUNDS CONTAINING 10 AT. CARBON.

FURFENE-SERIES. $C^{10}H^6$.a. Oxygen-nucleus. $C^{10}H^4O^2$.

Furfurol.



- DÖBEREINER. (1831.) *Schw.* 63, 368. — *Ann. Pharm.* 3, 141; *J. pr. Chem.* 46, 167.
- STENHOUSE. *Ann. Pharm.* 35, 301; also *Phil. Mag. J.* 18, 122. — Further: *Ann. Pharm.* 74, 278; *abstr. Pharm. Centr.* 1850, 625; *Phil. Mag. J.* 37, 226; *Instit.* 1850, 412.
- G. FOWNES. *Phil. Trans.* 1845, 253; also *Ann. Pharm.* 54, 52. — Further: *Pharm. J. Trans.* 8, 113.
- CAHOURS. *N. Ann. Chim. Phys.* 24, 277; also *Ann. Pharm.* 69, 82; also *J. pr. Chem.* 46, 45.

Artificial Oil of Ante, künstliches Ameisenöl.

Formation. 1. By heating sugar with moderately dilute sulphuric acid and peroxide of manganese. (Döbereiner.) — 2. By heating bran (Morson & Fownes) or flour (Stenhouse, Fownes) with moderately dilute sulphuric acid. — When sugar, starch, or saw-dust is distilled with dilute sulphuric acid without manganese, no furfurol is obtained. (Döbereiner.) — Cahours likewise obtained none from pure starch, woody fibre, or gluten with dilute sulphuric acid; and bran distilled merely with water, likewise yielded no furfurol. According to Stenhouse, on the other hand, chips or shavings distilled with dilute sulphuric acid, yield furfurol; also linseed cake, the woody shell of the cocoa-nut, and mahogany. The furfurol obtained from mahogany is very free from resin, and more easily purified than that obtained from other sources. According to Emmet (*Sill. Amer. J.* 32, 140; also *J. pr. Chem.* 12, 120), sugar, starch, gum, and wood, distilled with sulphuric acid, so far diluted as not to exert any carbonising action, yields at 100° , scarcely anything but furfurol; but as soon as the residue blackens, nothing but formic acid is obtained. — F. Fownes likewise obtained only indistinct indications of furfurol by distilling starch with dilute sulphuric acid, and from recently washed linen, not a trace. He is of opinion that the source of the furfurol is to be found in the matter which lines the interior of the vegetable cells, called by Payen, *matière incrustante*. — 3. By heating bran with a very strong solution of chloride of zinc. The greater the quantity of starch in the bran, the smaller is the quantity of furfurol obtained. Pure starch and pectin distilled with chloride of zinc, do not yield furfurol. Bran distilled with chloride of calcium does not yield furfurol, but possibly

4. Furfurol is likewise found among the products of the dry distillation of sugar. (Völckel, *Ann. Pharm.* 85, 59.) ¶.

Preparation. 1. One part of sugar is distilled with 3 pts. of manganese, 3 pts. of oil of vitriol, and 5 pts. of water; the formic acid in the distillate saturated with carbonate of soda; the liquid redistilled; the distillate saturated with chloride of calcium; and lastly, the furfurol distilled off. (Döbereiner.)— 2. One part of wheat-flour or saw-dust is distilled with 1 pt. of oil of vitriol diluted with an equal bulk of water in a copper still, which may be half filled with the mixture, the distillation being continued till the residue begins to char; the distillate, together with about as much water as was at first used, poured back into the still; the liquid redistilled nearly to dryness; the formic and sulphurous acids in the distillate—which is rendered milky by the furfurol—saturated with hydrate of potash, which colours the liquid yellow; one-fourth of the liquid then distilled off; the resulting distillate mixed with a large quantity of chloride of calcium and partially distilled; and this process repeated, if necessary, till the greater part of the oil, which is surmounted by an aqueous solution of itself—is obtained in the free state. By this process, 100 pts. of flour yield 0.52 pts. of furfurol. (Stenhouse.)— 3. Two parts of oatmeal are heated with 2 pts. of water and 1 pt. of oil of vitriol in a still, and the mixture stirred, till the pasty mass has become liquid from formation of dextrin; the liquid then distilled; 1 pt. more of water added as soon as sulphurous acid begins to escape; the distillation continued till sulphurous acid comes off in larger quantity; the whole distillate poured back into the still; half of it poured off; and this half neutralised as in (2), with hydrate of potash, &c. (Fownes.)— 4. Two pts. of bran are distilled in a similar manner with 2 pts. of oil of vitriol and 6 pts. of water: by this process, 100 pts. of bran yield 0.8 pts. of furfurol. (Fownes.) In subsequent experiments, Fownes obtained, by distilling 64 oz. (troy) of wheat-bran with 32 oz. sulphuric acid and an equal volume of water, 1 oz. of furfurol; and from 64 oz. wheat flour, treated in the same manner, about 1½ drms. of impure furfurol.— 5. Six pts. of bran are distilled with 5 pts. of oil of vitriol and 12 pts. of water in a capacious still, till a strong odour of sulphurous acid is emitted, and the distillate partially and repeatedly rectified over chloride of calcium. 100 pts. of bran yield by this process 2.6 pts. of furfurol in all, part of which is held in solution in the watery distillate, but may be precipitated by ammonia in the form of furfuramide. (Cahours.)— 6. To save the repeated rectifications, the first bran distillate may be immediately saturated with ammonia; the mixture set aside for 24 hours in a cool place, and shaken occasionally; the furfuramide which separates distilled with dilute hydrochloric acid not in excess, and the distillate rectified over chloride of calcium. (Döbereiner.)— ¶. 7. According to Stenhouse, the most advantageous process for preparing furfurol is to distil bran with more than half its weight of sulphuric acid previously diluted with 2 pts. of water. Hydrochloric acid may also be used, but it has the disadvantage of distilling over with the oil. To obtain furfurol in large quantity, Stenhouse mixes 32 pounds of wheat-bran with 20 pounds of sulphuric acid, diluted as just mentioned, in a capacious three-necked glazed earthenware Woulfe's bottle (such as are used in the preparation of nitric and hydrochloric acid on the large scale); distils by passing steam into the mixture; neutralises the strongly acid distillate with chalk; rectifies the distillate

salt and redistilling: this process yields from 12 to 13 ounces of crude furfural, containing a considerable quantity of acetone.

Bran and chloride of zinc (in the proportion of 3 to 2½ : 1), in the state of solution strong enough to form a damp mass cohering in lumps, are distilled together, whereupon water passes over first, then furfural, then hydrochloric acid, and lastly a solid fatty mass consisting of margaric acid, with a small quantity of a hydrocarbon. The distillate is strained through linen, neutralised with potash, saturated with common salt, and rectified; and the furfural, after being separated from the water which passes over with it, is dried over chloride of calcium and again rectified. The watery portion of the distillate still contains a little furfural, which may be converted into furfuranide as in (6). Six pounds of bran thus treated yielded from 1 to 2 oz., and sometimes more of furfural; bran containing a larger proportion of starch yielded less. (Babo, *Ann. Pharm.* 85, 100.)

Crude furfural obtained from any of the preceding sources is always contaminated with another aromatic oil, *Metafurfural*, which has a higher boiling point; oxidises very readily; is for the most part converted during the distillation into a brown resin; and when mixed with a few drops of strong sulphuric, hydrochloric, or nitric acid, immediately exhibits a purple colour, a reaction, formerly indicated by Stenhouse and Fownes as characteristic of furfural, erroneously, however, for pure furfural does not exhibit it. Furfural may be freed from metafurfural by repeated rectification; the latter being less volatile, and much more oxidable, remains behind. The purity of the product may be tested by boiling an aqueous solution of the furfural for a few minutes with caustic potash, and treating the dark yellow liquid with excess of sulphuric or hydrochloric acid; if metafurfural is present, a deep red colour is produced; if not, the colour remains unchanged. (Stenhouse.) ¶.

Properties. Colourless oil. (Stenhouse, Döbereiner.) Colourless when recently prepared, but soon turns yellow, even in the dark, and brown when exposed to light; under water these changes take place more slowly. (Fownes.) Refracts light strongly. (Döbereiner.) Sp. gr. 1·1006 at 16° (Stenhouse); 1·168 at 16°. (Fownes.) Boils steadily at 161·7° (Fownes); at 162° (Cahours); at 168°. (Stenhouse.) [*Later determinations:* Sp. gr. 1·1648 at 15·6°. (Fownes.) Boils at 162·8° to 163·3°, in metallic vessels, bar. 29·9 inches (Fownes); at 66°. (Stenhouse.) The lower boiling points found by Cahours and Fownes appear to be due to the presence of acetone. (Stenhouse.)] Volatilises unchanged. Vapour-density = 3·344 (Cahours); 3·49. (Fownes.) Smells like a mixture of the oils of cinnamon and bitter almonds (Döbereiner, Fownes), and has an aromatic taste like that of cinnamon-oil.

			Stenhouse.		Fownes.	Cahours.
10 C	60	62·50	62·34	62·33	62·35	
4 H	4	4·17	4·40	4·29	4·26	
4 O	32	33·33	33·26	33·38	33·39	
C ¹⁰ H ⁴ O ⁴	96	100·00	100·00	100·00	100·00	100·00
			Vol.	Density.		
C-vapour			10	4·1600		
H-gas			4	0·2772		
O-gas			2	2·2186		
Furfural vapour			2	6·6558		
			1	3·3279		

yellow, very smoky name. (Stenhouse.) — 2. When kept under water, it merely turns yellow, but by itself it turns brown in a few hours, and is converted in the course of years into a brown tar, which when distilled with water, gives off the undecomposed portion of the furfural, together with a small quantity of formic acid, and leaves a pitchy residue, insoluble in water, but soluble in potash, and precipitated therefrom by acids. (Fownes.) — 3. With *Chlorine* it merely forms black resinous products. (Cahours.) — 4. Hot *Nitric acid* (even when dilute, according to Cahours), converts it, with violent evolution of nitrous fumes, into oxalic acid. (Fownes.) — Metafurfural is converted by nitric acid into oxypicric or some similar acid. (Stenhouse.) — 5. By sulphuric acid with *Peroxide of Manganese*, or by *Chromic acid*, it is quickly converted into a brown substance. (Cahours.) — 6. The solution of furfural in cold *Oil of Vitriol* decomposes when heated, with formation of sulphurous acid and charcoal. (Fownes.) — 7. Cold *Hydrochloric acid* imparts to it a fine red, hot hydrochloric acid, a dark brown colour. (Stenhouse.) It behaves with strong hydrochloric acid in the same manner as with oil of vitriol. (Fownes.) [Pure furfural is converted by strong hydrochloric or sulphuric acid into a black-brown resin, without previous red colouring; metafurfural is coloured purple by those acids, and also by nitric acid. (Stenhouse, *Ann. Pharm.* 74, 282.)] — 8. It dissolves slowly in cold, more quickly in hot *potash-ley*, and is precipitated therefrom by acids, in the form of a resin. (Fownes.) It is not decomposed by aqueous or alcoholic potash, but when heated with solid hydrate of potash it is converted into a resin. (Stenhouse.) — 9. *Potassium* decomposes it with evolution of gas. (Stenhouse.) — Potassium acts but slowly upon it in the cold, but when heated with it, produces fiery explosion and separation of charcoal. (Fownes.) — 10. With *Ammonia*, furfural forms furfuralamide. (Fownes, p. 376.) — ¶. Other products, not of basic character, are likewise formed. When furfural purified by distillation over lime, was treated with ammonia, and the mother-liquor separated from the furfuralamide evaporated, it deposited long crystalline needles of a black-brown deliquescent substance, which exhibited an acid reaction when dissolved in water, and gave off ammonia on being heated with potash or with lime. In the latter case, a neutral, deliquescent, crystallisable lime-salt was formed, containing an acid not yet examined. (Svanberg & Bergstrand, *J. pr. Chem.* 66, 230.) ¶. — 11. With *Sulphide of Ammonium*, furfural forms thiofurfural. (Cahours, p. 374.) — [Metafurfural does not form any crystalline amide with ammonia, but is converted by that body into a brown resinous mass. (Stenhouse.)]

Combinations. Furfural dissolves pretty abundantly in *Water*, imparting its odour. (Döbereiner & Stenhouse.) — Metafurfural is less soluble. (Stenhouse.) — Furfural dissolves in 12 pts. of water at 15.6°; (Fownes,) in 11 pts. at 13° (Stenhouse).

Furfural dissolves in cold *Oil of Vitriol* with splendid purple-red colour, [without colour when free from metafurfural (Stenhouse),] and is separated from the solution by water. (Fownes.)

It dissolves *Iodine* abundantly, without violent action. (Stenhouse.)

It dissolves in 9 pts. of strong aqueous ammonia at 13.5°. (Stenhouse.)

It dissolves very readily in *Alcohol*. (Stenhouse, Fownes.)

¶. **FUCUSOL.** — Obtained by treating sea-weed, *e. g.* *Fucus nodosus*, *F. vesiculatus*, *F. serratus*, &c. with dilute sulphuric acid, in the same

manner as bran is treated for the preparation of furfural (p. 371, 7). The oil thus obtained contains a large quantity of acetone, which may be removed by washing with water, redistilling at a lower temperature, and rejecting the first portion which passes over. It also contains meta-furfural, or a similar impurity, from which it may be separated by repeated rectification with water, as in the purification of furfural. Lastly, it is dried over chloride of calcium and redistilled. The quantity of fucosol thus obtained from sea-weed, is only about a fourth of that of the furfural obtained from bran. (Stenhouse, *Ann. Pharm.* 74, 284.)

Fucosol resembles furfural in most of its properties. When recently prepared, it is colourless, but turns yellow and brown in a few days, especially when it contains meta-furfural. In the pure state, it may be kept unaltered for a long time in hermetically sealed tubes. Sp. gr. 1.150. Boiling point between 171° and 172°. (Stenhouse.)

							Stenhouse.		
10 C.....	60	62.50	62.19	...	62.59	62.32
4 H	4	4.17	4.43	...	4.59	4.48
4 O	32	33.33	33.38	...	32.82	33.20
C ¹⁰ H ⁴ O ⁴	96	100.00	100.00	...	100.00	100.00

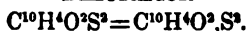
Isomeric with furfural; Stenhouse gives the formula C¹⁰H⁴O⁴; he does not appear to have determined the vapour-density.

Fucosol is much less stable than furfural. Sulphuric acid colours it yellowish brown, hydrochloric acid green, and nitric acid light yellow; if however it contains meta-furfural, all these acids colour it purple-red. Potash-ley colours it yellow at first, but the colour afterwards changes to dark-red. It imparts a deep yellow colour to the skin, and on moistening the yellow spots with aniline, a rose-colour is produced (the same reaction is exhibited by furfural). — With ammonia fucosol forms fucosamide isomeric with furfuramide, and with sulphide of ammonium it forms thio-fucosol isomeric with thiofurfal. (Stenhouse.)

Fucosol dissolves in 14 pts. of water at 13°, and in 12 pts. of strong aqueous ammonia at 13.5°. (Stenhouse.)

Moss (*Sphagnum*) and various species of lichen, *Cetraria islandica*, *Usnea*, *Ramalina*, &c., distilled as above with dilute sulphuric acid, yielded an oil which appeared to be identical with fucosol, inasmuch as it formed with ammonia an amide, which, when treated with boiling potash-ley, formed a difficultly crystallisable base whose platinum-salt crystallised in the same form as that of fucosine (p. 383). Fern (*Pteris aquilina*) yielded an oil which appeared to be intermediate in its properties between furfural and fucosol, the base formed by treating its amide with potash crystallising with facility and in the same form as furfurine, while the platinum-salt resembled that of fucosine. (Stenhouse.)

Thiofurfal.



CAHOURS (1848). *N. Ann. Chim. Phys.* 24, 281; also *Ann. Pharm.* 69, 85; also *J. pr. Chem.* 46, 45.

Formation. By the action of sulphide of ammonium on furfural; or of sulphuretted hydrogen on furfuramide.



and



... treated yields thiofucosol, isomeric with, and similar in every respect to, thiofurfol. (Stenhouse.)

Properties. Yellowish crystalline powder. If the sulphuretted hydrogen be passed quickly through a warm concentrated alcoholic solution of furfamide, the thiofurfol separates in the form of a resin, but with the same composition. (Cahours.)

		Cahours.		Stenhouse.	
		<i>pulverulent.</i>		<i>resinous.</i>	
				<i>Thiofucosol.</i>	
10 C.....	60	53.58	53.71	53.29	53.12
4 H	4	3.57	3.69	3.82	3.95
2 O	16	14.28	14.32	14.72	14.28
2 S.....	32	28.57	28.28	28.17	28.65
<hr/>					
C ¹⁰ H ⁴ O ² S ²	112	100.00	100.00	100.00	100.00

Stenhouse's thiofucosol was precipitated from a cold alcoholic solution of fucosamide.

Decompositions. 1. Thiofurfol melts when heated, and yields a sublimate of C¹⁰H¹⁰O⁴ (*vid. inf.*). [Probably thus:



2. When heated in contact with the air, it diffuses a strong repulsive odour, and burns with a bluish flame, somewhat smoky, and with the odour of sulphurous acid. (Cahours.)

The compound, C¹⁰H¹⁰O⁴, purified by two crystallisations from alcohol, appears in colourless or yellowish, iridescent, long, hard, easily friable needles.

It is violently attacked by nitric acid, and converted into oxalic acid.

It is insoluble in cold water, but dissolves sparingly in hot water, whence it crystallises on cooling; tolerably well in ether; and also in alcohol, especially when warm, forming a solution which slowly turns brown on exposure to the air. (Cahours.)

		Cahours.	
18 C	108	72.97	72.91
4 H	8	5.41	5.27
4 O	32	21.62	21.82
<hr/>			
C ¹⁰ H ¹⁰ O ⁴	148	100.00	100.00

[Doubtless belonging to the ketones (vii, 214) = C¹⁰H¹⁰O⁴ + C⁶H⁴.] Stenhouse obtained a similar compound from thiofucosol, but not in sufficient quantity for analysis.

*Conjugated Compounds of Furfurol.***Furfuramide.**

FOWNES (1845). *Phil. Trans.* 1845, 253; also *Ann. Pharm.* 54, 52.

Formation and Preparation. Furfurol set aside with five times its volume of aqueous ammonia, is converted partially in a few hours, and completely after a longer time, into a yellowish white, bulky, crystalline mass of furfuramide. A mixture of aqueous furfurol and ammonia yields the same compound in a few days, purer and whiter (Fownes):



Properties. The yellowish white crystalline mass, dissolved in hot alcohol, crystallises on cooling in short needles united in tufts. Fusible. Nearly inodorous when dry. (Fownes.)

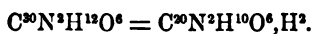
¶. Stenhouse obtained fucusamide from fucusol, in a similar manner to the above; but as fucusol is much less soluble in ammonia than furfurol, a larger quantity of ammonia must be used in the preparation, and the two liquids mixed by frequent agitation. Fucusamide thus obtained resembles furfuramide in appearance and properties, and crystallises from hot alcohol in groups of long needles. ¶¶.

				Fownes.	Stenhouse (mean)
				<i>Furfuramide.</i>	<i>Fucusamide.</i>
30 C.....	180	67·17 66·59 67·11
2 N.....	28	10·45 10·43 10·23
12 H.....	12	4·47 4·51 4·66
6 O.....	48	17·91 18·47 18·00
<hr/>					
C ⁵⁰ N ² H ¹² O ⁵	268	100·00 100·00 100·00

Decompositions. 1. Furfuramide burns with a smoky flame, and leaves a small quantity of charcoal. — 2. When exposed to damp air, or heated with water or alcohol, it is slowly resolved into ammonia and furfurol; acids produce this decomposition instantly. (Fownes.) Fucusamide is much less stable than furfuramide. (Stenhouse.) — 3. Furfuramide boiled with dilute potash-ley, is converted, without the slightest evolution of ammonia, into furfurine. (Fownes.) Similarly, fucusamide into fucusine. (Stenhouse.) — 4. Furfuramide treated with sulphuretted hydrogen yields thiofurfur (Cahours); and fucusamide yields thiofucusol. (Stenhouse.)

Combinations. Furfuramide is insoluble in cold water, but dissolves readily in alcohol and ether. (Fownes.)

Furfurine.



FOWNES. (1845.) *Phil. Trans.* 1845, 253; also *Ann. Pharm.* 54, 52.

STENHOUSE. *Ann. Pharm.* 74, 289.

SVANBERG & BERGSTRAND. — *Oefversigt af Akad. Förhandlingar*, 1854, 309; *J. pr. Chem.* 66, 239.

Formation and Preparation. 1. Dried furfuramide is added to a large quantity of dilute boiling potash-ley; the liquid left to cool slowly after 10 to 15 minutes, whereupon the furfurine which has separated in the form of a yellowish oil solidifies, and the portion remaining in solution crystallises out; the whole of the furfurine collected on a filter, washed with cold water, and dissolved in excess of boiling aqueous oxalic acid, from which impure acid oxalate of furfurine crystallises on cooling; this impure oxalate washed on the filter with cold water, and dissolved in boiling water; the solution boiled for a few minutes with animal charcoal previously purified by hydrochloric acid, then filtered at the boiling heat; the pure white salt which separates on cooling dissolved in boiling water; the solution supersaturated with ammonia, and filtered hot; and the crystals of furfurine which form on cooling washed with cold water. (Fownes.) — ¶. The crude base may also be purified by repeated solution in alcohol and precipitation with water. (Svanberg & Bergstrand.) — 2. Furfuramide is also readily converted into furfurine by heating it for half an hour to 110°–120°. The resulting brown mass dissolved in alcohol, and treated with excess of oxalic acid, yields acid oxalate of furfurine, from which the base may be obtained as above. By this means furfurine may be prepared directly from furfurol, viz., by passing dry ammoniacal gas into furfurol, heated to 110°–120°. The furfurol then turns brown, and in the course of half an hour to an hour, is converted into furfurine. (C. Bertagnini, *Ann. Pharm.* 88, 128.) ¶.

Properties. White soft, silky needles, resembling those of coffeine. Melts considerably below 100°, to a nearly colourless oil, which, on cooling, solidifies to a soft resin, and afterwards to a resinous crystalline mass. Permanent in the air. (Fownes.) When perfectly dry, it remains unaltered on exposure to the air; but when moist, it quickly turns greyish green, yellowish brown, and often red. (Svanberg & Bergstrand.) Inodorous; has but little taste. Has an alkaline reaction, which is particularly strong in the hot aqueous or alcoholic solution. (Fownes.) ¶. When a tolerably strong solution of neutral sulphate of furfurine is heated, the precipitated brown powder (p. 379) separated by filtration, and the filtrate treated with ammonia, furfurine is precipitated, not in the pulverulent or crystalline state, but in the form of a tough coherent mass, which, after a little kneading, becomes brittle and as hard as stone; the recently precipitated mass, when examined by the microscope, exhibits here and there crystalline groups like snow-flakes. Furfurine appears then when heated to pass, like quinine, into another modification. (Svanberg & Bergstrand.) ¶.

<i>Crystals dried in vacuo over oil of vitriol.</i>		<i>Fownes.</i>	
30 C	180	67·17	66·74
2 N	28	10·45	10·23
12 H	12	4·47	4·58
6 O	48	17·91	18·45
<hr/>			
$C^{30}N^2H^{12}O^6$	268	100·00	100·00

Therefore metameric with furfuramide.

Decompositions. 1. Furfurine, when heated in the air, burns with a red smoky flame, and leaves a trace of charcoal. (Fownes.)—2. Aqueous periodic acid decomposes it, with separation of iodine. (Bödeker, *Ann. Pharm.* 71, 64.)

Combinations. Furfurine dissolves in 137 pts. of boiling water, and separates out almost completely on cooling. (Fownes.)

Furfurine-salts.—Furfurine dissolves very readily in dilute acids and neutralises them completely. It expels ammonia from sal-ammoniac at a boiling heat, but at ordinary temperatures is itself precipitated from its combinations with acids, by ammonia, potash, or soda. The salts of furfurine have an extremely bitter taste. They are precipitated white by corrosive sublimate, yellow by bichloride of platinum, but give no precipitate with tincture of galls. (Fownes.)

Furfurine is capable of combining with carbonic acid. (Döbereiner.)

†. *Phosphate of Furfurine.*—*a. Basic.*—A solution of the salt *c*, mixed with a large excess of the alcoholic solution of furfurine, deposits this salt on cooling, in long, oblique, four-sided prisms, which are white and destitute of lustre; anhydrous; permanent in the air; may be heated to 120°—125° without decomposition, but at higher temperatures, behave like the two following salts. They dissolve readily in water and alcohol, but very sparingly in ether. The solutions have an alkaline reaction. (Svanberg & Bergstrand.)

<i>Crystals.</i>		<i>Svan. & Bergs.</i>	
$3(C^{30}N^2H^{12}O^6,HO)$	833·0	92·1	
PO^5	71·4	7·9	7·7
<hr/>			
$(C^{30}N^2H^{12}O^6,HO)^3,PO^5$	904·4	100·0	

b. Neutral.—Obtained by adding 1 At. furfurine dissolved in alcohol to a solution of 1 At. of the salt *c*, and heating the mixture. The filtrate on cooling deposits white shining, oblique four-sided, anhydrous prisms, which in the dry state are permanent in the air. They may be heated to 130°—135° without decomposition, but at higher temperatures behave like the salt *c*. Dissolves readily in boiling water or alcohol, but is nearly insoluble in ether. (Svanberg & Bergstrand.)

<i>Crystals.</i>		<i>Svanb. & Bergs.</i>	
$2(C^{30}N^2H^{12}O^6,HO)$	554·0	87·3	
HO	9·0	1·4	
PO^5	71·4	11·3	12·1
<hr/>			
$(C^{30}N^2H^{12}O^6,HO)^2$ } PO^5	634·4	100·0	

c. Acid.—A boiling alcoholic solution of furfurine, mixed with a large excess of ordinary phosphoric acid, deposits crystals on cooling,

liquor, but if quickly taken out and pressed between paper, retain their silvery lustre on subsequent exposure to the air. — Right four-sided prisms, so short that they appear like thin laminæ. The crystals do not diminish in weight or decompose at 150°; but when more strongly heated, they assume a blackish grey colour, and between 200° and 215°, melt into a black vitreous mass, which dissolves completely in warm alcohol, and then no longer exhibits the reactions of ordinary phosphoric acid. The salt dissolves sparingly in cold, readily in hot water and alcohol, but appears to be insoluble in ether. (Svanberg & Bergstrand.)

<i>Crystals.</i>		Svanb. & Bergs.	
$C^{20}N^2H^{12}O^4, HO$	277.0	75.6
2 HO	18.0	4.9
PO^5	71.4	19.5
<hr/>			
$C^{20}N^2H^{12}O^4, HO$ } PO^5	366.4	100.0
2 HO			

Pyrophosphate of Furfurine. — An alcoholic solution of furfurine, neutralised with pyrophosphoric acid and evaporated in the drying chamber, ultimately yields a glassy crystalline crust, which dissolves readily in water and alcohol, and has a neutral reaction. Gives off 1.5 p. c. water at ordinary temperatures, and 2.14 p. c. more at 100°. Hence if the 1.5 p. c. be regarded as hygroscopic, the salt may be supposed to contain 2 At. water. Between 115° and 120°, it assumes a greyish aspect, apparently from incipient decomposition. (Svanberg & Bergstrand.)

<i>Anhydrous.</i>		Svanb. & Bergs.	
2 $(C^{20}N^2H^{12}O^6, HO)$	554.0	88.6
PO^5	71.4	11.4
<hr/>			
$(C^{20}N^2H^{12}O^6, HO)^2, PO^5$	625.4	100.0
<hr/>			
<i>Hydrated.</i>		Svanb. & Bergs.	
$(C^{20}N^2H^{12}O^6, HO)^2, PO^5$	625.4	97.19
2 HO	18.0	2.81
<hr/>			
$(C^{20}N^2H^{12}O^6, HO)^2, PO^5 + 2Aq.$	643.4	100.00

Metaphosphate of Furfurine? — When strongly ignited phosphate of soda and ammonia was dissolved in water, the solution precipitated by chloride of barium, and the washed metaphosphate of baryta digested for 24 hours with neutral sulphate of furfurine, a filtrate was obtained which had a neutral reaction, but did not yield any crystallisable compound. When evaporated, it left a gummy mass, which became black and glassy when heated. (Svanberg & Bergstrand.)

Sulphate of Furfurine — a. Neutral. — Sulphuric acid saturated with furfurine deposits when evaporated, either by heat or under the exsiccator, a black-brown powder. When hydrochlorate of furfurine is decomposed with sulphate of silver, crystals are deposited from the coloured and acid mother-liquor; but they contain only 0.3 p. c. sulphuric acid, and therefore cannot consist of sulphate of furfurine.

b. Acid. — When furfurine is dissolved in somewhat dilute sulphuric acid, and a slight excess of the acid added after the solution has been warmed, short four-sided prisms are soon deposited, which dissolve readily in water, less readily in alcohol or ether, and least of all in water acidu-

lated with sulphuric acid. The solution has a sour and bitter taste, and is coloured red by strong sulphuric acid. The salt effloresces readily at ordinary temperatures, giving off all its water of crystallisation, amounting to 21.62 p. c. (7 At.) Between 80° and 90° , it loses $\frac{1}{2}$ of its weight, and appears to decompose; at a higher temperature, it cakes together, and then melts into a black mass, which no longer dissolves completely in water. (Svanberg & Bergstrand.)

Dried in a current of air.			Svanberg & Bergstrand.
$C^{50}N^2H^{12}O^4, HO$	277	...	75.68
HO	9	...	2.47
2 SO^2	80	...	21.85

$(C^{50}N^2H^{12}O^4, HO)$ } $2SO^2$	366	...	100.00
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Crystals.			Svanb. & Bergstr.
$C^{50}N^2H^{12}O^6, 2HO$	286	...	66.67
2 SO^2	80	...	18.65
7 Aq	63	...	14.68

$C^{50}N^2H^{12}O^6, 2HSO^4 + 7Aq.$	429	...	100.00	¶.
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Hydrochlorate of Furfurine. — Dilute hydrochloric acid, saturated with the base, yields delicate, silky, neutral needles united in tufts; they retain their lustre when dried in vacuo over oil of vitriol, and dissolve readily in water, less easily in hydrochloric acid. (Fownes.)

Crystals dried in vacuo over oil of vitriol.			Fownes.
30 C	180.0	...	55.83
2 N	28.0	...	8.68
15 H	15.0	...	4.66
8 O	64.0	...	19.85
Cl	35.4	...	10.98

$C^{50}N^2H^{12}O^6, HCl + 2Aq.$ 322.4	...	100.00	100.00
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Perchlorate of Furfurine. — Furfurine dissolved in warm very dilute perchloric acid, yields very long, thin, brittle prisms, having a glassy lustre and a disagreeable, saline, bitter taste; they effloresce at 60° , melt at 150° to 160° , solidifying on cooling to a glassy brittle mass, and explode at a higher temperature. They dissolve readily in water and alcohol. (Bödeker, *Ann. Pharm.* 71, 63.) — The crystals belong to the right prismatic system. Right rhombic prisms, having the angles of the lateral edges = $72^\circ 33'$ and $107^\circ 27'$, the obtuse lateral edges truncated, the acute bevelled; cleavage from one obtuse lateral edge to the other. (Dauber, *Ann. Pharm.* 71, 67.)

Crystals.			Bödeker.
$C^{50}N^2H^{12}O^6, HO$	277.0	...	71.69
ClO^7	91.4	...	23.65
2 HO	18.0	...	4.66

$C^{50}N^2H^{12}O^6, HO, ClO^7 + 2Aq.$	386.4	...	100.00	100.00
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Nitrate of Furfurine. — Transparent, colourless, highly lustrous, hard crystals, which effloresce in vacuo over oil of vitriol, and dissolve readily in water, slowly in nitric acid. (Fownes.) — ¶. Crystallises from

alcoholic solution, in very regularly developed rhombic of considerable size and peculiar lustre; if, however, very strongly used, the crystals, which are at first perfectly transparent and opaque, whereas those obtained from weak alcohol retain and transparency. (Stenhouse.) ¶.

<i>Dried in vacuo.</i>		Fownes.	
30 C	180	54.38	54.33
3 N	42	12.69	
13 H	13	3.93	3.96
12 O	96	29.00	

$C^{30}N^3H^{13}O^6, HO, NO^6$ 331 100.00

Stephens's salt was crystallised from alcohol; Fownes's had efflorescence.

Hydrochlorate of furfurine added to *aqueous mercuric chloride* throws down a white double salt. (Fownes.)

It also forms crystalline double salts with the *chlorides of potassium*, and iridium. (Döbereiner, *J. pr. Chem.* 46, 169.)

Platinum-salt. — Hydrochlorate of furfurine forms with *bichloride of platinum*, a light yellow precipitate, which, after drying, blackens, melts, and froths up strongly, giving *nitrogen gas*, and leaving a difficultly combustible charcoal. (Fownes.) *Bichloride of platinum* is poured into a hot solution of *hydrochlorate of furfurine* in weak alcohol, the double salt separates on cooling as light yellow needles resembling picrate of potash. (Stenhouse.)

		Fownes.	
30 C	180.0	37.96	38.06
2 N	28.0	5.90	
13 H	13.0	2.74	3.00
6 O	48.0	10.12	
Pt	99.0	20.88	20.45
3 Cl	106.2	22.40	

$C^{30}N^2H^{13}O^6, HCl, PtCl^2$ 474.2 100.00

Acetate of Furfurine. — Uncrystallisable or very difficultly crystallisable; very soluble in water. (Fownes.)

Oxalate of Furfurine. — *a. Neutral.* — Bundles of *crystals* easily soluble in water. (Fownes.)

b. Acid. — Thin transparent tables, which retain their luster in *vacuum*, redden litmus strongly, and dissolve very sparingly in water, more readily in warm water. (Fownes.)

<i>Crystals.</i>		Fownes.	
34 C	204	56.98	57.0
2 N	28	7.82	7.7
14 H	14	3.91	4.0
14 O	112	31.29	31.1

$C^{30}H^{14}N^2O^6, C^4H^2O^6$ 358 100.00 100.0

¶ *Mellitate of Furfurine.* — When aqueous mellitic acid is mixed with furfurine, this salt separates after a while in nodular crystals, which by crystallisation are obtained in beautiful plates.

ing to the monoclinic system. The salt gives off 5.7 p. c. water between 100° and 125° , and begins to turn yellow at 130° . (Karmrodt, *Ann. Pharm.* 81, 171.)

Acid Tartrate of Furfurine crystallises from a rather acid solution of furfurine in tartaric acid, in oblique four-sided prisms, which are permanent in the air, and do not give off water at 150° . They give off ammonia when heated with potash. Ammonia added to their solution does not precipitate furfurine. (Svanberg & Bergstrand.) ¶

Furfurine dissolves readily in cold *alcohol* or *ether*, and crystallises when the solvent is evaporated. (Fownes.)

¶. Fucusine. $C^{20}N^2H^{12}O^6$.

STENHOUSE. *Ann. Pharm.* 74, 289.

Formation and Preparation. When pure fucsamide (p. 376) is boiled for 20 minutes, with moderately concentrated potash or soda-ley, it melts, and is converted, without evolution of ammonia, into a slightly brown oil, which solidifies on cooling in the form of a yellowish resin. This substance contains fucusine, but does not yield that base in the crystalline form, even by solution in alcohol or ether. The best mode of obtaining the fucusine from it, is to digest the mass at a temperature a little above its melting point, with nitric acid; cool the liquid till the resin solidifies; decant the solution, and leave it to itself till the nitrate of fucusine crystallises out; purify this salt by recrystallisation from water; and decompose its pure aqueous solution with a slight excess of ammonia. The fucusine then slowly separates in small laminae united in stellate groups. This form of crystallisation distinguishes fucusine from furfurine.

				Stenhouse.
30 C	180	...	67.17	67.30
2 N	28	...	10.45	10.30
12 H	12	...	4.47	4.58
6 O	48	...	17.91	17.82
<hr/>				
$C^{20}N^2H^{12}O^6$	268	...	100.00	100.00

Therefore isomeric with furfurine.

Hydrochlorate of Fucusine. Very soluble; separates from highly concentrated solutions in short flexible needles.

Nitrate of Fucusine. — *Preparation (vid. sup.).* Crystallises from the hot aqueous solution in long prismatic needles united in stellate groups. When crystallised from alcohol, however, it forms large rhombic prisms of great regularity and peculiar lustre. (For details of the crystalline forms of the nitrates of fucusine and furfurine, as determined by Miller, *vid. Ann. Pharm.* 74, 293.) — The crystals obtained from strong alcohol become opaque after a while, but those which separate from a weak alcoholic solution retain their transparency. The salt when heated to 100° quickly becomes coloured, and decomposes.

3 N	42	12.69	31.00
13 H	13	3.93	4.26
12 O	96	29.00	

$C^{30}N^2H^{12}O^6, HO, NO^5$ 231 100.00

Platinum-salt. — When bichloride of platinum is added to a cold aqueous solution of hydrochlorate of fucusine, the double salt separates in the form of a yellow crystalline precipitate; but if the solutions are mixed hot, and especially if a little alcohol is added, broad four-sided prisms are obtained, having two wide and two narrow faces, and differing altogether from the long needle-shaped crystals of the corresponding furfurine-salt (p. 381).

	<i>Dried in vacuo.</i>		Stenhouse.	
30 C	180.0	37.96
2 N	28.0	5.90
13 H	13.0	2.74
6 O	48.0	10.12
Pt	99.0	20.88
3 Cl	106.2	22.40

$C^{30}N^2H^{12}O^6, HCl, PtCl^2$ 474.2 100.00 100.00

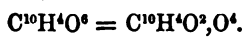
Oxalate of Fucusine. — *a. Neutral.* — Resembles the following salt in external appearance, but is much more soluble.

b. Acid. — When crude fucusine (p. 382) is digested with excess of oxalic acid, and the solution filtered hot, the acid oxalate is deposited in small needle-shaped crystals, which are generally coloured at first, but by repeated crystallisation and the use of animal charcoal, may be obtained in colourless silky needles. Not very soluble in cold water, but dissolves readily in boiling water and in alcohol. The solutions have a distinct acid reaction. (Stenhouse.)

	<i>Dried in vacuo.</i>		Stenhouse.	
34 C	204	56.98
2 N	28	7.82
14 H	14	3.91
14 O	112	31.29

$C^{30}N^2H^{12}O^6, C^4H^2O^8$ 358 100.00 100.00 ¶.

Pyromucic Acid.



HOUTON LABILLARDIÈRE. *Ann. Chim. Phys.* 9, 365; also *N. Tr.* 3, 2, 384.
BOUSSINGAULT. *Ann. Chim. Phys.* 58, 106; also *Pogg.* 36, 78; also
Ann. Pharm. 15, 184.

Brenzschleimsäure, brenzliche Schleimsäure, Acide pyromuictque. — First observed by Scheele (*Opusc.* 2, 114); pronounced by Trommsdorff (*A. Tr.* 17, 1, 59) to be a mixture of succinic and pyrotartaric acid; recognised as a peculiar acid by Houton Labillardière.

Preparation. Mucic acid is subjected to dry distillation; the resulting sublimate and distillate mixed with a fourfold quantity of water; the liquid filtered from the oil thereby separated; the filtrate evaporated — whereupon acetic acid is likewise given off — and cooled till it crystallises; the decanted mother-liquor repeatedly evaporated to the crystallising point; and the entire crop of still yellowish crystals purified by several crystallisations from water, and subsequent distillation at 130° , after which the acid still exhibits a yellow tint, but may be obtained perfectly white by recrystallisation from water. (Houton.) 100 pts. of mucic acid thus treated yield from 5 to 7 pts. of pyromucic acid. (Houton.) — ¶. According to Arppe (*Ann. Pharm.* 87, 238), the acid is most conveniently obtained by evaporating the tarry liquid obtained by the distillation of mucic acid to dryness over the water-bath, and subliming the residue in a porcelain basin covered with a paper cone, as in the ordinary mode of subliming benzoic acid. In the course of a few hours, the pyromucic acid condenses in the cone in the form of elongated crystalline laminæ of dazzling whiteness. ¶¶.

Properties. Crystallised from water: Long white laminæ (Houton); with a pearly lustre (Boussingault); — sublimed: long needles; or, if it first passes over as an oil and then crystallises on further cooling: white crystalline mass (Houton), exhibiting the granular fracture of loaf-sugar. (Boussingault.) The acid melts to an oil at 130° and volatilises at a somewhat stronger heat (above 135° , according to Boussingault), in white fumes having a pungent odour. (Houton.) It is inodorous, tastes very sour, and reddens litmus strongly. (Houton.)

		Houton.		Boussingault.		Malaguti.	
		a.		a. b.		c.	
10 C	60	53.57	52.12	54.0	54.1	54.10	
4 H	4	3.57	2.11	3.9	3.8	3.88	
6 O	48	42.86	45.77	42.1	42.1	42.02	
$C^{10}H^4O^2$	112	100.00	100.00	100.0	100.0	100.00	

a was crystallised from water, and b sublimed; the acid c analysed by Malaguti (*Ann. Chim. Phys.* 60, 200) was obtained by dry distillation of paramucic acid, and sublimed.

Decompositions. The acid burns with flame. (Scheele.) — It is not decomposed by being three times evaporated in contact with nitric-acid. (Houton.) — 2. The potash-salt dissolved in water and gradually mixed with bromine, is violently attacked, with separation of a heavy red oil, and emission of a penetrating odour, like that produced under similar circumstances by citraconate of potash. (Cahours, *N. Ann. Chim. Phys.* 19, 506; also *J. pr. Chem.* 41, 78.) — 3. The acid reduces oxide of silver to a black powder, with evolution of gas. (Stenhouse, *J. pr. Chem.* 32, 262.)

Combinations. With Water. — The acid does not become moist on exposure to the air; it dissolves in 28 pts. of water at 15° (Houton); in 4 pts. of boiling water, whence it crystallises on cooling. (Trommsdorf.)

The *Pyromucates* = $C^{10}H^8MO^4$.

Pyromucate of Ammonia. — The neutral compound gives off part of its ammonia when evaporated, and crystallises readily. (Houton.)

moist in the air; dissolves readily in water and alcohol.
Pyromucate of Soda. — Crystallises with difficulty; becomes slightly moist on exposure to the air; less soluble in alcohol than the potash-salt. (Houton.)

Pyromucates of Baryta, Strontia, and Lime. — Small crystals, which are permanent in the air, dissolve somewhat more readily in hot than in cold water, but are insoluble in alcohol. (Houton.)

	<i>Dry.</i>		Houton.
BaO.....	76.6	42.65	42.2
C ¹⁰ H ³ O ⁵	103.0	57.35
C ¹⁰ H ³ BaO ⁶	179.6	100.00	

The alkaline pyromucates do not precipitate the salts of magnesia, alumina, manganese or cobalt (Houton). According to Trommsdorff, they form a white precipitate with nitrate of *baryta*, crystalline after awhile with acetate of *lime*, white with manganous sulphate, and peach-blossom-coloured with cobaltous sulphate.

Pyromucate of Zinc. — The solution of zinc in warm pyromucic acid, the formation of which is attended with evolution of hydrogen, solidifies in a mass when evaporated. (Houton.)

Pyromucate of Tin. — Nitrate of tin yields a white precipitate with pyromucate of potash. (Houton.)

Pyromucate of Lead. — The free acid and its compounds with alkalis precipitate basic but not neutral acetate of lead (according to Trommsdorff, the soda-salt precipitates nitrate of lead). The hot aqueous acid forms with carbonate of lead a neutral solution, on the surface of which brown, transparent, oily drops form during evaporation, till the entire solution is converted into this oily mass, which consists of undecomposed pyromucate of lead, and on cooling first becomes viscid like pitch, then white, opaque, and hard. (Houton.)

Ferrous Pyromucate. — Iron dissolves in pyromucic acid with evolution of hydrogen, forming an easily soluble salt. (Houton.)

Ferric Pyromucate. — Alkaline pyromucates form with ferric salts a lemon-yellow precipitate (Houton); dingy brown-red (Trommsdorff); greenish black, loose granules (John, *Mag. Pharm.* 9, 292).

Pyromucate of Nickel. — The soda-salt forms an apple-green precipitate with nitrate of nickel. (Trommsdorff.)

Cupric Pyromucate. — Small greenish blue crystals sparingly soluble in water. (Houton.)

Mercurous Pyromucate. — The alkaline pyromucates form a white precipitate with mercurous nitrate. (Houton.)

Pyromucate of Silver. — The solution of silver-oxide in the aqueous acid turns brown when evaporated, and yields white scales of the salt. (Houton.) An aqueous mixture of the lime-salt with neutral nitrate of silver, deposits the salt after a few days; it must then be pressed between paper. (Boussingault.)

		Dried at 125°.		Boussingault.	
10 C	60 27.40	29.91
3 H	3 1.37	1.58
Ag	108 49.31	49.05
6 O	48 21.92	19.46
<hr/>					
$C^{10}H^3AgO^6$	219 100.00	100.00

Pyromucic acid dissolves in alcohol more readily than in water. (Houton.)

Conjugated Compound of Pyromucic Acid.

Pyromucate of Ethyl.



MALAGUTI (1837). *N. Ann. Chim. Phys.* 64, 279; also *Ann. Pharm.* 25, 276; also *J. pr. Chem.* 11, 227.

Pyromucic ether, Bremschleimsaures Aethyloxyd, Ether pyromucique.

Preparation. A mixture of 1 pt. hydrochloric acid, 2 pts. pyromucic acid and 4 pts. alcohol of sp. gr. 0.814, is distilled four or five times, being each time cohobated to one-half, and the last time till the distillate begins to pass over coloured; the distillate then mixed with water, which throws down an oil, solidifying in a few minutes in laminæ; and these laminæ washed on the filter with cold water, pressed between paper, and distilled several times, removing each time the moisture which collects in the neck of the retort at the beginning of the distillation, till the whole distils without leaving any residue in the retort.

Properties. Transparent, colourless, 4-, 6-, and 8-sided laminæ, derived from a rhombic prism; of sp. gr. 1.297 at 20°; unctuous to the touch. The ether melts at 34°, boils between 208° and 210°, under a pressure of 0.756 met. and volatilizes undecomposed and without residue. Vapour density = 4.859. Has a powerful odour resembling that of benzoate of methyl and also that of naphthalin; tastes cooling at first, then transiently bitter and pungent, afterwards agreeably like anise and camphor. Neutral to vegetable colours.

		Malaguti.		
14 C	84 60.00 60.26
8 H	8 5.71 5.86
6 O	48 34.29 33.88
<hr/>				
$C^{14}H^8O^6$	140 100.00 100.00
			Vol.	Density.
C-vapour	14	5.8240
H-gas	8	0.5546
O gas	3	3.3279
<hr/>				
Ether-vapour	2	9.7065
		1	4.8532

Decompositions. The ether is not set on fire by the flame of a candle. — 1. In a stream of dry chlorine gas, the dry ether melts, with great rise of temperature, turns yellow, and is converted into chloropyromucic

evolved, unless moisture is present. — 2. In cold nitric acid, the ether first liquefies and then dissolves with decomposition. — 3. Its solution in cold oil of vitriol or hydrochloric acid decomposes when heated. — 4. The ether is decomposed by aqueous potash or soda, like other compound ethers of the third class. Baryta, strontia, or lime-water forms with the alcoholic solution, a precipitate which dissolves in a small quantity of water. — 5. After keeping for some time, the ether becomes slightly coloured, and then leaves a residue when distilled.

Combinations. Pyromucic ether dissolves very sparingly in water, easily and without decomposition in cold oil of vitriol or hydrochloric acid, and in all proportions in alcohol and common ether. (Malaguti.)

Appendix.

Chloropyromucate of Ethyl.



MALAGUTI (1837). *Ann. Chim. Phys.* 64, 282; also *Ann. Pharm.* 25, 279; also *J. pr. Chem.* 11, 229. — *Ann. Chim. Phys.* 70, 371; also *Ann. Pharm.* 32, 41; also *J. pr. Chem.* 18, 53.

Chloropyromucic ether, Chlor-brenzschleimvinester, Ether chloropyromucique.

Preparation. Chlorine gas is passed at ordinary temperatures over dry pyromucic ether, as long as heat is evolved, and the resulting liquid freed from the excess of chlorine, which colours it yellow, by a current of dry air, and preserved in vacuo, or in well-closed bottles completely filled with it.

Properties. Transparent, colourless syrup, of sp. gr. 1.496 at 19°. Not volatile without decomposition. Has a strong and agreeable odour, like that of calycanthus; excites slowly a persistent, strongly bitter taste; neutral.

				Malaguti.
14 C	84.0	29.83 30.11
4 Cl	141.6	50.28 49.83
8 H	8.0	2.84 2.77
6 O	48.0	17.05 17.29
<hr/>				
$C^{10}Cl^4H^8O^6$	281.6	100.00 100.00

The acid which may be supposed to exist in this ether, but which has not been obtained in the separate, viz., chloropyromucic acid, would be $C^{10}Cl^4H^8O^6$. [Consequently a valerianic acid in whose nucleus part of the H is replaced by Cl and O, = $C^{10}Cl^4H^8O^2, O^4$. — Or might it be a hydrochlorate of chloropyromucic ether = $C^{14}Cl^2H^8O^6, 2HCl$?] Other views are given by Berzelius (*J. pr. Chem.* 14. 356.)

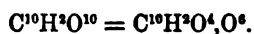
Decompositions. The ether when heated evolves a large quantity of hydrochloric acid, yields but little distillate, and thickens with deposition of charcoal. — 2. It is not affected by chlorine gas at ordinary temperatures, but when heated with it, gives off hydrochloric acid and other products, while the residue becomes continually poorer in chlorine. — 3. When exposed to moist air (or when water is added to it), it becomes milky, with formation of hydrochloric acid, but recovers its trans-

ley becomes coloured, and forms a white coagulated mass, which, when mixed with water and boiled, gives off alcohol and disappears, with formation of a dark-red liquid. From this liquid, sulphuric acid, after a considerable time, throws down yellowish grains, together with a black substance, soluble in potash, but nearly soluble in alcohol; but neither pyromucic nor pyruracemic acid can be afterwards detected in the liquid. — 5. When dry ammoniacal gas is passed through the alcoholic solution of the ether, the liquid becomes heated, sal-ammoniac is formed, together with a small quantity of hydrocyanate of ammonia and a large quantity of charcoal, but no gas is evolved.

Combinations. Chloropyromucic ether dissolves readily in alcohol and common ether. (Malaguti.)

b. *Oxygen-nucleus.* $C^{10}H^8O^4$.

Croconic Acid.



L. GMELIN (1825). *Pogg. Ann.* 4, 37. — *Ann. Pharm.* 37, 58.
LIEBIG, *Pogg.* 33, 90; also *Ann. Pharm.* 11, 182.
HELLER, *J. pr. Chem.* 12, 230; and in the memoirs cited in connection with Rhodizonic acid (p. 398).

Krokonäure, Acide croconique.

Formation. When carboxide of potassium is dissolved in water, the chief product formed is rhodizionate of potash, which, by exposure to the air and evaporation, is converted into croconate of potash, and possibly also into oxalate, the reddish yellow colour of the solution changing at the same time to pale yellow.

1. *Preparation of Neutral Croconate of Potash.* — Carboxide of potassium more or less pure, as it is deposited, in the preparation of potassium by Brunner & Wöhler's method (iii. 5, b.), partly in the copper receiver, partly in the tubes and bottles therewith connected, is dissolved in water, carefully, however, because an explosion may take place; the liquid filtered; the carbonaceous mass washed with warm water as long as the water acquires a reddish yellow colour, and rhodizionate of potash appears mixed with the charcoal, in the form of a red powder; and the filtrate evaporated over the water-bath, till it yields on cooling yellow needles of croconate of potash, which are collected on a filter. — The brown mother-liquor, evaporated and cooled as often as yellow needles are produced from it, becomes at length thick and dark brown, and yields by further evaporation crystals of oxalate and bicarbonate of potash; and the still darker mother-liquor obtained therefrom, yields, when supersaturated with dilute sulphuric acid, a copious, dark brown, flocculent precipitate, of a substance resembling humic acid, but dissolving with tolerable facility in hot water. The liquid containing sulphuric acid, filtered from this precipitate, yields by distillation, small quantities of hydrocyanic, formic, and acetic acids (vii, 41). — The yellow

repeated crystallisation from hot water (Gm.), this treatment being continued till the pulverised salt no longer imparts a brownish yellow colour to strong alcohol. (Heller.)

2. *Preparation of Croconic acid.*—Pulverised croconate of potash is digested and boiled for several hours, and with frequent agitation, with absolute alcohol, (or with spirit of 85 p. c. at last with addition of absolute alcohol,) and a very small quantity of oil of vitriol, till the turbidity, which a filtered sample produces with dilute chloride of barium, disappears completely on heating with dilute hydrochloric acid, after which the filtrate is evaporated. (Gm.)

[The acid obtained by boiling finely pounded acid croconate of potash with 85 p. c. spirit, is not quite free from potash.]

The acid cannot be obtained from croconate of lead by the action of dilute sulphuric acid, the decomposition thereby obtained being very far from complete. — When croconate of lead diffused in water is decomposed by sulphuretted hydrogen,—a reaction which takes place very slowly,—a brownish yellow filtrate is obtained containing sulphur. This filtrate assumes a deeper brown colour when exposed to the air or evaporated; continues to deposit sulphur even after all the sulphuretted hydrogen has evaporated; and ultimately dries up in the air to a brown extract containing combined sulphur, and yielding only a very few needles. The extract redissolves completely in water. The dark brown, litmus-reddening solution, forms with potash a similarly coloured mixture, which, when evaporated, yields needles of croconate of potash, and a dark brown mother-liquor. The above-mentioned solution precipitates baryta and lime-water in dark brown flakes, which dissolve in hydrochloric acid; from protochloride of tin, neutral acetate of lead, mercurous nitrate, and silver nitrate, it likewise throws down dark brown flakes; but from alum, corrosive sublimate and terchloride of gold, flakes of a lighter brown colour. — Croconate of copper yields similar results when treated with sulphuretted hydrogen. (Gm.)

Properties. When the aqueous solution is abandoned to spontaneous evaporation, the acid remains in transparent, orange-yellow (sometimes brown) prisms and granules, which undergo no alteration at 100°. When the solution is evaporated over the water-bath, the acid remains in the form of a lemon-yellow opaque film. It is inodorous, tastes very acid and rough, and reddens litmus strongly. (Gm.)

Calculation according to the analysis of croconate of potash.

10 C	60	42.25
2 H	2	1.41
10 O	80	56.34
<hr/>			
C ¹⁰ H ² O ¹⁰	142	100.00

Decomposition. The acid, when heated, gives off first white, and then yellow fumes, which smell like bitumen and excite coughing, and leaves a small quantity of charcoal, which burns away easily and completely (without leaving potash). (Gm.)

Combinations. In *Water*, the acid dissolves readily, forming a lemon-yellow liquid which becomes decolorised by time. (Gm.)

The *Croconates* are all coloured, generally lemon-yellow or orange-yellow; some of the crystallised croconates of the heavy metals transmit light of a brownish yellow colour, but reflect it from their crystalline faces with a violet-blue colour. They decompose below a red heat, with glowing and sparkling, yielding carbonic acid and carbonic oxide gases, and a mixture of charcoal and metallic carbonate or oxide, or of charcoal and metal. They withstand the action of air and light, even their aqueous solutions not being altered by exposure to the air. The croconates of the soluble alkalis in particular, are soluble in water; but all croconates dissolve in nitric acid, with decomposition of the croconic acid. (Gm.) Some of the croconates of the heavy metals likewise dissolve in alcohol and ether. (Heller.)

Croconate of Ammonia. — Obtained by spontaneous evaporation of the alcoholic solution of the acid saturated with ammonia. — Deep reddish yellow, transparent tables, soluble in water and alcohol. (Heller.)

Croconate of Potash. — *a. Neutral.* — *Preparation* (p. 388). The salt dehydrated at 100° is lemon-yellow and opaque. The hydrated crystals are six- or eight-sided needles of an orange-yellow colour, strongly lustrous, and translucent. The author sometimes obtained in the six-sided needles, two angles of the lateral edges = 106° and four = 127° ; sometimes two of the angles were = 144° , and four = 109° . All however mere rough approximations. Heller obtained rhombic prisms with lateral edges of 126° and 54° . — The crystals taste somewhat like nitre, are inodorous and neutral. They give off their water at a temperature considerably below 100° ; and the lemon-yellow residue, when moistened with a little water, immediately recovers its orange-yellow tint, but is again turned lemon-yellow by oil of vitriol, which abstracts the water; the crystals are likewise dehydrated by strong alcohol.

		Dried at 100° .		Gm.	Liebig.
10 C	60.0 27.47 28.09 27.41
2 K	78.4 35.90 36.06 35.72
10 O	80.0 36.63 35.85 36.87
<hr/>					
$C^{10}K^2O^{10}$	218.4 100.00 100.00 100.00
<hr/>					
		Crystals.		Gm.	
10 C	60.0 23.58 23.80	
2 K	78.4 30.82 30.55	
10 O	80.0 31.45 30.37	
4 HO	36.0 14.15 15.28	
<hr/>					
$C^{10}K^2O^{10} + 4Aq$	254.4 100.00 100.00	

The author formerly believed, on theoretical grounds, that the salt dried at 100° must contain 1 H more, although experiment indicated the contrary; but he retracted this view as early as 1826, in accordance with further investigations (*Schw.* 17, 262; *Mag. Pharm.* 15, 141; *Pogg.* 7, 525.)

The crystals when heated give off water and turn lemon-yellow; at a stronger heat, they again assume their orange-yellow colour without change of form; and at a temperature below redness, even out of contact of air, suddenly exhibit a glimmering light extending through the entire mass, rapidly giving off at the same time about 2 vol. carbonic acid gas to 1 vol. carbonic oxide, and leaving 66.90 p. c. of a mixture of 53.81 p. c. carbonate of potash and 13.09 charcoal. — The salt dissolves without effervescence in hot oil of vitriol, forming a yellow liquid, which on

temperature gives on sulphurous acid, becomes black-brown, swells up strongly, and finally, at a heat near redness, becomes decolorised and is converted into sulphate of potash. — Nitric acid instantly decolorises the aqueous solution of croconate of potash, with slight evolution of nitric oxide; it dissolves the crystallised salt, with brisk evolution of nitric oxide, but without separation of carbonic acid, forming a colourless liquid, which when evaporated yields neither nitrate nor oxalate of potash, but a yellowish white, indistinctly crystalline, saline mass, which at a stronger heat turns brown and detonates with moderate force. The colourless aqueous solution of this mass acquires when mixed with potash, a yellow colour disappearing on exposure to the air; precipitates an abundance of pale yellow flakes from baryta-water, lime-water, and neutral acetate of lead; and produces a rather strong white turbidity in a solution of mercurous nitrate, weaker in nitrate of silver. — Chlorine immediately decolorises the aqueous solution of the salt, which then precipitates baryta-water and neutral acetate of lead in pale yellow flakes, and leaves a pale yellow mass when evaporated. (This mass is very acid, and its aqueous solution heated with mercuric oxide reduces the mercury to the metallic state.) On the other hand, chlorine gas exerts no action on the heated crystallised salt. — From terchloride of gold, croconate of potash slowly precipitates metallic gold, especially with the aid of heat; from corrosive sublimate, it throws down, after some time, a white powder, probably consisting of calomel.

Croconate of potash dissolves in moderate quantity and with pale yellow colour in cold water, and in much larger quantity in hot water, so that the solution solidifies on cooling. If the quantity of boiling water is not sufficient to dissolve the whole quantity, the undissolved portion becomes lemon-yellow from loss of water. The cold aqueous solution mixed with potash-ley deposits needles of the salt; it dissolves iodine without further alteration. Aqueous alcohol dissolves a very small quantity of the salt; absolute alcohol none. (Gm.)

b. Acid. — When 10 pts. oil of vitriol are added to the pale yellow solution of 26 pts. of the neutral salt in the smallest possible quantity of boiling water, the liquid acquires a deep brownish yellow colour, and deposits immediately, or as it cools, crystals which nearly convert the mixture into a solid mass, and may be freed from bisulphate of potash by draining, washing with cold water, and repeated crystallisation. The acid salt is not obtained by treating the neutral salt with acetic acid. — The prisms in which this salt crystallises appear thicker than those of the neutral salt, do not form such delicate needles, and have a darker colour, more inclining to hyacinth-red. They redden litmus slightly. They retain their colour at 100°, and when more strongly heated leave a black mixture of charcoal and carbonate of potash, exhibiting incandescence. (Gm.)

<i>Air-dried crystals.</i>				Gm.
20 C	120.0	27.61 26.92
5 H	5.0	1.15 1.08
3 K	117.6	27.06 26.86
24 O	192.0	44.18 45.14
$C^{10}HKO^{10} + C^{10}K^2O^{10} + 4Aq$				434.6 100.00 100.00

As only one analysis was made and with a very small quantity of salt, there may possibly be an error.

The brown-yellow aqueous solution of this salt slowly turns pale yellow on exposure to the air, and yields very pale yellow crystals when evaporated. The aqueous solution of these crystals forms, with neutral acetate of lead, an orange-yellow precipitate which becomes pasty during washing; and this precipitate decomposed by sulphuretted hydrogen not in excess, yields a colourless filtrate which leaves thin colourless prisms when evaporated. These prisms are likewise obtained by heating the aqueous solution of neutral croconate of potash with a quantity of nitric acid just sufficient to decolorise it, and treating the lead-salt as above. If the sulphuretted hydrogen be used in excess, the filtrate acquires a yellow colour and yields a brown extract besides the colourless prisms. These colourless crystals are quietly carbonised by heat and yield a white, strongly acid sublimate. Their aqueous solution reddens litmus strongly, and no longer precipitates neutral acetate of lead. (Gm.)

Croconate of Soda. — By saturating the acid with carbonate of soda. Rhombic prisms, having a lighter orange-yellow colour than the potash-salt, giving off water of crystallisation when heated, dissolving readily in water, sparingly in alcohol. (Heller.)

Croconate of Lithia. — Pale yellow, amorphous, soluble in water and alcohol. (Heller.)

Croconate of Baryta. — The acid and the potash-salt form with baryta-water or chloride of barium, a thick, pale yellow, pulverulent precipitate, which coagulates by boiling into a deep, lemon-yellow, curdy mass, insoluble in a large quantity of hot water, and dissolving but sparingly in hot hydrochloric acid. (Gm.) It is not soluble in water, alcohol, or ether. (Heller.)

Croconate of Strontia. — The acid forms with chloride of strontium a yellow crystalline precipitate, which crystallises from the solution in alcohol by spontaneous evaporation. The potash-salt forms with chloride of strontium, transparent crystalline laminæ. Easily soluble in water and alcohol. (Heller.)

Croconate of Lime. — Croconate of potash forms with lime-water or chloride of calcium, after a few hours, a large quantity of lemon-yellow crystals, which dissolve in water very sparingly and with very pale yellow colour. (Gm.) The free acid forms with chloride of calcium yellow, translucent, flat prisms, bevelled at the ends, sparingly soluble in water and alcohol. (Heller.)

Croconate of Magnesia. — The clear aqueous mixture of croconate of potash and sulphate of magnesia, yields, by spontaneous evaporation, dark brown prisms acuminate at the ends. (Heller.)

Ceric Croconate. — Croconate of potash forms a copious precipitate with hydrochlorate of ceric oxide and ammonia, and a scanty precipitate with acid hydrochlorate of ceric oxide. (Heller.)

Croconate of Yttria. — Yellowish brown, micaceous, crystalline scales, easily soluble in water. (Berlin, Pogg. 43, 116.)

Croconate of Glucina. — The mixture of the alcoholic solution of croconic acid with acetate of glucina, forms yellow crystals, easily soluble in water and alcohol. (Heller.)

with acetate of alumina, leaves yellow crystals, easily soluble in water and alcohol. (Heller.)

Croconate of Zirconia. — Prepared like the alumina-salt. Yellow, transparent crystals, soluble in water and alcohol.

Uranic Croconate. — The hyacinth-red aqueous mixture of the acid or the potash-salt with uranic nitrate, yields, by spontaneous evaporation, yellowish red, transparent crystals, easily soluble in water and alcohol. (Heller.)

Manganous Croconate. — By evaporating the acid with manganous acetate, or leaving the potash-salt for some time in contact with manganous sulphate, dingy yellow crystals are obtained, having a faint blue reflex. (Heller.)

Croconate of Antimony. — The potash-salt forms, with hydrochlorate of chloride of antimony, a thick lemon-yellow precipitate, soluble in excess of the chloride of antimony. (Gm.)

Croconate of Bismuth. — The thick lemon-yellow precipitate formed by the potash-salt in a solution of bismuth-nitrate, dissolves in an excess of the bismuth-solution. (Gm.) It contains 55.68 p. c. bismuth-oxide, and is not soluble either in water or in alcohol. (Heller.)

Croconate of Zinc. — The alcoholic solution of the acid forms, with acetate of zinc, on evaporation, and the potash-salt forms, with acetate or sulphate of zinc, when set aside for several hours, yellow crystals and crystalline grains, soluble in water and alcohol.

Croconate of Cadmium. — The potash-salt added to sulphate of cadmium, throws down a large quantity of powder, having a fine yellow colour, and soluble in water and alcohol. (Heller.)

Stannous Croconate. — The potash-salt throws down from protochloride of tin, a large quantity of an orange-yellow powder (Gm.), which decomposes with violence when heated, and is sparingly soluble in water. (Heller.)

Bichloride of tin is not precipitated by the potash-salt. (Heller.)

Croconate of Lead. — The free acid and its potash-salt precipitate neutral acetate of lead abundantly in lemon-yellow flakes, which dissolve with decomposition in nitric acid, forming a colourless liquid, and when digested for some time with water and a small quantity of sulphuric acid, still leave a portion of free sulphuric acid in the liquid, which turns yellow. (Gm.) The precipitate, when dry, is a powder of a fine yellow colour, containing 64.06 p. c. oxide of lead, [therefore = $C^{10}Pb^2O^{10}$], dissolving without colour in nitric acid, but insoluble in water and alcohol. (Heller.)

Ferrous Croconate. — The potash-salt imparts a dark yellowish brown colour to ferrous sulphate, and afterwards forms brown flakes, which change over night to dark brown crystals. These crystals exhibit a blue reflex on the crystalline faces, like the copper-salt, which they also resemble in form, and are soluble in water and alcohol. (Heller.)

Ferric Croconate. — The potash-salt forms with aqueous sesquichloride of iron, a clear black mixture, exhibiting a garnet-red colour in thin

layers (Gm.); and depositing indistinct, very dark-coloured crystals, which are soluble in water and alcohol. (Heller.)

Croconate of Cobalt.—The brown-red, slightly turbid mixture of the potash-salt with an aqueous cobalt-salt, yields, after a few hours, dark brown transparent crystals with beautiful violet reflex, soluble in water and alcohol. (Heller.)

Croconate of Nickel.—By evaporating croconic acid with sulphate of nickel, light brown grains are obtained, soluble in water and alcohol. (Heller.)

Cupric Croconate—The clear bluish green mixture of warm aqueous croconate of potash with cupric sulphate or hydrochlorate, deposits crystals on cooling, which must be washed with water and dried between paper. Crystals belonging to the right prismatic system. Right rhombic prisms (*Fig. 61*) $u : u = 108^\circ$ and 72° ; the obtuse lateral edges and summits replaced by the faces m and y ; the acute summits bevelled with two faces in the direction of the terminal edges; cleavage parallel to u . (Blum.) The crystals transmit light with brownish orange-yellow colour, but reflect it from their faces with dark blue colour and brilliant metallic lustre. Masses of small crystals appear violet-red; the powder is lemon-yellow, brighter in proportion to its fineness, and imparts the same colour to a large quantity of cupric oxide when triturated therewith. The crystals heated in the water-bath for several days, give off 13.51 p. c. water, then a small additional quantity at 162° , in all 13.81 p. c. (4 At. while 2 At. water are obstinately retained), and appear but little altered, only more brownish and duller. When the crystals are heated in a small retort, water escapes at first, and then, at a temperature below redness, one crystal after another suddenly decomposes without appearance of light, and with percussive evolution of gas and projection of single particles, which burn with emission of sparks, on coming in contact with the air. The gas thereby evolved consists of carbonic acid and carbonic oxide, at first in the volume-ratio of 1 : 1.2, at last of 1 : 1.8. A very small quantity of distillate is obtained, having the odour of wood-vinegar, the first portions being pale yellow, and reddening litmus slightly; the latter portions brownish yellow and strongly acid, and after neutralisation with ammonia, imparting a darker colour to dilute sesquichloride of iron, and forming an immediate black precipitate with nitrate of silver. The residue of copper and charcoal which remains after heating the crystals, amounts to 30.8 per cent. if the crystals have been heated in a retort containing air; to 32.8 per cent. if carbonic acid has been passed through the apparatus before and during the heating; and to 36.8 p. c. if hydrogen has been passed through it. It is a brown-black, dull, somewhat fibrous powder. Heated in the air to a temperature somewhat below redness, it burns away with a glimmering light and slight emission of sparks, leaving first a red powder of metallic copper and afterwards cupric oxide. Fuming nitric acid sets it on fire, with vivid sparkling. The crystals heated in the air decompose one after another with a slight hissing noise, appearance of fire, sparkling and projection of individual particles, and throw out slender threads of dull red metallic copper, which is then quickly converted, with a glowing light, into oxide. In oxygen gas, the sparkling and projection of the particles are very violent. (Gm.)

The salt dissolves very sparingly in cold water; somewhat more abundantly and with lemon-yellow colour, in boiling water, but separates

yellow tint. The solution, mixed with potash (even out of contact of air), forms croconate of potash, and a blue precipitate soluble in excess of potash. Similarly with ammonia, which also dissolves the crystals with blue colour, whereas potash-ley acts but feebly on the crystals. The aqueous solution exhibits, with sulphuretted hydrogen, ferrocyanide of potassium, sulphocyanide of potassium, ferrous sulphate, and also with hydrocyanic acid and tincture of guaiacum, the same reactions as other cupric salts (v. 413). It coppers iron but slightly, unless hydrochloric acid be added. (Gm.)

<i>Crystals.</i>		<i>Gm.</i>	
10 C	60	23·26	23·36
2 Cu.....	64	24·80	24·80
6 H	6	2·33	2·23
16 O	128	49·61	49·61
<hr/>			
$C^{10}Cu^2O^{10} + 6Aq.$	258	100·00	100·00
<i>Or:</i>		<i>Gm.</i>	
10 C	60	23·26	23·26
2 Cu.....	64	24·80	24·80
10 O	80	31·01	31·83
6 HO	54	20·93	20·11
<hr/>			
$C^{10}Cu^2O^{10} + 6Aq.$	258	100·00	100·00

Mercurous Croconate. — The free acid and its potash-salt form, with mercurous nitrate, copious lemon-yellow flakes, which dissolve in nitric acid, forming a colourless liquid. (Gm.) The flakes are reddish yellow at first; but the colour quickly changes to yellow. (Heller.)

Mercuric Croconate. — Mercuric nitrate also forms, with the potash-salt, a precipitate of a fine yellow colour. (Heller.)

Croconate of Silver. — The free acid and the potash-salt precipitate from nitrate of silver, an abundance of aurora-red flakes, which still contain potash (perhaps $C^{10}KAgO^{10}$?), are quickly and completely resolved by hydrochloric acid into chloride of silver and croconic acid containing potash, and dissolve in nitric acid to a colourless liquid, with slight evolution of gas. (Gm.) The precipitate turns brown on exposure to light, throws out sparks with violence when heated, and dissolves sparingly in water. (Heller.)

Croconic acid is soluble in *alcohol*.

Appendix to Croconic Acid.

1. Carboxide of Potassium.

L. GMELIN. *Pogg.* 4, 35.

LIEBIG. *Pogg.* 33, 90.

HELLER. *Ann. Pharm.* 34, 232.

Kohlenoxyd-Kalium. — First observed by Wöhler and Berzelius. (*Pogg.* 4, 31 to 34.)

Charcoal at a white heat decomposes potash into carbonic oxide and potassium; but at a dull red heat, the potassium again decomposes the

carbonic oxide gas into charcoal and potash; and at a still lower heat, the potassium and carbonic oxide unite into a grey flocculent mass, which may provisionally be regarded as a compound of carbonic oxide and potassium, and designated as carboxide of potassium.

The following observations are recorded:

When potassium is prepared by Brunner and Wöhler's method (iii. 7), in which the mixture of carbonic oxide gas and potassium-vapour is passed from the white-hot iron bottle through an iron tube into a copper receiver, and thence through a long tube, the half-ignited iron tube becomes filled with a hard black mass, which behaves like a mixture of charcoal, potash, and potassium. But the gas which escapes from the copper receiver is accompanied by grey vapours. If this cloudy gas is not too much cooled, it burns slowly in the air with a dull red light, but on the approach of a flaming body, or in many instances spontaneously, takes fire and burns rapidly with a bright reddish white flame and white fumes. When, on the other hand, the gas is passed through tubes and vessels in which it cools, the cloud condenses in these vessels, in grey flakes of carboxide of potassium. These flakes are likewise found in the copper receiver, mixed, however, with charcoal, potash, and potassium. The formation of carboxide of potassium is equally abundant when the potassium is prepared from a mixture of charcoal and carbonate of potash instead of burnt tartar, and no rock-oil is put into the receiver. Consequently, the cooling of the carbonic oxide gas, mixed with potassium-vapour stops the separation of charcoal, and induces the formation of carboxide of potassium. (Gm.)

When Gay-Lussac & Thénard (*Recherch.* 1, 250, and 267,) heated potassium in carbonic oxide gas over a spirit-lamp, the gas, at a certain temperature [probably near redness,] was almost instantly absorbed, with ignition of the potassium, separation of charcoal and formation of potash; sodium heated nearly to dull redness, acted nearly in the same manner, but without appearance of fire.

On the other hand, when Liebig passed dry carbonic oxide gas over potassium, heated just to its melting point in a wide iron tube, the potassium absorbed the gas without appearance of fire, becoming green at first, spreading itself out on the side of the tube, and being finally converted into a black mass, which was easily separated when cold, and exhibited the characters of the carboxide of potassium obtained in the preparation of potassium. Heller obtained the same mass, but found that the crust which formed above the potassium, prevented the complete penetration of the carbonic oxide.

Preparation. The preparation of potassium is conducted with a larger quantity of charcoal than usual, whereby the yield of potassium is diminished, but that of the carboxide is increased; and the gaseous mixture is made to pass from the copper receiver, which contains a little rock-oil, through tubes into three bottles successively, the first two of which contain rock-oil, and the third water. The black mass which condenses in the copper receiver, contains, besides carboxide of potassium, a large quantity of charcoal, potash, and potassium, together with a resinous matter, and a brown substance soluble in water, and serves for the preparation of rhodizonate and croconate of potash. The product in the first bottle consists of porous lumps, often as big as hazlenuts, and contains small quantities of potassium and charcoal (perceptible on dissolving the mass in water); that in the second is free from charcoal; that

carboxide of potassium in the second bottle is separated from the admixed potassium (which remains in a more coherent state) by trituration and levigation with rock-oil; collected on a filter; strongly pressed between paper; and preserved in well closed bottles. The compound thus obtained is not however pure; alcohol and ether extract potassium from it in the form of potash, besides rock-oil and a resinous substance, which may be precipitated from the water by alcohol; and the residue forms with water, not only rhodizonate of potash, but also a brown substance [resembling humate of potash] which dissolves in the water. (Heller.)

Also, when the gas which issues from the copper receiver is passed through a tube of tinned iron, an inch wide and three feet long, into a wide open iron bottle, the greater part of the carboxide of potassium is deposited tolerably pure in the tube and bottle. Bottles and tubes of glass are dangerous; because the carboxide of potassium contained in them may explode, after the air has acted upon it for a short time, and shatter the glass, especially on dissolving the mass in water. (Gm.)

Properties. Carboxide of potassium is a grey or black, loose pulverulent mass. (Berzelius, Gm., Heller.) Under the microscope, it sometimes exhibits four-sided prisms with truncated summits. (Edm. Davy.)

Decompositions. The mass distilled at a red heat gives off potassium, and leaves charcoal. (Edm. Davy.) — The carboxide of potassium obtained by heating potassium in carbonic oxide gas, if exposed to the air while still warm, takes fire with detonation. (Liebig.) — The carboxide obtained in the preparation of potassium takes fire in the air, and burns like a pyrophorus. (Berzelius.) — The product condensed in the copper receiver without rock-oil, takes fire in the air with emission of sparks, projection of the mass, and dangerous explosion, especially if rubbed. (Heller.) — The grey loose mass which condenses in the glass or tinned iron tube connected with the copper receiver, becomes soft and pasty on exposure to the air, and rises almost to a red heat, which gradually extends throughout the mass, the reddish grey colour changing at the same time to grey. (Gm.) — The greenish grey powder, shaken out of the tube into a porcelain dish, after the tube has been closed air-tight for 10 days, immediately reddens, and, after a few seconds, takes fire with tremendous detonation and shatters the basin. (Wöhler, *Ann. Pharm.* 49, 361.) Moistening with rock-oil prevents it from taking fire. — Carboxide of potassium takes fire when thrown on water, [from the presence of free potassium?] and acquires a vermilion colour when brought in contact with water under rock-oil. (Berzelius.) — Exposed to the air, after complete cooling, it sometimes turns green here and there, and afterwards yellow, with formation of croconate of potash, sometimes red. (Gm. Liebig.) It acquires a fine red colour, from formation of rhodizonate of potash. (Heller.) — When recently prepared, it dissolves quietly in water, with slight evolution of combustible gas, and forms a brownish yellow liquid, containing croconate (or rather rhodizonate, according to Heller), and neutral carbonate of potash. If the quantity of water present is not very large, a cochineal-coloured powder (rhodizonate of potash, according to Heller), remains undissolved. Carboxide of potassium which has been exposed to the air till it has turned yellow and red, likewise dissolves quietly in water; but that which has been

exposed to the air for a few hours only, is set on fire by water, with violent detonation, and shattering of the glass vessels. (Gm. iii. 8.) — The combustible gas eliminated by water is C^2H^2 . (Edm. Davy, *Ann. Pharm.* 23, 144; see viii. 150.) — Carboxide of potassium, placed in contact with water over mercury, so as to exclude the air, dissolves quietly, giving off first olefiant gas, then carbonic oxide. (Heller.) — When the quantity of water is large, the whole dissolves with deep reddish yellow colour; when less water is used, part of the rhodizionate of potash produced remains undissolved, in the form of a red powder; and with a still smaller quantity of water, a pale yellow solution is obtained, because the strong caustic alkali contained in it, converts the rhodizionate of potash into croconate. (Heller.) — The black compound produced by heating potassium in carbonic oxide gas, dissolves in water, with the exception of a few black flakes, and gives off a gas, part of which takes fire spontaneously; the gas evolved out of contact with the air, burns when set on fire, with the bright flame of olefiant gas. The solution obtained with a small quantity of water is pale yellow; that obtained with a large quantity of water, reddish yellow and alkaline; when evaporated, it turns pale yellow, and yields, first croconate of potash, then about an equal quantity of oxalate. (Liebig.)

2. Rhodizonic Acid.

HELLER. *J. pr. Chem.* 12, 193; abstr. *Ann. Pharm.* 24, 1. — *Zeitschr. Phys. v. W.* 6, 54; abstr. *Ann. Pharm.* 34, 232.
A. WERNER. *J. pr. Chem.* 13, 404.

Berzelius and Wöhler noticed the red substance produced by the action of water on carboxide of potassium. Gm. found that the aqueous solution of this substance yields croconate of potash when evaporated in contact with the air, and supposed it to contain an acid different from croconic acid. Heller, in 1837, ascertained the properties of this acid more distinctly, and gave it the name of Rhodizonic acid.

Preparation of Rhodizionate of Potash. — Carboxide of potassium, collected in the copper receiver under rock-oil, freed from the greater part of the charcoal and potassium by levigation with rock-oil, then collected on a filter and pressed, is repeatedly shaken up with alcohol, — which extracts potash, rock-oil, and a resinous substance precipitable by water, — till the alcohol no longer becomes strongly coloured; the black viscid mass which remains after pouring off the alcohol, agitated with one-third of its bulk of water, and then with a sufficient quantity of alcohol to produce separation; the aqueous alcoholic liquid containing potash and a dark brown substance precipitable by water, decanted; the residual mass repeatedly treated in the same manner with water and alcohol, till the water is no longer coloured brown but light yellow, from the presence of a small quantity of rhodizionate of potash; the substance which remains after decanting the liquid, exposed to the air, under which circumstances it turns red, the more quickly as it has been more completely freed from potash; the mass, which has the consistence of honey, diluted with a little water, then treated with successive small portions of a mixture of 1 pt. oil of vitriol and 15 pts. water, which eliminates carbonic acid,

strongly alkaline liquid decanted, and the mass repeatedly treated in this manner with water containing sulphuric acid and with alcohol, till the decanted liquid is no longer alkaline, — a sign that the mass is completely converted into rhodizionate of potash; it must then be thrown on a filter with the aid of alcohol, and dried. If too much sulphuric acid has been used, and the mass has consequently acquired the power of reddening litmus, from separation of rhodizonic acid, it must be neutralised with carbonate of potash. An admixture of sulphate of potash renders the dark red colour of the rhodizionate paler.

Preparation of Rhodizonic acid. — 1. The potash-salt is suspended in alcohol of sp. gr. 0·81 to 0·82; a mixture of alcohol with sufficient oil of vitriol to saturate the potash then added; the whole digested at a gentle heat; the filtrate, if it still contains sulphuric acid, cautiously digested with baryta-water, till a pale red precipitate of rhodizionate of baryta just begins to form; the filtrate evaporated at a gentle heat to a small bulk; the acid left to crystallise; and the crystals freed by washing with alcohol from the dark brown mother-liquor, which has an offensive odour of rock-oil. (Heller.) — When the potash-salt is decomposed by alcohol containing a small quantity of sulphuric acid, a deep purple-red filtrate is obtained, containing no sulphuric acid, and leaving on evaporation, blue-black needles united in tufts. (Werner.) — 2. The acid obtained by (1) is dissolved in alcohol and precipitated by carbonate of potash in the form of rhodizionate of potash; the aqueous solution of this salt precipitated by neutral acetate of lead acidulated with acetic acid; the dark violet lead-salt washed on the filter with water, and decomposed by sulphuretted hydrogen after suspension in water or alcohol; and the dark hyacinth red filtrate evaporated to a small bulk and left to crystallise. — The mother-liquor then remaining, which contains scarcely any more rhodizonic acid, is very dark coloured. (Heller.) — The lead-salt suspended in water may be easily and completely decomposed by sulphuretted hydrogen, and yields a pale yellow filtrate, which exhibits the reactions of rhodizonic acid, and becomes continually darker by evaporation, ultimately acquiring a deep red colour and yielding brown-black dodecahedrons. (Werner.)

Properties. Prepared by (1): Short slender needles of a pale orange-yellow colour; by (2): Very dark coloured needles having a bluish green metallic lustre. This dark colour arises from enclosed mother-liquor. (Heller.) — (Heller has withdrawn his former statement that the acid is colourless; but respecting the colour of its aqueous, alcoholic, or ethereal solution, which was likewise stated to be colourless, nothing is said in his second memoir. Liebig regards these colourless crystals formerly obtained by Heller, as sulphovinate of potash.) Werner obtained: by (1), needles; by (2) dodecahedrons of brown-black colour, which reflected the sun's rays with brilliant, deep purple-red metallic lustre. — Inodorous, with slightly acid and astringent taste, reddening litmus permanently. (Heller, Werner) — The crystals do not decompose, even by long keeping; but if exposed to the air, especially in vessels which are frequently opened, they turn red, and when rubbed between the fingers, exhibit a blood-red colour, with green metallic lustre, in consequence of the great affinity of the acid for organic substances. (Heller.) [Or from taking up ammonia?]. — The aqueous solution colours the skin yellowish-red (Heller); deep brown-red. (Werner.)

From the contradictory analyses of the rhodizonates of potash and

lead, it is impossible to establish with certainty the formula of rhodizonic acid; we can only indeed deduce from these analyses that all the hydrogen which can be supposed to exist in the acid, together with C and O is (as in croconic and oxalic acid) replaceable by a metal. Liebig (*Ann. Pharm.* 24, 16), starting from the fact that rhodizionate of potash acid dissolved in water, splits up into croconate and oxalate, suggests for rhodizionate of potash the formula $3KO, 7CO$, which, when doubled and written in a different form, becomes $C^{14}K^2O^{20}$; such a compound may yield $C^{10}K^2O^{10}$ (croconate of potash), $C^4K^2O^8$ (oxalate of potash), and $2KO$. This view is corroborated, on the one hand, by Thaulow's observation, that the solution of rhodizionate of potash, when thus decomposed, becomes alkaline, and on the other hand, approximately, by Heller's analysis of the potash-salt, in which he found 62 p. c. potash, the formula $C^{14}K^2O^{20}$ requiring 59 p. c. According to this view, the formula of rhodizonic acid would be $C^{14}H^2O^{20}$. It is not yet, however, satisfactorily explained why rhodizionate of potash immediately splits up into croconate and oxalate when free potash is added to it, whereas, without this addition, the change does not take place unless the air has access to the liquid.

Decompositions. The crystallised acid heated considerably above 100° , turns greenish black and volatilises in the decomposed state without residue. (Heller.) When heated, it gives off water, then a yellowish-red vapour which forms a sublimate of the same colour and appears to consist of undecomposed acid;—it then turns black and yields a grey, and afterwards a yellow vapour smelling of empyreumatic organic matter, and burns away in the air leaving only a trace of alkaline ash. (Werner.)—2. It is quickly decomposed by concentrated mineral acids (Heller); even in the state of aqueous solution. (Werner.)—3. The alcoholic solution of the acid and the aqueous solution of the potash-salt reduce the metal from a solution of gold. (Heller.)—The acid dissolved in water and exposed to the air for several weeks, is resolved into croconic and oxalic acid. (Werner.)

Combinations. The acid dissolves readily in water. (Heller.) The concentrated solution is red, the dilute solution yellow. (Werner.)

Rhodizonates.—The potash-salt is the only one which crystallises. The colour of the salts passes from light rose-red through carmine and blood-red to dark chocolate-brown, and is lighter the more finely the salts are divided. Many exhibit a green metallic lustre. They are not decomposed by exposure to the air, but merely acquire a darker colour. They decompose at a temperature considerably below redness, without any or with only a faint glow, and leave a mixture of charcoal with metal, oxide, or carbonate. Most of them dissolve in water with orange-yellow, or in case of greater concentration, with red-brown colour. Some of these solutions become pale yellow on exposure to the air, the rhodizionate being then resolved into croconate and oxalate.

Rhodizionate of Ammonia.—Precipitated as a dark yellowish powder, on mixing the alcoholic solution of the acid with a small quantity of ammonia, and as a violet powder on mixing the aqueous potash-salt with hydrosulphate of ammonia. It dissolves readily in water, sparingly in alcohol, and in the state of aqueous solution splits up into croconate and oxalate of ammonia. (Heller.)

conque rhodizone powder, whose base is a bright green metallic lustre; the velvety, bright red powder, rubbed on paper with the polishing stone immediately acquires a blue-green metallic lustre. Inodorous, tasteless, permanent in the air. Contains 61.96 p. c. potash. Becomes greyish black when heated, and ultimately leaves carbonate of potash. Insoluble in alcohol and ether, but dissolves readily in water. The deep red aqueous solution, when left to stand [in contact with the air] turns pale yellow in a few hours (immediately on the addition of potash or ammonia) from formation of croconate and oxalate of potash, and with liberation of potash; it is also decolorised and decomposed by sulphuric, hydrochloric, and nitric acid. (Heller.) — The alcoholic solution of the acid, yields, when alcoholic potash is dropped into it, a cherry-red precipitate, with greenish metallic lustre, which, after being collected on a filter and dried between paper, becomes brown-red, and exhibits the green metallic lustre in a fainter degree. It dissolves sparingly in cold, not much more readily in hot water, and is not altered by remaining for many weeks under water in contact with the air. (Werner.)

[From the author's notes of former experiments (*Pogg.* 4, 59) with impure rhodizonate of potash, as obtained in the form of a cochineal-coloured powder by the action of water on carboxide of potassium which has been exposed to the air, the following passage is extracted: It burns with resinous flame and white smoke. Its reddish yellow aqueous solution is immediately decolorised by nitric acid, and reduces gold from the solution of the chloride. With aqueous ammonia it forms a reddish yellow solution, which again leaves a red residue when evaporated, but forms with potash a yellow solution of croconate of potash; its aqueous solution also immediately turns reddish on addition of a small quantity of potash, and then deposits needles of croconate of potash. The reddish-yellow aqueous solution, if kept from contact with the air, retains its colour, even in sunshine, and again leaves a red mass when evaporated; but the solution, when exposed to the air, becomes pale yellow in a few hours, and then leaves on evaporation needles of croconate of potash. The reddish yellow aqueous solution throws down from baryta-water, brown-red flakes which turn yellow on exposure to the air; from lime-water, pale red flakes; from protochloride of tin or neutral acetate of lead, dark red; from mercurous nitrate, carmine-coloured; and from nitrate of silver, reddish black flakes.]

Rhodizonate of Soda. — Obtained by adding a concentrated solution of carbonate of soda to the solution of the acid in strong alcohol, and washing the dark carmine-coloured powder thereby precipitated, on the filter with alcohol, to remove the excess of alkali. The dried salt is brown. Its reddish yellow aqueous solution decomposes like the potash-salt on exposure to the air or on addition of soda. (Heller.)

Rhodizonate of Lithia. — The dark crimson-red salt, which is prepared like the soda-salt, forms with water a reddish yellow solution, which becomes very pale on exposure to the air, depositing a light violet powder and forming croconate and oxalate of lithia. (Heller.)

Rhodizonate of Baryta. — 1. The alcoholic acid forms with baryta-water, a light carmine-coloured precipitate, and with a small quantity of aqueous chloride of barium, after a while, an extremely beautiful carmine-coloured precipitate, which transmits light of the same colour, but, under different circumstances, reflects it with yellowish green colour.

precipitate with baryta-water, and an immediate cherry-red precipitate with chloride of barium. The salt is insoluble in water, alcohol, and ether; it is not altered by immersion in water, but in baryta-water it turns yellow, with formation of croconate of baryta. (Heller.) The aqueous acid likewise precipitates hydrochlorate and acetate of baryta; the latter is the best test for rhodizonic acid, and forms with dilute solutions a rose-coloured, with concentrated solutions a deep purple-red precipitate. (Heller.) — The salt, after drying, is yellowish red, with greenish iridescence. Dilute sulphuric acid decomposes it only in the recently precipitated state. When finely divided and suspended in water, it is coloured carmine-red by a few drops of hydrochloric acid, and exhibits after washing the characters of the unaltered salt; the yellow liquid filtered therefrom contains hydrochlorate of baryta, as well as rhodizonate (precipitable by a small quantity of potash). Rhodizonate of baryta suspended in water is coloured light-red by a small quantity of nitric acid, yellowish-red by phosphoric acid. When the salt suspended in water is heated with phosphoric, hydrochloric, or nitric acid, the liquid acquires a yellow colour from formation of croconic acid, but is decolorised by boiling, in consequence of the further decomposition of the croconic acid. Rhodizonate of baryta likewise dissolves sparingly in strong acetic acid, but is insoluble in water. (Werner.)

Rhodizonate of Strontia. — The alcoholic acid forms, with chloride of strontium, a splendid violet-carmine-red precipitate, and the potash-salt a cherry-red precipitate, with yellowish green metallic lustre, sparingly soluble in water, insoluble in alcohol. (Heller.) The aqueous acid likewise precipitates chloride of strontium. (Werner.)

Rhodizonate of Lime. — The alcoholic acid forms with lime-water a garnet-brown, and with acetate of lime a light blood-red precipitate; the aqueous potash-salt forms with lime-water a deep carmine-red, and with acetate of lime a dark red precipitate, but does not precipitate chloride of calcium. The precipitate turns yellow under lime-water; it dissolves in water, but not in alcohol. (Heller.)

Rhodizonate of Magnesia. — Obtained by precipitating acetate of magnesia with the alcoholic solution of the acid. Has a fine garnet-red colour; dissolves easily in water and alcohol. (Heller.)

Ceric Rhodizonate. — By dissolving ceric oxide in the alcoholic acid, and evaporating, a purple-red amorphous mass is obtained, easily soluble in water and alcohol. (Heller.)

Rhodizonate of Glucina. — By evaporating the alcoholic acid with acetate of glucina, a garnet-red powder is obtained, which dissolves very readily in water and alcohol. (Heller.)

Rhodizonate of Alumina. — Prepared in a similar manner. Red-brown powder which dissolves very readily in water and alcohol. (Heller.)

Rhodizonate of Zirconia. — Obtained by dissolving zirconia in the alcoholic acid, and evaporating. The residue has a deep garnet-brown colour, and dissolves easily in water and alcohol. (Heller.)

Rhodizonate of Titanium. — The alcoholic acid colours the oxide red, dissolves it, and then leaves a red salt when evaporated. (Heller.)

precipitate not yet further examined. (Heller.)

Uranic Rhodizionate. — The alcoholic acid precipitates from uranic nitrate, a light blood-red powder easily soluble in water and alcohol. [?] (Heller.)

Rhodizionate of Manganese. — The alcoholic acid forms, with acetate of manganese, a dark red precipitate which increases on boiling, and dissolves with yellow colour in water and alcohol. (Heller.)

Rhodizionate of Tellurium. — The solution of telluric oxide in the alcoholic acid leaves a red salt when evaporated.

Rhodizionate of Bismuth. — The potash-salt dissolved in a small quantity of water forms, with nitrate of bismuth, a pale-red precipitate which quickly loses colour; the alcoholic acid forms a yellow precipitate which contains croconic acid, and, if left in the liquid, gradually turns white. (Heller.)

Rhodizionate of Zinc. — The alcoholic acid colours zinc-oxide red, and then dissolves it with yellow colour; with acetate of zinc, it forms a dark red precipitate, soluble in water and alcohol. (Heller.)

Stannous Rhodizionate. — The potash-salt forms, with protochloride of tin, a carmine-red precipitate which afterwards becomes darker; it dissolves sparingly in water and is insoluble in alcohol. — The *Stannic salt* is darker. (Heller.)

Rhodizionate of Lead. — The alcoholic acid forms a deep red-brown precipitate with acetate and nitrate of lead. The dark carmine-red precipitate obtained on adding the potash-salt to an acidulated solution of acetate of lead, assumes, when left for some time in the liquid, a red-brown, and afterwards a black-brown colour; it does not dissolve in water or alcohol. (Heller.) The aqueous acid forms, with acetate of lead, a deep violet precipitate which has a splendid metallic lustre; it is easily decomposed by sulphuric acid while moist, and by sulphuretted hydrogen, even after drying. (Werner.) The precipitate formed by the potash-salt with excess of neutral acetate of lead, is dark red, and leaves, when ignited in an open dish, a mixture of lead-oxide and metallic lead. (Thaulow, *Ann. Pharm.* 27, 1.)

				Heller.
3 PbO	336	85.28 85.00
3 C	18	4.57 4.67
5 O	40	10.15 10.33
			394 100.00
			 100.00

				Thaulow.
3 PbO	336	77.42 77.20
7 C	42	9.68 9.87
7 O	56	12.90 12.93
			434 100.00
			 100.00

Rhodizionate of Iron. — The alcoholic acid forms, with ferrous sulphate, a red-brown precipitate soluble in water and alcohol, and with ferric salts, a brown precipitate, likewise soluble in water, and therefore imparting a brown colour to the liquid. (Heller.)

Rhodizionate of Cobalt. — The alcoholic acid added to nitrate of cobalt, precipitates a small portion of the salt, forming a carmine-red precipitate soluble in water, while the greater portion remains dissolved with red colour in the alcoholic liquid. (Heller.)

Rhodizionate of Nickel. — Brown, soluble in water and alcohol. (Heller.)

Cupric Rhodizionate. — The alcoholic acid forms, with cupric salts, a red-brown precipitate soluble in water; from concentrated aqueous solutions, the potash-salt throws down the same precipitate. (Heller.)

Mercurous Rhodizionate. — The alcoholic acid forms, with mercurous nitrate, a scarlet precipitate which soon becomes darker in colour; and the potash-salt forms, with mercurous nitrate or acetate, a dark carmine-red precipitate, which, when immersed in the liquid, soon turns brown, and ultimately yellow. The precipitate is insoluble in water and alcohol. (Heller.)

Mercuric Rhodizionate. — The red-brown precipitate which the potash-salt forms with mercuric salts is insoluble in water, and soon turns yellow when immersed in the liquid. (Heller.)

Rhodizionate of Silver. — Nitrate of silver forms, with the alcoholic acid, a brownish red precipitate which quickly blackens, and after drying, exhibits the metallic lustre; and with the potash-salt, a deep carmine-red precipitate which dissolves but very sparingly in water, and soon assumes a brown colour, changing to black on exposure to the air. (Heller.) The aqueous acid likewise precipitates a solution of nitrate of silver. (Werner.)

The alcoholic acid does not precipitate *Bichloride of Platinum*. (Heller.)

Rhodizonic acid dissolves readily and without colouring in *alcohol* and *ether*. (Heller.) The concentrated alcoholic solution is red, the dilute yellow. (Werner.)

c. *Nitrochlorine-nucleus* C¹⁰XClH⁴.

St. Evre's Acid.



ST. EVRE. (1849.) *N. Ann. Chim. Phys.* 25, 493; also *J. pr. Chem.* 46, 456.

The solution of chloroniceic acid in fuming nitric acid, deposits on cooling, crystals of nitrochloroniceic acid; and the mother-liquid decanted therefrom, yields, on evaporation, long white needles of a peculiar acid, containing:

				St. Evre.		
10 C	60.0	33.82	33.77
N	14.0	7.89	8.14
Cl	35.4	19.95	19.67
4 H	4.0	2.25	2.29
8 O	64.0	36.09	36.13
<hr/>						
C ¹⁰ XClH ⁴ O ⁴	177.4	100.00	100.00

d. *Amidogen-nucleus.* $C^{10}AdH^3O^3$

Pyromucamide.



MALAGUTI. (1846.) *Compt. rend.* 22, 856.

[Malaguti has not described the formation and preparation of this compound; but it is probably obtained by the dry distillation of monomucate of ammonia = $C^{12}NH^2O^{16}$.]

Properties. Right-angled, four-sided prisms, which melt between 130° and 132° , and have a very slightly sweet taste.

Decompositions. Heated a little above its boiling point, it acquires a green colour, changing as the temperature rises, to blue, and afterwards to violet, and then yields a brown distillate, which after being decolorised by animal charcoal, again exhibits the characters of pyromucamide.

Combinations. Dissolves in water, alcohol, and ether. (Malaguti.)

e. *Amidogen-nucleus.* $C^{10}Ad^2H^2O^3$.

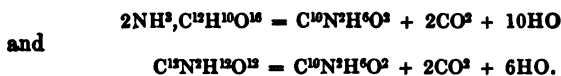
Bipyromucamide.



MALAGUTI. (1846.) *Compt. rend.* 22, 856.

Pyromucamide biamidés.

Formation and Preparation. By the dry distillation of dimucate of ammonia or of mucamide:



The sublimate is repeatedly crystallised from water to free it from adhering pyromucic acid, which remains in the mother-liquor.

Properties. Six- and eight-sided laminæ, which melt and become coloured at 175° , and have a very sweet taste.

Decompositions. 1. Heated above the melting point, it decomposes; and at 250° enters into a kind of ebullition, giving off carbonate of ammonia, besides other products. — 2. With potash-ley, it gives off ammonia only at the boiling heat.

Combinations. It dissolves sparingly in cold water, more readily in alcohol and ether.

f Nitrogen-nucleus. $C^{10}NH^6$.

¶. Pyridine; $C^{10}NH^6$.

ANDERSON. *Ed. Phil. Trans.* 20, ii. 247; *Phil. Mag.* [4], 2, 257; *Ann. Pharm.* 80, 55; *Jahresber.* 1851, 478.

Formation. By the destructive distillation of azotised organic substances; being found: (a) in bone-oil (Anderson); (b) among the products obtained by the dry distillation of the bituminous shale of Dorsetshire (C. G. Williams, *Phil. Mag.* [4] 8, 24); (c) among the volatile bases obtained by the destructive distillation of cinchonine. (C. G. Williams, *Ed. Phil. Trans.* 21, ii. 315.)

Preparation. The more volatile oily portion of rectified bone-oil is set aside for some days with dilute sulphuric acid, and frequently shaken up; and the strongly acid liquid separated from the oil, is kept for a long time in a state of ebullition in a still, whereupon a series of bases resembling Runge's pyrrol, and called pyrrol-bases, pass over. The acid liquid separated from these bases and cooled, is then distilled with excess of slaked lime, and the oily bases which pass over separated from the aqueous solution by means of solid hydrate of potash, (*comp.* p. 160) and then subjected to fractional distillation. The fraction obtained between 65° and 100° contains propylamine and butylamine, and perhaps also ethylamine, amylamine, and caproamine. The portion which boils above 115° contains another series of bases, which may be approximately separated by repeated fractional distillation, the receiver being changed at every 55° . The portion which distils over at about 115° consists chiefly of pyridine. (Anderson.)

Properties. Transparent, colourless liquid, which does not become coloured by exposure to the air. It dissolves in all proportions in water, and readily in oils, both fixed and volatile. Acids dissolve it with great rise of temperature, and form easily soluble salts. (Anderson.)

Calculation.

10 C	60	75.95
N	14	17.72
5 H	5	6.33
$C^{10}NH^6$ 79 100.00			

Homologous with picoline ($C^{12}NH^7$) and belonging to a series of bases called by Anderson *Picoline-bases*, whose general formula is C^nNH^{n-2} .

Platinum-salt. — On mixing the solution of the hydrochlorate with bichloride of platinum, the double salt separates in flattened prisms, which are easily soluble in boiling water, less soluble in alcohol, and quite insoluble in ether. They are decomposed by boiling with water, with separation of a yellow salt. (*vid. inf.*) (Anderson.)

10 C	60.0	21.03	21.48	20.29
N	14.0	4.93				
6 H	6.0	2.10	2.30	2.24
3 Cl	106.2	37.33				
Pt	99.0	34.61	34.30	34.71
$C^{10}NH^5, HCl, PtCl^2$ 285.2		100.00				

The salt *a* analysed by Anderson was in the recently precipitated state; *b* had been boiled with water till a tolerably large portion remained undissolved. — Williams's salt *c* was obtained by saturating with hydrochloric acid the portion of the volatile bases from shale-naphtha which boiled below 98°; adding bichloride of platinum; diluting the liquid till the precipitate disappeared; and then evaporating over oil of vitriol, to avoid the decomposition which always takes place when the solutions of these platinum-salts are heated. The first and second crops of crystals thus obtained consisted of the platinum-salt of lutidine ($C^{14}NH^9$); the third and fourth of the platinum-salt of picoline ($C^{12}NH^7$); and the fifth and last of the platinum-salt of pyridine. The crystals, before ignition, were pulverised and washed with alcohol and ether to remove a resinous impurity. — *d* was obtained in a similar manner from the mixture of volatile bases produced by distilling cinchonine with caustic potash.

PLATINOPYRIDINE. $C^{10}NH^3Pt = C^{10}N \left\{ \begin{matrix} H^3 * \\ pt. \end{matrix} \right\}$ — When chloroplatinate of pyridine, carefully freed from excess of bichloride of platinum, is dissolved in hot water, and the solution boiled for several days, it deposits a sulphur-yellow crystalline powder, which is the bihydrochlorate of platinopyridine:



After five or six days' boiling, the whole of the chloroplatinate is transformed into this new compound; but if the yellow powder be separated before the decomposition is complete, the mother-liquor deposits on cooling another compound, consisting of golden-yellow laminæ, resembling iodide of lead. (*vid. inf.*)

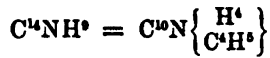
The hydrochlorate of platinopyridine is insoluble in water and in acids. It is decomposed by potash, with separation of pyridine. Platinopyridine cannot, therefore, be obtained in the free state by treating the hydrochlorate with alkalis; but on mixing the solution of that salt with silver-salts, chloride of silver is precipitated, and salts of platinopyridine are obtained. It is very difficult to prepare these salts in a definite state. The *chromate* is however obtained by adding bichromate of potash to sulphate of platinopyridine, in the form of an orange-red precipitate, containing $C^{10}NH^3Pt, HO, CrO^3$.

The yellow scales obtained by stopping the ebullition of the solution of chloroplatinate of pyridine, before the decomposition is complete, consist of a compound of chloroplatinate of pyridine with hydrochlorate of platinopyridine: $C^{10}NH^5, HCl, PtCl^2 + C^{10}NH^3Pt, 2HCl$. (Anderson, *N. Ann. Chim. Phys.* 44, 366.)

PLATOSOPYRIDINE. $C^{10}N \left\{ \begin{matrix} H^4 \\ Pt. \end{matrix} \right\}$ — When chloroplatinate of pyridine is boiled with excess of pyridine, the liquid becomes strongly coloured; and on evaporating to a syrup and digesting in water, a dark-coloured solution is obtained, together with a residue very sparingly soluble in water. This residue treated with boiling alcohol yields a solution, which, on cooling, deposits small needles of hydrochlorate of platosopyridine, $C^{10}NH^4Pt, HCl$. (Anderson.)

* pt. = $\frac{1}{2}$ Pt. = 49.5.

¶. Ethylopyridine.



Formed by the action of iodide of ethyl on pyridine. On gently heating the mixture of the two liquids an action ensues, attended with considerable rise of temperature, and hydriodate of ethylopyridine rises to the surface in the form of an oily layer, which crystallises on cooling. By decomposing this salt dissolved in water with moist oxide of silver, the base C¹⁴NH⁵O, is obtained, in the form of a colourless, strongly alkaline, aqueous solution, which has a caustic taste, absorbs carbonic acid from the air, and exhibits, for the most part with metallic salts, the same reactions as potash or soda.

Hydriodate of Ethylopyridine, crystallises in tables having a silvery lustre, easily soluble in water, and somewhat deliquescent; they likewise dissolve readily in alcohol and ether.

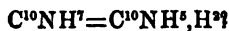
				Anderson.
14 C	84	35.90 36.17
N	14	5.98 5.70
10 H	10	4.27 4.59
I	126	53.85 53.54
C ¹⁴ NH ⁵ .HI or C ¹⁴ NH ¹⁰ .I 234			 100.00 100.00

Chloro-aurate. C¹⁴NH¹⁰Cl, AuCl³. Yellow tables, sparingly soluble in cold water, and decomposed by boiling with water.

Chloroplatinate. Obtained by decomposing the hydriodate with nitrate of silver; precipitating the excess of silver with hydrochloric acid; and mixing the filtrate with a concentrated solution of bichloride of platinum. Garnet-red rhombic tables, sparingly soluble in cold water, insoluble in a mixture of alcohol and ether. (Anderson.)

				Anderson.
14 C	84.0	26.82 26.33
N	14.0	4.47 4.47
10 H	10.0	3.19 2.92
3 Cl	106.2	33.91 33.91
Pt	99.0	31.61 31.62
C ¹⁴ NH ¹⁰ Cl, PtCl ³				313.2 100.00 ¶.

Stenhouse's Alkaloid.



STENHOUSE. *Ann. Pharm.* 70, 200.

Kidney beans are subjected to dry distillation in an iron cylinder, at the lowest possible heat; the distillate supersaturated with hydrochloric acid; the watery liquid decanted from the tar, which is then exhausted several times with water containing hydrochloric acid; the hydrochloric

spirit, acetone and neutral, and acid empyreumatic oil; and the liquid filtered through charcoal powder, supersaturated in a large distilling apparatus with lime or carbonate of soda, and distilled. A *first* watery distillate then passes over, with oily alkaloïds floating upon it, which increase but then diminish again, so that at last nothing passes over but an aqueous solution of these oils, which must be collected apart as a *second* distillate. — The oil is removed from the *first* distillate, and dissolved in hydrochloric acid; the hydrochloric acid solution separated from the neutral oil by means of a wet filter; the filtrate distilled in a large retort with excess of carbonate of soda; and the oily alkaloïd which passes over separated with the pipette from the ammoniacal liquid. The *second* distillate, after neutralisation with hydrochloric acid, is then concentrated at a gentle heat, (at a boiling temperature a large quantity of the alkaloïd would be resinised,) distilled with carbonate of soda, and the oily alkaloïd which is removed from the distillate, rectified several times with water, a small quantity of resin then remaining behind. The united oily alkaloïds from the *first* and *second* distillates are repeatedly shaken up with strong potash-solution to remove the ammonia, being each time separated from the ammoniacal potash-ley, till all the ammonia is expelled, which is not effected without loss; they are then freed from water, which amounts to half their bulk, by repeated agitation and several days' standing with hydrate of potash, till that substance no longer becomes moist; the clear oil poured off and carefully rectified; and the last third, which passes over no longer colourless but yellowish, collected apart, repeatedly rectified, till it also becomes colourless, then added to the first two-thirds, and slowly rectified in a retort provided with a thermometer. The boiling begins at 108°; a small quantity passes over between 108° and 130°; a large quantity between 150° and 165°; and the last between 165° and 220°. The distillates thus obtained are further separated, according to their different degrees of volatility, by repeated fractional distillation.

All these oily alkaloïds agree with each other in the following respects: They are transparent and colourless, with strong refracting power; lighter than water; have a pungent, slightly aromatic odour and a burning taste; redden turmeric, and turn reddened litmus blue; and produce fumes with hydrochloric acid. In closed vessels they do not alter in the dark, but on exposure to light they become yellow and less volatile. When boiled, they turn brown, and are resolved into a colourless distillate and a dark-brown resinous residue. When passed through a red-hot tube filled with charcoal, they are converted into ammonia. They are also decomposed, with evolution of ammonia, by boiling with potash-ley, or by the continued boiling of their aqueous solutions. By nitric acid they are converted into resins of a deep yellow colour, not into picric acid, and by aqueous chloride of lime into brown resins without exhibiting the reaction of aniline. They dissolve in water with tolerable facility, the more volatile more readily than the less. They neutralise acids, and their salts are mostly crystallisable; but those of the more fixed alkalis are contaminated with a brown resin and crystallise less readily. They precipitate the salts of iron and copper, but the copper-precipitate dissolves with blue colour in excess of the alkalis. With mercury, gold, and platinum, they form double salts, which are about as soluble as the corresponding double salts of ammonia.

The alkaloid which boils between 150° and 155° forms crystallisable

salts with sulphuric, nitric, and hydrochloric acid. The *hydrochlorate* forms easily soluble, transparent prisms. The *gold double salt* dissolves readily in water, and separates in light yellow needles on cooling. The *platinum double salt* forms four-sided prisms of a deep yellow colour, which dissolve in water with tolerable facility; they contain 34.66 p. c. platinum. (Stenhouse.)

		Alkaloid, boiling at 150°—155°,		at 160°—165°,		at 170°,		at 200°—210°	
10 C 60 74.07 74.69 74.08 75.42 75.63			
N 14 17.29							
7 H 7 8.64 7.97 8.06 8.52 8.73			
C ¹⁰ NH ⁷ 81 100.00							

[May not these several volatile oils be merely the same alkaloid in different degrees of purity?]

The same or similar alkaloids are obtained by dry distillation, at the gentlest possible heat, of bones, wheat, linseed-oil cake, coal, peat, and the entire plant of *Pteris aquilina*, whereas wood yields only a trace. (Stenhouse.)

Kidney-beans or linseed-oil cake distilled with strong soda-ley, likewise evolve, together with ammonia, a tolerably large quantity of a similar alkaloid, which may be obtained by rectifying the distillate, neutralising with hydrochloric acid, filtering from the neutral oil, &c.; ox-liver similarly treated yields but a small quantity. (Stenhouse.)

Similar alkaloids are likewise obtained by digesting kidney-beans with a mixture of 1 pt. oil of vitriol and 3 to 4 pts. water, the process being stopped before sulphurous acid begins to escape. (Stenhouse.)

In the dry distillation of *Semen Lycopodii*, an oily alkaloid of peculiar and very pungent odour passes over first, then an alkaloid resembling that obtained from kidney-beans. If, on the other hand, the lycopodium be first boiled to dryness with strong soda-ley and then distilled, only the former alkaloid is obtained, together with a large quantity of ammonia.

Lastly, similar alkaloids may be formed by the putrefaction of azotised compounds. Horse-flesh which had been repeatedly boiled with water for a different purpose, on being left to putrefy, and then exhausted with water containing hydrochloric acid, yielded a hydrochlorate of an alkaloid and sal-ammoniac. By concentrating the liquid, distilling with carbonate of ammonia, and repeatedly rectifying the distillate over hydrate of soda, a light, colourless, oily mixture of alkaloids was obtained, having a rather agreeable aromatic odour, easily soluble in water, and capable of neutralising acids; the quantity was however much less than that which had been obtained by dry distillation of the flesh. (Stenhouse, *Ann. Pharm.* 72, 86.)

LIKENE-SERIES.

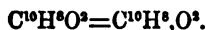
Primary Nucleus. C¹⁰H⁸.

The illuminating gas obtained on the large scale by dry distillation of resin and a small quantity of fixed oil, deposits under strong pressure a brown oily mixture having the odour of phosphuretted hydrogen. This oily mixture when distilled, leaves a sooty matter, bituminous tar, and a small quantity of naphthalin, and yields a nearly colourless distillate, which, when dehydrated over chloride of calcium and repeatedly subjected to fractional distillation, is resolved into six oils of various degrees of volatility (boiling from 28° to 140°.) (Couverbe.) After the most volatile, which boils at 28° [and is perhaps amylene], follows the oil, probably belonging to this place, and called by Couverbe, *Pentacarbure quadrihydrique*.

It is colourless, of sp. gr. 0·709 at 14°, boils at 50° [calculation, according to Gerhardt's law (vii. 57), gives 45°], and its vapour-density is 2·354. (Couverbe, *Ann. Chim. Phys.* 69, 184; *J. pr. Chem.* 18, 165.)

				Couverbe.			Vol.	Density.	
10 C	60	88·24	88·14	C-vapour	10	4·1600
8 H	8	11·76	11·59	H-gas	8	0·5546
C ¹⁰ H ⁸	68	100·00	99·73	Oil-vapour	2	4·7146
							1	2·3573

Guajacene.



DEVILLE. (1843.) *Compt. rend.* 17, 1143; 19, 134.

C. VÖLCKEL. *Ann. Pharm.* 89, 345.

Guajol. (Völckel.)

The oily mixture of guajacene, pyroguajacic acid, nacreous laminæ, and certain other empyreumatic products, obtained by dry distillation of guajac resin, yields, when it is rectified, and only the most volatile portion collected, guajacene, which appears to be formed, with elimination of 2 At. carbonic acid, by decomposition of the guajacic acid contained in the resin. (Deville.)

Colourless oil (Deville); yellow, even after repeated distillation. (Völckel.) Sp. gr. 0·874 (Deville); 0·871 at 15°. (Völckel.) Boils at 118° (Deville); from 115° to 120° (Völckel); giving off a vapour whose density is 2·92. (Deville.) Smells like bitter almond oil (Deville), somewhat also like the yellow oils which pass over in the distillation of sugar between 80° and 120°. Its taste is very strong, pungent, and burning.

Calculation, acc. to Deville.			Calc. acc. to Völckel.			Völckel.
10 C	60	71.42	9 C	54	70.13	69.91
8 H	8	9.53	7 H	7	9.10	9.40
2 O	16	19.05	2 O	16	20.77	20.69
$C^{10}H^{16}O^2$	84	100.00	$C^9H^{14}O^2$	77	100.00	100.00
				Vol.	Density.	
C-vapour			10	4.1600		
H-gas			8	0.5546		
O-gas			1	1.1093		
Guajacene-vapour			2	5.8239		
			1	2.9119		

[If the formula $C^{10}H^{16}O^2$ be correct, guajacene may be regarded as the aldide of angelic acid (Gerhardt, *Compt. rend.* 26, 226.) — Völckel's formula, which agrees better with the analysis, should perhaps be doubled to make the number of carbon-atoms even.]

The oil, when exposed to the air, is converted by oxidation into beautiful crystalline laminæ. (Deville.) [Of angelic acid ?] — ¶. Each time that it is distilled, a small quantity of a yellowish brown substance is formed. — Nitric acid dissolves it with violent action, and water added to the solution throws down a yellow resinous body. Strong sulphuric acid also dissolves it, forming a solution from which water precipitates a small quantity of resinous matter. The oil absorbs a small quantity of hydrochloric acid gas, and acquires thereby a darker colour. It absorbs chlorine, with formation of a heavy yellow oil. When shaken up with potash, it is at first decolorised, but quickly passes through successive shades of blue, red, and brown, and is ultimately converted into a resinous body of yellow, brownish yellow, yellowish brown, or red-brown colour, according to the strength of the potash-ley. The red-brown substance dissolves in water, forming a solution of the same colour from which it is reprecipitated by water. It also dissolves in alcohol. (Völckel.)

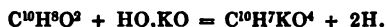
Guajacene is but sparingly soluble in *water*, but dissolves in all proportions in *alcohol* and ether. (Völckel.)

Essential Oil of Roman Camomile (Anthemis nobilis). — This oil is a mixture of the aldide of angelic acid $C^{10}H^{16}O^2$ [or hydride of angelyl $C^{10}H^{16}O^2, H$] with a hydrocarbon, $C^{10}H^{16}$, isomeric with oil of turpentine, and a small quantity of angelic acid. It is greenish, slightly acid, and has a pleasant odour. It begins to boil at about 160° ; but the boiling point gradually rises to 180° and even to 190° , at which temperature two-thirds of the oil pass over. Towards the end of the distillation, the boiling point rises to 210° , but this rise is due merely to the presence of a resinous impurity and of a less volatile oil; for the first and last portions of the distillate exhibit the same reactions and very nearly the same boiling point. Three portions of the oil collected between 200° and 210° , gave by analysis :

	Gerhardt.		
Carbon	75.57	76.61	76.00
Hydrogen	10.57	10.66	10.78
Oxygen	13.86	12.73	13.22
	100.00	100.00	100.00

The oil is not acted upon by aqueous potash; but when gently heated with pulverised hydrate of potash, it is entirely converted, without

oil in its original state. On continuing the heat, however, a sudden rise of temperature takes place, and hydrogen is evolved; and if the external heat be then removed, the action goes on spontaneously to the end; the hydrocarbon contained in the oil volatilises, and angelate of potash remains behind :



If the heating be still further continued, hydrogen is more abundantly evolved, and the angelate of potash is converted into acetate and propionate of potash :



(Gerhardt, *N. Ann. Chim. Phys.* 24, 96; also *Traité de Chimie organique*, 2, 445; Chiozza, *N. Ann. Chim. Phys.* 39, 435.)

Oil of camomile does not form any crystalline compound with alkaline bisulphites. (Bertagnini.) ¶.

Angelic Acid.



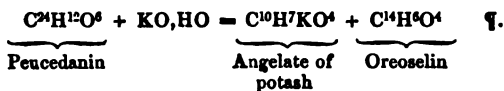
L. A. BUCHNER. (1843.) *Repert.* 76, 161; abstr. *Ann. Pharm.* 42, 226.

H. MEYER & D. ZENNER. *Ann. Pharm.* 55, 307.

REINSCH. *Jahrb. pr. Pharm.* 7, 79;— & Hopf. 11, 217;— & Recker, 16, 12.

Angelic acid, Sumbuloläure, Angeliksäure, Acide angélique.

Sources and Formation. In the root of *Angelica Archangelica* (Buchner), and more abundantly, as it appears, in the Sumbul or Moschus-root, which likewise appears to belong to an umbelliferous plant. (Reinsch.) The less volatile portion of the essential oil of *Anthemis nobilis* is converted by boiling with alcoholic potash into angelate and valerate of potash. (Gerhardt, *N. Ann. Chim. Phys.* 24, 96.) — ¶. The supposed valerianic acid obtained by decomposing this potash-salt with sulphuric acid, was probably nothing but angelic acid, rendered uncrystallisable by the presence of certain products of its decomposition, viz., acetic and propionic acid; in fact, the angelates and the valerates exhibit nearly the same composition per cent. (Gerhardt, *Traité de Chimie organique*, 2, 450.) The oil is also converted into angelate of potash when gently heated with pulverised hydrate of potash. (Chiozza, *vid. sup.*) — 2. Peucedanin treated with alcoholic potash, is converted into angelic acid and oreosilin (Wagner *J. pr. Chem.* 62, 275):



Preparation. a. From Angelica-root. 1. The root is exhausted with alcohol; the filtrate evaporated to a small bulk; the residual angelica-balsam freed from the subjacent layer of extract, which has the consistence of honey; then washed with water, and digested with aqueous potash; the filtrate evaporated; the mass redissolved in water; the liquid filtered to

separate a waxy substance; the filtrate then set aside as long as needles of angelicin continue to separate from it; the liquid separated therefrom and containing angelate of potash, distilled with dilute sulphuric acid; and the distillate, consisting partly of aqueous acid, partly of oily drops of the pure acid saturated with potash, evaporated and distilled with strong phosphoric acid: pure angelic acid then passes over in the form of an oil. (Buchner.) The liquid obtained by boiling the balsam with dilute potash may also be supersaturated when cold with dilute sulphuric acid, decanted from the precipitated resin, and distilled; and the distillate, which smells of valerianic acid, redistilled; the turbid distillate then deposits crystals of angelic acid, surmounted by an oily layer of valerianic acid. (Meyer & Zenner.)— 2. Fifty pounds of the dry root are boiled with 4 pounds of lime and with water; the liquid strained by pressure through linen; the brown solution evaporated, and distilled in a copper still with excess of dilute sulphuric acid; the turbid and acid distillate, which is covered with a neutral oil, and smells like fennel, supersaturated with potash and evaporated, whereby the fennel odour, which proceeds from neutral oil, is destroyed; the brown residue again distilled with sulphuric acid in the copper still, with a condensing tube not kept too cold; the residue repeatedly mixed with small quantities of water and redistilled; and the turbid distillate, containing a large quantity of oily drops, set aside for several days in the cold, as long as angelic acid continues to separate from it in needles and prisms, while valerianic and acetic acid remain dissolved in the water. The crystals are then washed with a small quantity of water, and repeatedly crystallised to free them from the still adhering valerianic acid, which remains in the mother-liquor, together with a small quantity of angelic acid. 100 pts. of the root thus treated, yield from 0.25 to 0.38 pt. of pure angelic acid. (Meyer & Zenner.)

b. From Sumbul-root.— Sumbul-balsam obtained by exhausting the root with alcohol and evaporating the filtrate, is boiled with concentrated potash, whereupon a volatile oil evaporates; the brown-red alkaline filtrate mixed with sulphuric acid, which separates a dark brown oil; and this oil distilled with water, which is added at intervals as the distillation goes on, as long as it passes over turbid, and mixed with drops of oil. (Sumbulamic acid remains in the retort). The oily-watery distillate set aside in the cold, deposits angelic acid (amounting to 3.5 per cent. of the root) in transparent colourless needles, while a small quantity of valerianic acid remains in solution. The crystallised acid is purified by twice saturating it with carbonate of soda, and distilling with sulphuric acid, then by distilling it *per se*, and finally, by keeping it for a long time in a state of ebullition. (Reinsch.) If the acid has not been completely freed by sufficient distillation from the sumbulamic acid likewise occurring in the sumbul-root, the alcoholic solution acquires a fine blue colour when mixed with sulphuric acid; whereas, if sumbulamic is not present, the solution remains colourless. (Reinsch.)— *c.* By heating the essential oil of *Anthemis nobilis* with hydrate of potash. (Gerhardt, Chiozza, p. 418.)

Properties. Large, long, transparent, colourless prisms and needles. (Meyer & Zenner, Reinsch). Melts at 45° (Meyer & Zenner), between 43° and 45° (Reinsch), to a transparent oil which floats on water, and at a few degrees above 0°, solidifies in a radiated mass of needles. (Buchner.) Boils at 190° (191° according to Reinsch), and may be distilled without

& Zenner), a pungent odour like that of valerianic and glacial acetic acid. (Reinsch, Buchner.) Tastes very sour and at the same time burning and aromatic (Buchner, Reinsch), and when placed on the tongue, produces a white spot which soon disappears. (Reinsch.) Reddens litmus.

Crystals.		Meyer & Zenner.	Reinsch & Ricker.	Gerhardt.
		a.	b.	c.
10 C	60	59.42	59.79	59.69
8 H	8	8.04	8.03	7.98
4 O	32	32.54	32.18	32.33
<hr/>				
C ¹⁰ H ⁸ O ⁴	100	100.00	100.00	100.00

a is the acid from angelica-root; b that from sumbul-root; c that obtained by fusing the oil of Roman camomile with hydrate of potash.

Decompositions. 1. The acid burns, when set on fire, with a bright and somewhat smoky flame. — 2. The potash-salt fused with excess of potash is resolved into acetate and propionate of potash, with evolution of hydrogen (Chiozza, p. 413).

Combinations. Angelic acid dissolves sparingly in cold, abundantly in hot water, whence it separates in needles on cooling. (Meyer & Zenner.)

Angelic acid decomposes the alkaline carbonates. The *Angelates* give off part of their acid when their aqueous solutions are evaporated. (Meyer & Zenner.)

Angelate of Ammonia. — Soluble in water and alcohol (Meyer); the solution smells like saffron. (Reinsch.)

Angelate of Potash. — Soluble in water and alcohol (Reinsch.)

Angelate of Soda. — Soluble in water and alcohol. (Meyer.) The concentrated solution mixed with alcohol yields deliquescent crystals. (Reinsch.)

Angelate of Lime. — Shining laminæ, which dissolve very easily in water, and give off 12.1 p. c. water at 100°. (Meyer & Zenner.)

Crystals.		Meyer & Zenner.	
CaO	28	20.44	20.56
C ¹⁰ H ⁷ O ⁴	91	66.42	
2 HO	18	13.14	12.10
<hr/>			
C ¹⁰ H ⁷ CaO ⁴ , 2Aq	137	100.00	

Angelate of Lead. — Alkaline angelates form, with lead-salts, a white precipitate soluble in a large quantity of water. (Buchner.) The precipitate likewise dissolves on heating the mixture, and then separates in nodules on cooling. (Reinsch.) The solution of lead-oxide in excess of the aqueous acid, yields, when evaporated by heat, beautiful crystals of the neutral salt. The salt is very much inclined to give up a portion of its acid, and pass into the condition of a basic salt, which crystallises in laminæ. The neutral salt cakes together when heated, and gradually melts into a semi-transparent mass, while part of the acid volatilises. (Meyer & Zenner.)

PbO	112	...	55.17	54.95
10 C	60	...	29.55	29.37
7 H	7	...	3.44	3.66
3 O	24	...	11.84	12.02

$C^{10}H^7PbO^4$ 203 100.00 100.00

The alkaline angelates form, with *Ferric salts*, a flesh-coloured precipitate insoluble in water (Buchner, Meyer), a yellowish brown precipitate (Reinsch); with *Cupric salts*, a bluish white precipitate, soluble in a large quantity of water (Buchner); and with *Mercurous nitrate*, a white precipitate, which soon turns grey (Buchner), and redissolves. (Reinsch.) They do not precipitate corrosive sublimate.

Angelate of Silver.— Alkaline angelates precipitate from silver-solution, a white salt (crystalline according to Reinsch), which dissolves in a large quantity of water, forming a solution whence silver is deposited, after a while, in the form of a black powder. (Buchner.) The somewhat acid solution of silver-oxide in the boiling aqueous acid, yields by evaporation at the gentlest possible heat, small crystals of the neutral salt, having usually a greyish white colour, and soluble in water and alcohol—or sometimes, if the acid volatilises during the evaporation, laminae of a basic salt. (Meyer & Zenner.)

<i>Neutral crystals, dried cold in vacuo.</i>		<i>Meyer & Zenner.</i>			
10 C	60	...	28.99	29.08
7 H	7	...	3.38	3.54
Ag	108	...	52.17	52.26
4 O	32	...	15.46	15.12

$C^{10}H^7AgO^4$ 207 100.00 100.00

Angelic acid dissolves very readily in *alcohol* and *ether*. (Meyer & Zenner, Reinsch.)

It dissolves easily in *oil of turpentine* and in *fixed oils*. (Meyer & Zenner.)

¶. Anhydrous Angelic Acid. $C^{10}H^7O^3$ or $C^{10}H^7O^2\}O^3$

CHIOZZA. *N. Ann. Chim. Phys.* 39, 210; *Compt. rend.* 36, 630; *Ann. Pharm.* 86, 260.

Obtained by the action of oxychloride of phosphorus on angelate of potash. The viscid oil thus produced yields, when treated with dilute carbonate of soda and then with ether, an ethereal solution, which, when evaporated, leaves the anhydrous acid.

Perfectly neutral, limpid oil, heavier than water; does not crystallise even in a mixture of ice and salt; has a peculiar odour differing altogether from that of the hydrated acid. It is but very slowly rendered acid by the action of water; but strong alkaline solutions dissolve it readily with the aid of heat.

		<i>Chiozza.</i>			
20 C	120	...	65.93	65.92
14 H	14	...	7.70	7.88
6 O	48	...	26.37	26.20

$C^{20}H^{14}O^6$ 182 100.00 100.00

rises to 250°, where it remains nearly stationary. Towards the end of the distillation, the liquid emits a penetrating odour, like that of citraconic acid; becomes continually darker in colour; and ultimately leaves a carbonaceous residue. The distillate contains hydrated angelic acid, part of which condenses in needles in the neck of the retort; also a neutral oil, having an odour like that of peppermint. The anhydrous acid, heated with a small piece of hydrate of potash, becomes strongly acid, and gives off vapours of the hydrated acid. — Aqueous ammonia first converts it into a buttery mass, and then dissolves it. — In contact with aniline, it becomes strongly heated, and, after a while, deposits crystals of angelanilide. (Chiozza.)

Conjugated Compound.

Angelic Ether.

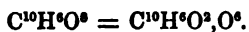
When angelate of soda is distilled with a mixture of 1 pt. of oil of vitriol and 2 pts. of 94 per cent. alcohol, angelic ether passes over in oily stræ, which may be separated by water and common salt.

It is colourless, smells like sour apples, and when inhaled excites coughing and violent head-ache; its taste is sweetish, burning, and aromatic. It burns with a bluish flame. (Reinsch & Ricker.)

SECONDARY NUCLEI.

a. Oxygen-nucleus. C¹⁰H⁶O².

Citraconic Acid.



LASSAIGNE. (1822.) *Ann. Chim. Phys.* 21, 100; also *J. Pharm.* 8, 490; also *Schw.* 36, 428; also *N. Tr.* 7, 2, 111.

DUMAS. *Ann. Chim. Phys.* 52, 295; also *Schw.* 68, 331; also *Pogg.* 29, 37; also *Ann. Pharm.* 8, 17.

ROBIQUET. *Ann. Chim. Phys.* 65, 78.

LIEBIG. *Ann. Pharm.* 26, 119, and 152.

CRASSO. *Ann. Pharm.* 34, 68.

ENGELHARDT. *Ann. Pharm.* 70, 246.

GOTTLIEB. *Ann. Pharm.* 77, 265; abstr. *Pharm. Centr.* 1851, 353; *Compt. chim.* 1851, 113; *N. J. Pharm.* 19, 476; *Chem. Gaz.* 1851, 233; *Jahresber.* 1851, 394.

Pyrocitric acid, Brenzcitronsäure, Acide pyrocitrique, Ac. citribique. (Baup.)

Formation. By the dry distillation of citric acid (Lassaigne), and of lactic acid. (Engelhardt.)

Preparation. Citric acid subjected to dry distillation yields a watery acid liquid, and below it an oily liquid [anhydrous citraconic

immediately saturated with lime. The oil is repeatedly shaken up with water, which then takes up an additional quantity of citraconic acid, and leaves a brown pitchy mass, having a very decided empyreumatic odour. The aqueous acid obtained in this manner from the oily liquid, is also saturated with lime, and the solution either freed from lime by precipitation with oxalic acid, and afterwards filtered and evaporated; or the liquid mixed with acetate of lead, whereby citraconate of lead is precipitated, and this precipitate decomposed by sulphuretted hydrogen. (Lassaigne.) — Dumas dilutes with water the distillate obtained by dry distillation of citric acid, neutralises with carbonate of soda, and precipitates with acetate of lead. — Crasso purifies by rectification the oily distillate obtained by dry distillation of citric acid [citraconic anhydride], and converts it by exposure to moist air into the crystallised acid, which may be freed from the excess of water which it has absorbed, by pressure between paper and drying at 50°.

2. To obtain the small quantity of citraconic acid in the liquid obtained by dry distillation of lactic acid, and consisting chiefly of lactide, lactic acid, and aldehyde, this distillate is freed from aldehyde by heating it to 100°; the residue, which solidifies to a crystalline magma on cooling, washed with absolute alcohol, which leaves the lactide-crystals undissolved; the alcoholic filtrate distilled, whereupon the lactic acid remains behind; the portion which distils over at 220°, neutralized with carbonate of baryta; and the baryta-salt, which separates from the alcoholic liquid as a crystalline magma, purified by recrystallisation from hot water. (Engelhardt.)

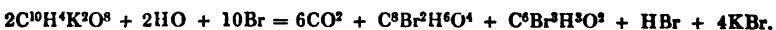
Properties. Colourless, four-sided prisms belonging to the right prismatic system (Crasso); mass composed of interlacing needles. (Lassaigne.) Melts at 80°. (Crasso.) Inodorous; has a sour and slightly bitterish taste, and reddens litmus. (Lassaigne.)

	<i>Crystals.</i>		Crasso.	Lassaigne.
10 C	60	46·15	46·24	47·5
6 H	6	4·62	4·60	9·0
8 O	64	49·23	49·16	43·5
$C^{10}H^6O^8$	130	100·00	100·00	100·0

Decompositions. 1. The acid heated in a retort above its melting point, evaporates, and passes over, first as water, afterwards as citraconic anhydride, without leaving any residue. (Crasso.)



2. When bromine is gradually added to the concentrated solution of neutral citraconate of potash in water, carbonic acid gas is evolved with effervescence, the liquid becomes turbid, and deposits a yellow oil, the quantity of which is about equal to that of the decomposed citraconic acid. This oil is a mixture of 1 pt. tribromopropylaldehyde (ix. 428), and 5 pts. bibromobutyric acid (p 136) (Cahours):



[According to this, however, the quantity of tribromopropylaldehyde should exceed that of the bibromobutyric acid.] — If the solution of the citraconate of potash contains excess of potash, the bromine likewise separates an oily mixture, with copious evolution of carbonic acid; but the acid extracted therefrom by alkalis is bromopropionic acid (ix. 428), and the insoluble

— ¶. 3. When a dilute solution of citraconic acid is boiled with about $\frac{1}{2}$ pt. of dilute nitric acid, a quiet action takes place, attended with slow evolution of gas; and the solution left to cool after a quarter to half an hour's boiling, deposits porcelain-like crystalline masses of *mesaconic acid* (p. 427). The mother-liquor yields by evaporation a small additional quantity of mesaconic acid, and lastly oxalic acid; there is also formed a yellow nitrocompound, which adheres obstinately to the mesaconic acid, and colours it yellow, but may be removed by repeatedly crystallising the acid, or by boiling with animal charcoal. (Gottlieb.)— When a saturated solution of citraconic acid is gently heated with nitric acid of sp. gr. 1.47, a violent action takes place, attended with the formation of numerous products. (Gottlieb.) When citraconic acid is treated with strong nitric acid, there is formed, among other products, an oily substance which, on cooling, solidifies in a crystalline mass. On boiling this mass with water, an odour of mint is evolved, and the liquid acquires a sweet taste. By repeatedly boiling the crystalline mass with water, and then treating it with hot alcohol of 88 per cent., a solution is obtained which, on cooling, deposits two substances of different degrees of solubility, both of which are colourless nitrocompounds, without taste or smell. The more soluble of these two bodies crystallises from alcohol, in white, striated, silky prisms; from ether in small transparent, highly lustrous crystals. It dissolves readily in hot alcohol of 88 p. c., in 170 parts of the same at 10°, and in 10,000 pts. of water at 10°. In boiling water, it melts into transparent globules, which, on cooling, often remain soft and transparent, but immediately become hard and opaque on being touched. This substance solidifies after fusion to a laminated crystalline mass, provided it has not been heated too long; at a higher temperature, it volatilizes completely, emitting an odour like that of amyrrin; gives off nitrous fumes when heated in a tube; burns with flame when set on fire. Dissolves in warm oil of vitriol, and crystallises out for the most part again on cooling. — The less soluble substance crystallises from alcohol in small, shining, transparent needles; also from ether in needles. It dissolves at 10° in 2200 pts. of 88 p. c. alcohol, in 1500 pts. of 97 p. c. alcohol, and in 24,000 pts. of water. Does not melt in boiling water, but dissolves to a certain extent in that liquid. Solidifies in shining prisms, even after long-continued fusion. Sublimes completely in small shining crystals, giving off a peculiar odour, like those of cumin and of mint. Dissolves also in oil of vitriol. (Baup, *Ann. Pharm.* 81, 103.) ¶.

Combinations. The acid dissolves in 3 pts. of water at 10° (Lassaigne; in 0.42 pt. at 15° (Baup); it deliquesces in the air, and its concentrated solution is viscid (Crasso).

The neutral *Citraconates* or *Pyrocitrates* are = $C^{10}H^6M^2O^8$, and the acid salts = $C^{10}H^5MO^8$.

CITRACONATE OF AMMONIA. — *Acid.* — Obtained by supersaturating ammonia with the aqueous acid. Shining crystalline laminae. (Crasso.)

	<i>Crystals.</i>		<i>Crasso.</i>	
10 C	60	40.81	41.01	
N	14	9.53	9.16	
9 H	9	6.12	6.12	
8 O	64	43.54	43.71	
$C^{10}H^4(NH^4)O^8$	147	100.00	100.00	

CITRACONATE OF POTASH — *a. Basic or Neutral.* — Carbonate of potash neutralised with the aqueous acid, dries up on evaporation to a pulverulent mass, easily soluble in water. — (Crasso.) — *b. Monobasic or Acid.* — If twice as much acid be used as is required to neutralise the potash, shining laminæ are obtained, very easily soluble in water. (Crasso.) — Lassaigue describes a potash-salt which crystallises in needles, permanent in the air, and soluble in 4 pts. of water. According to Baup (*Ann. Pharm.* 29, 169), there is also a salt containing 1 At. potash with 2 At. acid.

CITRACONATE OF SODA. — The bibasic and monobasic salts cannot be obtained in the crystalline form, but dry up to a white powder, which dissolves very easily in water. (Crasso.)

CITRACONATE OF BARYTA. — *a. Neutral.* — The acid neutralised with baryta-water, deposits, after some hours, a crystalline powder, soluble in 150 pts. of cold, and 50 pts. of hot water. (Lassaigue.) The concentrated acid saturated at a boiling heat with carbonate of baryta, deposits on cooling a white crystalline powder, sparingly soluble in cold, readily in hot water. (Crasso.) The salt obtained by dry distillation of lactic acid (p 418), crystallises on cooling in beautifully nacreous laminæ which give off 14.62 p. c. (5 At.) water, at 100°, retaining their lustre, and are decomposed only at a strong heat. (Engelhardt.)

	Dried at 100°.		Engelhardt.		Crasso.	Lassaigue.
2 BaO	153.2	57.77	57.67	57.21	56.1	
10 C	60.0	22.62	22.69			
4 H	4.0	1.51	1.86			
6 O	48.0	18.10	17.78			
<hr/>						
C ¹⁰ H ⁴ Ba ² O ⁵	265.2	100.00	100.00			

b. Acid. — Crystallises from the aqueous solution in large nodules, composed of delicate needles with a silky lustre. They contain 37.01 p. c. baryta, do not give off anything at 100°, and swell up before burning. (Crasso.)

CITRACONATE OF STRONTIA. — *a. Neutral.* — Obtained by saturating the boiling acid with carbonate of strontia. Does not crystallise distinctly, and effloresces strongly when the solution is evaporated. — *b. Monobasic.* — Large, colourless, shining crystals, which give off 26.19 p. c. water and acid, and become opaque at 100°; emit a distinct odour of acid at 120°, and swell up at a stronger heat. (Crasso.)

	Crystals.		Crasso.
SrO	52	26.0	26.1
C ¹⁰ H ⁴ O ⁷	121	60.5	
3 HO	27	13.5	
<hr/>			
C ¹⁰ H ⁴ SrO ⁶ + 3Aq.	200	100.0	

CITRACONATE OF LIME. — *a. Neutral.* — Needles united in arborescent groups, having a sharp taste, soluble in 28 pts. of water, containing in the air-dried state 30 per cent. of water, and in the anhydrous state 66 p. c. lime. (Lassaigue.) The acid saturated with carbonate of lime dries up with efflorescence when evaporated, and leaves a white mass, very soluble in water. (Crasso.)

water, and crumble to a white powder, at 120°, give off in air 15.54 p. c. (3 At.) water; at 140° give off also a small quantity of acid; afterwards turn black, swell up into a brownish mass, and finally burn away. (Crasso.)

	<i>Crystals.</i>		<i>Crasso.</i>	
CaO	28	15.91	16.21	
C ¹⁰ H ⁵ O ⁴	121	68.75		
3 HO	27	15.34	15.54	
<hr/>				
C ¹⁰ H ⁵ CaO ⁸ + 3Aq.....	176	100.00		

CITRACONATE OF MAGNESIA. — The solution dries up on evaporation to a translucent mass, exhibiting a radiated structure on the fractured surface, and very soluble in water. (Crasso.)

MANGANOUS CITRACONATE. — Opaque viscid mass. (Crasso.)

STANNOUS CITRACONATE. — Alkaline citraconates form a white precipitate with protochloride of tin. (Crasso.)

CITRACONATE OF LEAD. — *a. Quadribasic.* — Obtained by precipitating subacetate of lead with bibasic or monobasic citraconate of potash. White crystalline powder, nearly insoluble in water. (Crasso.)

			<i>Crasso.</i>	
4 PbO	418	80	79.48	
C ¹⁰ H ⁴ O ⁶	112	20		
<hr/>				
2 PbO, C ¹⁰ H ⁴ Pb ² O ⁸	560	100		

b. Neutral. — a. Anhydrous. — 1. A hot aqueous solution of bibasic citraconate of soda is precipitated by an insufficient quantity of nitrate of lead; and the sandy precipitate, as it is somewhat soluble, washed with not too large a quantity of cold water. (Dumas.) — 2. The aqueous acid, mixed with a small quantity of ammonia, is precipitated with neutral acetate of lead, and the mixture heated to the boiling point, whereby the smaller portion of the bulky precipitate is dissolved, and the greater portion converted into a crystalline powder, which is thrown boiling hot on the filter, and washed with boiling water. It gives off nothing at 100°, but blackens at a stronger heat, and then burns away quietly. (Crasso.)

	<i>Anhydrous.</i>		<i>Dumas.</i>		<i>Crasso.</i>		<i>Lassaigne.</i>	
2 PbO	224	66.67	66.46	66.60	66.60	66.60		
10 C	60	17.86	18.21					
4 H	4	1.19	1.22					
6 O	48	14.28	14.11					
<hr/>								
C ¹⁰ H ⁴ Pb ² O ⁸	336	100.00	100.00					

Dumas dried the salt in vacuo at 180°.

β. Bi-hydrated. — 1. The liquid filtered at a boiling heat from the anhydrous salt (*vid. sup.*), deposits on cooling a bulky white powder, which does not exhibit any crystalline structure when dry, swells up when heated, and dissolves sparingly in cold, but very readily in hot water. (Crasso.)

γ. Tetra-hydrated. — Obtained by precipitating a cold solution of neutral acetate of lead with bibasic citraconate of potash. White, trans-

lucent, gelatinous mass, which shrinks together in drying, and then contains 8 p. c. water. (Lassaigne.) Similarly with a cold solution of bibasic citraconate of ammonia. The jelly, when exposed to the air, dries up to a pale yellow gum, which at 100° becomes opaque, and gives off 9.27 p. c. water, and when further heated, burns away with intumescence. When the gelatinous precipitate is boiled with the liquid, it dissolves completely, but after a few seconds deposits the anhydrous salt, in the form of a crystalline powder, which does not redissolve by longer boiling. (Crasso.)

<i>Bihydrated.</i>				Crasso.
2 PbO	224	63.28 63.68
$C^{10}H^{10}O^8$	112	31.64	
2 HO	18	5.08	
<hr/>				
$C^{10}H^8Pb^2O^8 + 2Aq.$	354	100.00	
 <i>Tetrahydrated.</i>				 Crasso.
2 PbO	224	60.22 59.66
$C^{10}H^{10}O^8$	112	30.11	
4HO	36	9.67 9.27
<hr/>				
$C^{10}H^4Pb^2O^8 + 4Aq.$	372	100.00	

c. Acid. — The solution of the bibasic salt in a large excess of the aqueous acid deposits small pale yellow crystals (Dumas); beautiful, loosely aggregated crystalline geodes, having a silvery lustre. (Gottlieb.)

<i>Dried in vacuo at 140°.</i>				Dumas.	Gottlieb.
PbO	112	48.07 47.89 48.04
10 C	60	25.75 25.85	
5 H	5	2.15 2.24	
7 O	56	24.03 24.02	
<hr/>					
$C^{10}H^8PbO^8$	233	100.00 100.00	

Gottlieb's salt was dried at 100° .

Hydrated *Sesquioxide of Iron* dissolves very slowly in the aqueous acid.

The bibasic *Cobalt*-salt is red and crystallo-granular.

The bibasic *Nickel*-salt is a green gum, and the monobasic salt forms green crystalline crusts. (Crasso.)

The acid forms a precipitate with mercurous nitrate. (Lassaigne.)

CITRACONATE OF SILVER. — *a. Neutral.* — The aqueous acid forms, with nitrate of silver, on the addition of a small quantity of ammonia, a bulky precipitate, which dissolves very readily in hot water, and separates out on cooling, in long, slender, shining needles. These crystals give off nothing at 100° , and burn with slight detonation at a stronger heat. The mother-liquor from which this anhydrous salt has crystallized, yields by slow evaporation, transparent, colourless, irregular six-sided prisms, which have an adamantine lustre, become opaque at 100° , with loss of 4.1 p. c. water, and when further heated, burn away with projection of silver. (Crasso.) The salt may be set on fire with a glowing slip of wood, burns with bright flame, and leaves shining silver. (Liebig.) The solution of the silver-salt in ammonia dries up in vacuo over oil of vitriol to a transparent, somewhat viscid mass, which dissolves readily in water.

10 C	60	17.44	16.99
4 H	4	1.17	1.47
6 O	48	13.95	14.84
$C^{10}H^4Ag^2O^8$	344	100.00	100.00

<i>Hydrated crystals.</i>			
2 AgO	232	64.09	63.02
$C^{10}H^4O^8$	112	30.94	
2 HO	18	4.97	4.20

$C^{10}H^4Ag^2O^8 + 2Aq.$ 362 100.00

¶. The crystals analysed by Gottlieb were obtained by precipitating the acid saturated with ammonia as above with nitrate of silver, dissolving the precipitate in hot water, leaving the solution to cool, whereupon it deposited delicate colourless needles, and then evaporating the liquid filtered from these crystals; somewhat larger needles were thus obtained, which when dried at 100°, yielded 61.98 p. c. silver. Gottlieb regards these crystals as the neutral silver-salt contaminated with a small quantity of acid salt.

b. *Acid.* — 1. The mother-liquor of the crystals of the neutral salt yields, by spontaneous evaporation, short, shining crystals, united in groups, and differing considerably in appearance from the neutral salt. — 2. By dissolving the neutral salt in aqueous citraconic acid at a gentle heat, and leaving the solution to evaporate, tolerably large crystals are obtained, united in tuft-like groups: they contain no water of crystallisation, and are much more soluble in water than the neutral salt. (Gottlieb.)

<i>Crystals dried at 100°.</i>				Gottlieb.	
				(1)	(2)
AgO	116	48.94	49.51	49.03	
10 C	60	25.31		25.10	
5 H	5	2.12		2.42	
7 O	56	23.63		23.45	
$C^{10}H^4AgO^8$	237	100.00	100.00	¶.	

Citraconic acid dissolves very readily in *alcohol*. (Lassaigne.)

Citraconic Ether.



MALAGUTI. (1837.) *Ann. Chim. Phys.* 64, 275; also *Ann. Pharm.* 25, 272; also *J. pr. Chem.* 11, 225.
 CRASSO. *Ann. Pharm.* 34, 65 and 71.

Preparation. By distilling citraconic acid with alcohol and hydrochloric acid, cohobating five times, and washing the distillate with water. (Malaguti.) — Crasso proceeded in the same manner both with citraconic and with itaconic acid, from each of which he obtained an ether of the same composition.

Properties. Transparent, colourless liquid of sp. gr. 1.040 at 18.5° (Malaguti), 1.05 at 15°. (Crasso.) The boiling point, which is 225°, at 0.758 met. bar. rises rapidly, in consequence of partial decomposition of the ether. (Malaguti.) Boils at 227°. (Crasso.) Smells somewhat like

Calamus aromaticus (Malaguti); has an agreeable aromatic odour (Crasso); tastes pungently bitter. (Malaguti, Crasso.) Neutral to vegetable colours. (Malaguti.)

					Malaguti. with citraconic acid.	Crasso. with itaconic acid.
18 C	108	58.06	58.44	57.74	57.46	
14 H	14	7.53	7.66	7.51	7.53	
8 O	64	34.41	33.90	34.75	35.01	
<hr/>						
C ¹⁰ H ⁸ O ²	186	100.00	100.00	100.00	100.00	

Decompositions. — 1. When the ether is boiled, a small portion of it suffers decomposition, while the greater portion passes over unaltered. (Malaguti, Crasso.) — 2. Nitric acid does not decompose citraconic ether in the cold, and but slowly when heated. (Malaguti.) — 3. Oil of vitriol heated with citraconic ether, immediately gives off sulphurous acid and separates charcoal. (Malaguti.) — Bromine, iodine, and hydrochloric acid exert no decomposing action on the ether; and chlorine (*Ann. Chim. Phys.* 70, 359) acts upon it but slightly. (Malaguti.) — 4. By continued contact with water, the ether is resolved into citraconic acid and alcohol. (Malaguti.) — 5. Potash resolves it into alcohol and citraconate of potash. Baryta, strontia, and lime-water, as well as nitrate of silver, form with it precipitates soluble in nitric acid. (Malaguti.) — Dry ammoniacal gas has no action on the ether. (Malaguti.)

Combinations. Citraconic ether dissolves in water to a scarcely perceptible extent. It dissolves without decomposition in cold oil of vitriol. — Mixes in all proportions with alcohol and common ether. (Malaguti.)

Appendix to Citraconic Acid.

1. Itaconic Acid.



BAUP. (1836.) *Ann. Chim. Phys.* 61, 182; also *Ann. Pharm.* 19, 29; abstr. *J. pr. Chem.* 8, 418. — *Bibl. univ.* 1838, Aug.; also *Ann. Pharm.* 29, 166.

CRASSO. *Ann. Pharm.* 34, 61.

According to Baup, the liquid obtained by dry distillation of citric acid contains, besides the citraconic or pyrocitric acid discovered by Lassaigne, and called by Baup, *citribic acid*, another less soluble acid, his *citric acid* or *itaconic acid*, which appears to be isomeric with citraconic acid. Although the separate identity of these two acids is likewise admitted by Crasso, it is nevertheless very doubtful. Liebig, (*Ann. Pharm.* 26, 120) was not able to discover two different acids in the distillate of citric acid. According to Cahours, itaconate of potash is decomposed by bromine in exactly the same manner as citraconate. According to Gerhardt (*Précis Chim. org.* 1, 558, and *N. J. Pharm.* 13, 293) the citraconates and itaconates do not exhibit any points of difference. [In his more recent *Traité de Chimie organique*, ii. 118, however, Gerhardt treats itaconic acid as distinct from citraconic.]

their different crystalline forms and their different degrees of solubility in water, and on the differences exhibited by some of their salts with regard to crystalline form and amount of water. But the crystals of citraconic acid require to be more exactly determined; their different solubility appears doubtful, considering the mode of preparation given by Baup; and the salts of the two acids have not yet been sufficiently investigated to enable us to regard the assigned differences as well established. Of greater importance appears to be distinction, that the crystals of itaconic acid, as stated by Baup and Crasso, do not melt at 100° , whereas those of citraconic acid melt at 80° .—According to Gottlieb, itaconic acid is monobasic and citraconic acid bibasic.

Preparation.—1. The watery liquid obtained in the dry distillation of citric acid is evaporated and repeatedly cooled till the citraconic acid crystallises out; the mother-liquor then yields, by further evaporation, needles of itaconic acid, which may be freed from the more soluble citraconic acid by repeated solution and crystallisation. (Baup.) [It is inconceivable that the citraconic acid should crystallise out first, and then the itaconic acid from the mother-liquor of the former, seeing that citraconic acid, according to Baup, dissolves in 0.42 pts. cold water, while itaconic acid requires 17 pts. of water to dissolve it; and it is nowhere stated that the quantity of the itaconic acid bears but an extremely small ratio to that of the citraconic.]—2. Twenty grammes of citric acid are heated in a retort capable of holding twice as much over a large spirit-lamp, the flame of which acts only on the bottom of the retort, while the upper part is protected from the heat, till yellow vapours of empyreumatic oil begin to pass over; the oily distillate, which soon solidifies, is then dissolved in a six-fold quantity of water; the solution crystallised by evaporation, the citraconic acid then remaining in the mother-liquor; or the resulting crystals are freed from the empyreumatic oil which colours them, by recrystallisation from alcohol or ether, and pressure between paper heated to 100° , and afterwards between paper moistened with absolute alcohol. If the oily distillates obtained by distilling citric acid, be dissolved in twice its volume of absolute alcohol, the itaconic acid separates out after a few hours in crystalline crusts, which, by solution in water and slow evaporation, may be converted into the rhombic octohedrons described by Baup. (Crasso.)—According to Gottlieb, citraconic acid heated for some time to 100° , is converted into itaconic acid; but to render the change distinct, it is necessary to operate with small quantities only.

Properties. Colourless rhombic octohedrons, (*Fig. 41.*) $a : a' \text{ and } a' : a'' = 136^{\circ} 20'$; $a : a' = 73^{\circ} 15'$; $a' : a \text{ behind} = 124^{\circ}$; also with the *p*-, *t*-, and *u*-faces of *Fig. 42*; the *p*-face often predominates to such a degree that a bevelled rhombic table is produced; cleavage very distinct parallel to *t*; less distinct parallel to *m*. (Baup; *comp. Schabus, Jahresber. 1854, 403.*) The crystals do not give off anything at 120° ; they melt at 161° , to a colourless liquid, which crystallises in a laminated form on cooling; evaporates, even somewhat below the melting point, in white, irritating vapours, having a peculiar odour and often condensing in white needles; and leaves no residue when gently heated and in small quantities. (Baup.) The acid is inodorous, but has a very sour taste. (Baup, Crasso.)

6 H	6	4.62	4.67
8 O	64	49.23	48.61
$C^{10}H^6O^8$	130	100.00	100.00

Decomposition. Itaconic acid heated to the boiling point distils over completely in the form of anhydrous citraconic acid, and a supernatant layer of water. (Crasso.)

Combinations. The crystals dissolve in 17 pts. of water at 10° , in 12 pts. at 20° , and much more abundantly in hot water. (Baup.)

ITACONATE OF AMMONIA. — *a. Neutral.* — Does not crystallise; gives off ammonia when its solution is evaporated. — *b. Acid.* — Crystallises from the concentrated solution at 20° , in transparent tables and prisms = $NH^3, C^{10}H^6O^8$, which are permanent in the air and dissolve in $1\frac{1}{4}$ pt. water at 12° , — and from a more dilute solution in the cold, in bihydrated needles = $NH^3, C^{10}H^6O^8, + 2Aq$, which on exposure to the air quickly effloresce from loss of 2 At. water. (Baup.)

ITACONATE OF POTASH. — *a. Neutral.* — Uncrystallisable, deliquescent, insoluble in alcohol. (Baup.) — *b. Acid.* — Small prisms permanent in the air. (Baup.) The air-dried crystals give off 7.08 p. c. water at 100° , and the residue contains 28.06 p. c. potash. (Crasso.)

ITACONATE OF SODA. — *a. Neutral.* — Deliquescent. (Baup.) — *b. Acid.* — Opaque, very soluble, fibrous crystals. (Baup.)

ITACONATE OF BARYTA. — *a. Neutral.* — Crystalline crusts more soluble than the lime-salt. (Baup.) The aqueous acid saturated with carbonate of baryta yields by evaporation long delicate needles united in stellate groups, which do not give off any water at 100° , contain at that temperature 54.92 per cent. of baryta (therefore = $C^{10}H^6Ba^2O^8, 2Aq$.) and swell up slightly at a stronger heat. (Crasso.) — *b. Acid.* — Small rhombic tables, with the obtuse summits rounded; = $C^{10}H^6BaO^8, Aq$.; they dissolve easily in water, especially when hot. (Baup.) Indistinct crystals. (Crasso.)

ITACONATE OF STRONTIA. — *a. Neutral.* — Crystalline crusts composed of needles, soluble in a few parts of water. (Baup.) Delicate needles, exactly resembling the baryta-salt, and not giving off water at 100° ; they contain 45.69 p. c. strontia (therefore $C^{10}H^6Sr^2O^8, 2Aq$.) (Crasso.) — *b. Acid.* — Laminæ permanent in the air, easily soluble in water. (Baup.)

ITACONATE OF LIME. — *a. Neutral.* — Needles growing into one another, = $C^{10}H^6Ca^2O^8, 2Aq$., soluble in 45 pts. of water at 18° , not more abundantly in hot water, and quite insoluble in alcohol. (Baup.) — *b. Acid.* — Small laminæ, permanent in the air, = $C^{10}H^6CaO^8, 2Aq$., Soluble in 13 pts. of water at 12° . (Baup.)

ITACONATE OF MAGNESIA. — *a. Bibasic.* — Gummy. — *b. Acid.* — Very soluble shining laminæ. (Baup.)

soluble in water. (Baup.)

ITACONATE OF LEAD. — The free acid precipitates both neutral and basic acetate of lead; the alkali-salts precipitate nitrate of lead when added in equivalent proportion, but the precipitate disappears if either salt is added in excess. White powder = $C^{10}H^4Pb^2O^8$, 2 Aq. (Baup.)

FERRIC ITACONATE. — The free acid imparts a reddish colour to ferric salts, and its alkali-salts form a red precipitate therewith. (Baup.)

ITACONATE OF NICKEL. — Pale bluish-green powder, very soluble in water. (Baup.)

CUPRIC ITACONATE. — Very slender, greenish-blue, sparingly soluble needles. (Baup.)

MERCUROUS ITACONATE. — Alkaline itaconates form a white precipitate with mercurous nitrate. (Baup.)

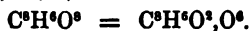
ITACONATE OF SILVER. — Alkaline itaconates form a white crystalline powder with nitrate of silver. (Baup.) The free acid does not precipitate the solution of nitrate of silver; the white powder obtained on adding a small quantity of ammonia burns with a kind of explosion when heated, and throws out vermicular shoots. Dissolves readily in ammonia and very sparingly in hot water. (Crasso.)

	Dried at 100°.		Baup.		Crasso.
10 C.....	60	17.44	17.49	17.57	
4 H.....	4	1.16	1.24	1.22	
2 Ag.....	216	62.79	62.73	62.36	
9 O.....	64	18.61	18.54	18.85	
$C^{10}H^4Ag^2O^8$	344	100.00	100.00	100.00	

¶. Itaconic acid does not appear to form an acid silver-salt. According to Gottlieb (*Ann. Pharm.* 77, 268), the neutral salt dissolves but very sparingly when boiled with aqueous itaconic acid, and the liquid then deposits a mixture of hydrated itaconic acid with a small quantity of the neutral salt. Gottlieb thence concludes that itaconic acid is monobasic, and its formula $C^8H^3O^4$. Gerhardt on the other hand (*Compt. chim.* 1851, 120,) does not think that there are sufficient grounds for this opinion. Wurtz also (*N. J. Pharm.* 19, 479,) regards itaconic acid as bibasic. The existence of the neutral and acid salts of baryta, strontia, lime, &c., (p. 426) is certainly in favour of this view. ¶.

Itaconic acid dissolves in 4 pts. of alcohol and in ether. (Baup.)

¶. 2. Meseaconic Acid.



GOTTLIEB. 1851. *Ann. Pharm.* 77, 268.

PEBAL. *Ann. Pharm.* 78, 129.

BAUP. *N. Ann. Chim. Phys.* 33, 192; *Ann. Pharm.* 81, 96.

Citraconic acid. (Baup.)

Formation and Preparation. By the action of dilute nitric acid (*Scheidewasser*) on aqueous citraconic acid, (*vid.* p. 419). — In this

reaction, the greater portion of the citraconic acid is not decomposed, but merely undergoes an isomeric transformation, the only products formed besides mesaconic acid, being oxalic acid and the yellow nitro-compound already mentioned, both of which occur in small quantity only. The nitro-compound appears to be a substitution-product of citraconic acid, inasmuch as a perfectly similar substance is formed by passing hyponitric acid into a concentrated solution of citraconic acid, its formation in this case not being accompanied by that of mesaconic acid. The formation of mesaconic from citraconic acid appears to be analogous to that of elaidic from oleic acid (*q. v.*) Itaconic acid treated with dilute nitric acid, does not yield mesaconic acid. (Gottlieb.) — Baup uses nitric acid diluted with four times its weight of water.

Properties.—Slender crystalline needles, having a faint lustre. (Gottlieb.) When crystallised from alcohol, it forms transparent flattened prisms. (Baup.) Crystallises by slow cooling from a hot saturated aqueous solution, in very slender needles, having a silky lustre; an alcoholic solution boiled and evaporated to dryness over the water-bath, yields the acid in brownish scales, the colour arising probably from a superficial decomposition. (Pebal.) Tastes harsh and sour. (Gottlieb.) Melts at 208° to a clear liquid, and when heated a few degrees above that point, sublimes without decomposition in crystals, (Gottlieb); sublimes before fusion. (Baup.) The fused acid solidifies in a crystalline mass on cooling. The vapour is pungent and excites coughing. The solutions redden litmus strongly, and decompose carbonates. (Gottlieb.)

<i>Dried at 100°.</i>				Gottlieb.	
10 C	60	46.15	45.73	45.77	
6 H	6	4.61	4.61	4.57	
8 O	64	49.24	49.66	49.66	
$C^{10}H^6O^8$	130	100.00	100.00	100.00	
<i>Dried at 100°.</i>				Pebal.	
			a.		b.
10 C	60	46.15	45.80	45.96	45.41
6 H	6	4.61		4.66	4.65
8 O	64	49.24		49.38	49.94
$C^{10}H^6O^8$	130	100.00		100.00	100.00

Isomeric with citraconic and itaconic acids; Pebal's acid *a* was crystallised from hot water; *b* was sublimed and dried at 150° .

Decomposition. Mesaconic acid heated in a platinum spoon and set on fire, burns with a blue flame, and without leaving any carbonaceous residue. (Baup.)

Combinations. The acid dissolves sparingly in cold, abundantly in hot water (Gottlieb), in 38 pts. water at 14° , and in 29 pts. water at 22° (Baup), in 14.29 pts. at 18.2° , and in 0.85 pts. at 100° (Pebal).

The acid is bibasic, forming neutral salts = $C^{10}H^4M^2O^8$, and acid salts = $C^{10}H^5MO^8$.

MESACONATE OF AMMONIA. — *a. Neutral.* — Does not crystallise. (Baup.) — *b. Acid.* — Very small prisms, with triangular summits, soluble in 8 pts. of water at 15° . (Baup.) On boiling a solution of the acid neutralised with ammonia, an evolution of ammonia takes place; and from the concentrated solution, the acid salt separates in crystalline geodes, which dissolve very readily in water. (Pebal.)

N	14	9.54	40.00
9 H	9	6.12	6.10
8 O	64	43.53	
<hr/>			
C ¹⁰ H ⁵ (NH ⁴)O ⁸	147	100.00	

Baup, by neutralising the acid with ammonia, obtained for the atom this salt, the numbers 146.3 and 145°.

MESACONATE OF POTASH. — The *neutral* salt, obtained by the acid with carbonate of potash, is very soluble in water, less soluble in alcohol, and crystallises from a highly concentrated solution after standing for some time in delicate needles, having lustre. (Pebal.) It is very deliquescent. (Baup.) The *acid* tallises in small micaceous laminæ, dissolves readily in water, and in alcohol. (Baup.)

MESACONATE OF SODA. — The *neutral* salt, prepared like salt, is also very soluble in water, and crystallises in small prisms, with truncated summits. (Pebal.) Baup did not obtain crystalline form. The *acid* salt crystallises in small rhomb which do not alter by exposure to the air. (Baup.)

MESACONATE OF BARYTA. — *a. Neutral.* — Obtained by boiling solution of the acid with carbonate of baryta. Separated concentrated solutions by spontaneous evaporation, in crystals to the oblique prismatic system, having a vitreous and some lustre. (Pebal.) Forms transparent, compressed, four-sided tables, which do not alter by exposure to the air, or only in very dry air, or when they are slightly warmed; they then rewater of crystallisation on exposure to the air. At a high temperature, the salt decomposes, swelling up to five times its original volume. (Baup.) The crystals give off the greater part of their water becoming partially opaque, and the whole at 130°. (Pebal.)

<i>Anhydrous, dried at 130°.</i>				Pebal.
2 BaO	153.2	57.75	58.00	57
10 C	60.0	22.63	22.29	
4 H	4.0	1.51	1.70	
6 O	48.0	18.11	18.01	
<hr/>				
C ¹⁰ H ⁴ Ba ² O ⁸	265.2	100.00	100.00	
<hr/>				
			Baup.	Pel
2 BaO	153.2	45.59		
C ¹⁰ H ⁴ O ⁸	112.0			
8 HO	72.0	21.18	21	
<hr/>				
C ¹⁰ H ⁴ Ba ² O ⁸ + 8 Aq.	337.2			

b. Acid. — By saturating one-half of an aqueous solution with carbonate of baryta, then adding the other half, decoloring with animal charcoal, and concentrating the liquid, the acid salt is obtained either in crystalline nodules or in nacreous six-sided tables, however, assuming the prismatic form by elongation in one direction. The purification of this salt is attended with considerable difficulty.

portion of the free acid adheres obstinately to the crystals, and cannot be completely removed by recrystallisation. Alcohol, either cold or boiling, decomposes the salt into the neutral salt and free acid. (Pebal.) Small crystals permanent in the air. (Baup.) The crystals give off their water, amounting to 6.35 p. c. ($1\frac{1}{2}$ At.), at 140° . (Pebal.)

<i>Tabular crystals, dried at 140°.</i>				Pebal.
BaO	76.6	38.74		38.08
10 C	60.0	30.38		30.65
5 H	5.0	2.53		2.89
7 O	56.0	28.35		28.38
$C^{10}H^4BaO^8$	197.6	100.00		100.00

<i>Tabular crystals, air-dried.</i>				Pebal.
2 BaO	153.2	36.27		36.51
20 C	120.0	28.43		28.60
13 H	13.0	3.08		3.33
17 O	136.0	32.22		31.56
$2C^{10}H^4BaO^8 + 3Aq.$	422.2	100.00		100.00

Or:

				Pebal.
2 $C^{10}H^4BaO^8$	395.2	93.6		
3 HO	27.0	6.4	6.4	
$2C^{10}H^4BaO^8 + 3Aq.$	422.0	100.0		

Baup found the crystals of the acid salt to contain 36.71 p. c. baryta, whence he deduces the formula $C^{10}H^4BaO^8 + 2Aq.$ which requires 37.07 BaO.

MESACONATE OF LIME. — Very small needle-shaped crystals, aggregated in white fibrous crusts. Give off their water at a somewhat elevated temperature, and recover it on exposure to the air. Swell up when decomposed by heat, but not so much as the baryta-salt. Soluble in $16\frac{1}{2}$ pts. of water at 20° ; insoluble in alcohol. (Baup.)

<i>Crystals.</i>				Pebal.
2 CaO	56	30.11		30.13
$C^{10}H^4O^8$	112	60.21		
2 HO	18	9.68		
$C^{10}H^4Ca^2O^8 + 2Aq.$	186	100.00		

MESACONATE OF LEAD. — *a. Basic.* — $4PbO, C^{10}H^4O^8 + 6Aq?$ — $2PbO, C^{10}H^4Pb^2O^8 + 6Aq?$ — Tribasic acetate of lead added to a solution of a neutral mesaconate, forms a flocculent or pulverulent precipitate, which diminishes in bulk considerably after a while, gives off 6 p. c. water when heated, and then turns yellow. Gives by analysis 72.35 p. c. PbO, the above formula requiring 72.96. (Baup.)

b. Neutral. — A solution of a neutral mesaconate forms, with neutral acetate of lead, a curdy precipitate, which gradually changes to small crystals; when the solutions used are very dilute, the neutral salt separates slowly in small transparent prisms. (Baup.). — Neutral mesaconate of ammonia or baryta forms, with lead-salts at ordinary temperatures, a white crystalline precipitate, and at a boiling heat a resinous viscous mass, which becomes hard and brittle on cooling; from the supernatant liquid the neutral salt crystallises in short needles. The precipitate (*a*)

tures, gives off 7.24 to 7.86 p. c. (3 At.) water at 100°; with hot water, it gives off at the same temperature only 5.63 to 6.12 p. c. (2 At.) water. (Pebal.)

<i>Dried at 180°.</i>				Pebal.
10 C	60	17.86	17.44	
4 H	4	1.19	1.28	
2 Pb	208	61.90	61.75	
8 O	64	19.05	19.53	
<hr/>				
$C^{10}H^4Pb^2O^8$	336	100.00	100.00	
<hr/>				Baup.
2 PbO	224	66.67	66.73	
$C^{10}H^4O^6$	112			
<hr/>				
$C^{10}H^4Pb^2O^8$	336			
<hr/>				Pebal.
<i>Hydrated salt (α).</i>				
$C^{10}H^4Pb^2O^8$	336	92.56		
3 HO	27	7.44	7.41	
<hr/>				
$C^{10}H^4Pb^2O^8, 3Aq.$	363	100.00		
<hr/>				Pebal.
<i>Hydrated salt (β).</i>				
$C^{10}H^4Pb^2O^8$	336	94.92		
2 HO	18	5.08	5.87	
<hr/>				
$C^{10}H^4Pb^2O^8, 2Aq.$	354	100.00		

Baup found the crystals to give off 7.9 to 8.2 p. c. water in drying; a quantity somewhat too great for the terhydrated salt (α), the excess being probably due to efflorescence.

c. Acid. — Crystallises in small colourless needles from a solution of the neutral salt in boiling aqueous mesaconic acid, an excess of which must be avoided. (Pebal.) It is also obtained by adding acetate of lead to a solution of mesaconic acid: it then separates, more or less quickly, according to the strength of the solution, in small prismatic crystals, acuminate at the ends. (Baup.) Gives off a mere trace of water at 100°. (Pebal.) Swells up and decomposes when more strongly heated. (Baup.)

<i>Dried at 100°.</i>				Pebal.
10 C	60	25.77	25.87	
5 H	5	2.15		
Pb	104	44.58	44.68	
8 O	64	27.50		
<hr/>				
$C^{10}H^8PbO^6$	233	100.00		
<hr/>				Baup.
PbO	112	48.07	47.90	
$C^{10}H^4O^6$	112	48.07		
HO	9	3.86		
<hr/>				
$PbO, HO, C^{10}H^4O^6$	233	100.00		

From a solution of *sesquichloride of iron*, mesaconic acid throws down red flakes. (Baup.)

CUPRIC MESAONATE. — A mixture of cupric acetate and mesaconic acid yields, more or less quickly, according to the degree of concentration, very small granular crystals of a deep sky-blue colour. (Baup.)

		<i>Air-dried.</i>		<i>Baup.</i>	
2	CuO	80	35.09	34.80	35.03
	$C^{10}H^4O^8$	112	49.12		
4	HO	36	15.79		15.53
$C^{10}H^4Cu^2O^8 + 4Aq.$		228	100.00		

On mixing the solution of a neutral mesaconate with cupric sulphate or acetate, there is obtained, besides the neutral salt just described, a basic salt, which effloresces rapidly on exposure to the air. (Baup.)

Mercurous nitrate forms a white precipitate with aqueous mesaconic acid. (Baup.)

Mercuric chloride forms a precipitate with soluble mesaconates. (Baup.)

MESACONATE OF SILVER. — *a. Neutral.* — *a. Anhydrous.* — Obtained by adding nitrate of silver to a solution of mesaconic acid exactly neutralised with ammonia (Gottlieb, Pebal); or by mixing a dilute solution of baryta with nitrate of silver. (Pebal.) Heavy, white crystalline precipitate, which is not altered by exposure to light, or by heating to 100° . (Gottlieb.) Curdy precipitate, which soon subsides in the form of a granular powder consisting of microscopic crystals. Sparingly soluble in water, more soluble in the mother-liquor. When treated with hot water, especially if exposed to light, it assumes a reddish tint. (Pebal.) When somewhat suddenly heated, it is decomposed with violence, throwing out vermicular shoots of metallic silver, like the itaconate under similar circumstances. (Gottlieb, Pebal.)

		<i>Dried at 100°.</i>		<i>Gottlieb.</i>		<i>Pebal.</i>	
10	C	60	17.44	17.72	17.33	17.28	
4	H	4	1.17	1.24	1.43	1.18	
2	Ag	208	62.79	62.49	62.80		
8	O	64	18.60	18.55	18.44		
$C^{10}H^4Ag^2O^8$		336	100.00	100.00	100.00		

β . Hydrated. — $C^{10}H^4Ag^2O^8 + 2Aq.$ — On adding nitrate of silver to neutral mesaconate of soda, filtering from the resulting precipitate of anhydrous salt, and mixing the filtrate with alcohol, a very bulky translucent precipitate is obtained, which does not subside in the granular form, even after long standing, and when separated from the mother-liquor, dries up to an amorphous mass. This salt washed with alcohol, pressed between bibulous paper, and dried over oil of vitriol, gave by ignition, 60.23 p. c. silver, agreeing nearly with the above formula, which requires 59.70 p. c. (Pebal.)

b. Acid. — Obtained by dissolving the neutral silver-salt in boiling aqueous mesaconic acid, avoiding an excess of the acid, as it would adhere to the crystals which separate from the cooling solution. The salt does not become coloured by exposure to light; when heated, it behaves like the neutral salt. Dissolves pretty easily in hot water. Gives off but a trace of water at 100° . (Pebal.)

		<i>Dried at 100°.</i>		<i>Pebal.</i>	
10	C	60	25.30	25.03	
5	H	5	2.11	2.24	
	Ag	108	45.61	45.59	
8	O	64	26.98	27.14	
$C^{10}H^4AgO^8$		237	100.00	100.00	

Mesaconic Ether.



PEBAL. *Ann. Pharm.* 78, 145.

Formation and Preparation. 1. By distilling mesaconic acid with sulphuric acid and alcohol of 90 per cent., the quantities of the two latter being twice as great as should be required, according to calculation, to convert the whole of the mesaconic acid into mesaconic ether, and the distillation being continued till the residue begins to blacken. The distillate thus obtained consists of common ether mixed with mesaconic ether the proportion of the latter being, however, but small. A fresh quantity of alcohol is therefore added to the liquid in the retort, the mixture again distilled, and these operations repeated as long as mesaconic ether continues to form. The crude product thus obtained is purified by heating it in the water-bath to expel the vinic ether, distilling the residue with water, treating the new distillate with carbonate of soda to remove free acid, then washing with water, and drying with chloride of calcium. — 2. By passing hydrochloric acid gas into an alcoholic solution of mesaconic acid; a portion of the latter always, however, remains unacted upon.

Properties. Colourless mobile liquid, having an agreeable fruity odour and bitter taste. Sp. gr. 1.043 at 20°. Boils constantly at 220°, from platinum, at 737 mm. bar., and distils without decomposition. Does not redden litmus.

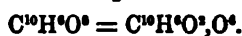
				Pebal.
18 C	108	...	58.06	57.85
14 H	14	...	7.53	7.52
8 O	64	...	34.41	34.63
$C^{18}H^{14}O^8$	186	...	100.00	100.00

Decomposition. Mesaconic ether is decomposed by baryta-water, with formation of mesaconate of baryta. Ammoniacal gas has no action upon it.

Combinations. The ether dissolves sparingly in cold, somewhat more readily in hot water, from which it separates on cooling, rendering the liquid milky. Mixes in all proportions with alcohol and vinic ether. (Pebal.)

An attempt to prepare *mesaconic acid* was not successful. ¶.

3. Lipic Acid.



LAURENT. (1837.) *Ann. Chim. Phys.* 66, 169. — *Revue Scientif.* 10, 125; also *J. pr. Chem.* 27, 316.

Preparation. 1 pt. of oleic acid is boiled with 1 pt. of concentrated nitric acid for 12 hours, with cohobation; the watery liquid in the retort separated from the oily portion; the latter again boiled with fresh nitric acid, as above; the acid liquid again separated from the oil, &c., so that, after 12 hours' boiling of the oily liquid with nitric acid, the operation has been repeated seven times, and 7 pts. in all of nitric acid have been used. The watery acid liquids separated after the several boilings are then united; the whole evaporated down to one-fourth, and cooled till the *suberic acid* solidifies, mixed with *azelaic acid* and a peculiar oil; the solidified matter separated from the acid mother-liquor, and washed with cold water; and these liquids further evaporated and frequently cooled to separate more *suberic acid*; they then yield, by still further evaporation and three days' cooling, a crystalline mass of *pimelic acid*, rougher to the touch, and consisting of harder grains, which product is freed from the acid mother-liquor and washed with cold water. This last mother-liquor is evaporated at a very gentle heat (so that no decomposition or blackening may occur) to expel the greater part of the nitric acid; set aside for two or three days after each evaporation; separated from the resulting brownish crystalline mixture of *lipic* and *adipic* acid; and, together with the cold wash-water of the latter, carefully evaporated and set aside in the cold, as long as it deposits crystals. (An acid not yet examined remains in solution.) These brownish crystals are dried, and dissolved in ether; the solution filtered from a brown substance, left to evaporate to one-half, and decanted from the resulting crystals of *adipic acid*, which may be purified by two or three crystallisations from hot alcohol and then separate in warty granules; and the ethereal mother-liquor left to evaporate: it then yields crystals of *lipic acid*, which, when purified in a similar manner by recrystallisation from alcohol, is obtained in somewhat elongated laminae. (Laurent.) — *Caprylic alcohol* is converted, by the continued action of nitric acid, into *butyric*, *succinic*, *pimelic*, and *lipic acid*. (Bouis, *Compt. rend.* 33, 141.)

Properties. The acid crystallised from alcohol, and still retaining 2 At. water, forms longish laminae, terminated by two lines inclined to one another at an obtuse angle. When the acid is heated on glass till it partly fuses, it solidifies in a fibrous mass on cooling. By rapid heating, it may be distilled without alteration, or sublimed in beautiful six-sided needles. But when slowly heated, it gives off water, and distils over as anhydrous acid, which does not melt below 140° to 145° . The vapours of the acid strongly excite coughing.

	Dehydrated by slow distillation.		Laurent.
10 C	60	46.15	46.59
6 H	6	4.62	4.39
8 O	64	49.23	49.02
$C^{10}H^{16}O^2$	130	100.00	100.00

8 H	8	...	5.41	5.50
10 O	80	54.05	53.35
<hr/>					
C ¹⁰ H ⁴ O ⁸ + 2Aq.....	148	100.00	100.00

Isomeric, therefore, with citraconic, itaconic, and mesaconic acid.

Combinations. The acid dissolves in cold water more readily than adipic or pimelic acid.

The anhydrous *Lipates* yield, when heated with oil of vitriol, an acicular sublimate of lipic acid.

The *Ammonia-salt* crystallises in long needles.

Its aqueous solution forms after a while with chloride of barium, square prisms of the *Baryta-salt*, which change to octohedrons and continue to increase for 24 hours. — With chloride of *strontium*, it forms crystalline groups resembling crowns; and with chloride of *calcium*, after a while, small square prisms. It precipitates the salts of *iron*, *copper*, and *silver*, but not those of magnesium or manganese.

<i>Baryta-salt dried in vacuo at 140°.</i>				Laurent.
2 BaO	153.2	57.77 57.7
10 C.....	60.0	22.62	
4 H.....	4.0	1.51	
8 O.....	64.0	18.10	
<hr/>				
C ¹⁰ H ⁴ Ba ² O ⁸	265.2	100.00	

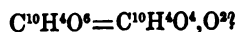
<i>Silver-salt.</i>				Laurent.
10 C.....	60	17.44	
4 H	4	1.16	
2 Ag	216	62.80 62.9
8 O	64	18.60	
<hr/>				
C ¹⁰ H ⁴ Ag ² O ⁸	344	100.00	

Lipic acid dissolves in *alcohol* and *ether*. (Laurent.)

Compare Bromeis. (*Ann. Pharm.* 35, 108.)

b. *Oxygen-nucleus.* C¹⁰H⁴O⁴.

Citraconic Anhydride.



ROBIQUET. *Ann. Chim. Phys.* 65, 78.

CRASSO. *Ann. Pharm.* 34, 68.

Anhydrous Citraconic acid, wasserfreie Citraconsäure, Acide pyrocitrique anhydre.

Formation and Preparation. 1. In the dry distillation of citric acid, an aqueous solution of citraconic acid first passes over, then the impure anhydride, in the form of a heavy yellow or greenish-yellow oily liquid, which, if the distillate has been carried too far, is contaminated with a

small quantity of empyreumatic oil, and in that case has an odour like that of rock-oil. (Lassaigne, Robiquet.) When the crude oil is distilled in the water-bath, the pure anhydride gradually distils over. (Robiquet.) There then remains a brown oil mixed with crystals of the acid; and this oil, distilled for several days in the water-bath, yields a distillate [probably water mixed with the anhydride] which changes after a while to colourless crystals; and in the retort there remains an oil [probably impure anhydride] which solidifies below 0° in a laminated mass, melts above 0°, has a burning taste, and is converted by exposure to the air into the crystallised acid. (Robiquet.) The crude oil is resolved by heat into a watery and an oily layer; and the latter, when rectified *per se*, yields first water, then at 200° a milky distillate, and when the receiver is changed, the clear oily anhydride. (Crasso.) — 2. Crystallised citraconic acid may be completely converted by heat into water and the oily anhydride, which pass over one after the other. (Crasso.)

Properties. Thin colourless oil (pale yellow, according to Robiquet), of sp. gr. 1·241 at 14°. (Crasso.) The crude oil has a density of 1·30. (Robiquet.) Remains liquid even in vacuo over oil of vitriol. Boils at 150° (Robiquet), at 212° (Crasso), but volatilises even at 90°. (Crasso.) It is nearly inodorous, and has a very sour and burning taste, like that of a volatile oil (Robiquet); it is inodorous and has a caustic, sour, and rough taste (Crasso); scarcely reddens thoroughly dried litmus paper, but reddens the moistened paper strongly. (Robiquet.)

				Robiquet.	Crasso.
10 C	60	...	53·57 53·17 54·24
4 H	4	...	3·57 3·69 3·67
6 O	48	...	42·86 43·14 42·09
<hr/>					
C ¹⁰ H ¹⁰ O ⁴	112	...	100·00 100·00 100·00

Decompositions. 1. The anhydride leaves a black residue when too rapidly distilled. (Crasso.) — 2. When shaken up with water, it distils slowly in the form of citraconic acid, which crystallises on evaporation; the unaltered portion settles down in oily drops every time the vessel is shaken, but after repeated treatment with water, finally disappears altogether. On exposure to moist air also, the anhydride is gradually converted into the crystallised acid, which then deliquesces. (Robiquet, Crasso.) The anhydride, in passing to the state of the crystallised acid, increases by 13·21 p. c. (Robiquet.) [100 : 113·21 = 112 (1 At. anhydride) : 126·8 (1 At. citraconic acid weighs 130).]

Citraconamide. C¹⁰NH¹⁰O³,O² + 2Aq.f

Citraconic anhydride heated in a stream of dry ammoniacal gas becomes heated; absorbs a large quantity of the gas; becomes covered at first with a coriaceous skin; then solidifies entirely in the form of a yellowish solid body; and is finally converted, with further absorption of ammonia, into a yellow viscid mass, which becomes brittle and glassy on cooling. This mass deliquesces in moist air, dissolves very abundantly

ration crystals of acid citraconate of ammonia. (Crasso.)

				Crasso.
10 C	60	46.51	47.57	
N	14	10.85	11.60	
7 H	7	5.43	5.58	
6 O	48	37.21	35.25	
<hr/>				
C ¹⁰ NH ⁷ O ⁶	129	100.00	100.00	

¶. Citraconimide. C¹⁰NH⁶O⁴.

Formed by the action of heat on acid citraconate of ammonia :



When citraconic acid is mixed with excess of ammonia and evaporated to dryness in the water-bath, there remains a mixture of neutral and acid citraconate of ammonia, which is better adapted for preparing the imide than the pure acid salt. When this mixture is gradually heated in a retort, ammoniacal water passes over at first; and, as soon as the temperature approaches 180°, the liquid, which has become yellow, swells up considerably, the evolution of water ceases, and the whole solidifies to a tumented, amber-colored mass of citraconimide, which at a higher temperature turns black, melts, and decomposes.

Citraconimide has a conchoidal fracture; it is tough and difficult to pulverize; the powder is white and highly hygroscopic, and does not part with the absorbed water till heated to 180°, at which temperature it bakes together without fusion; under water it melts at 100°.

	Powder dried at 180°.		Gottlieb.
10 C	60	54.05	54.18
N	14	12.61	12.59
5 H	5	4.51	4.66
4 O	32	28.83	28.57
<hr/>			
C ¹⁰ NH ⁶ O ⁴	111	100.00	100.00

Citraconimide is insoluble in cold water, but is dissolved by boiling water, the excess melting to a viscid liquid, while the greater portion separates, as the liquid cools, in small drops which afterwards solidify. It likewise dissolves to a certain extent in alcohol, and with similar phenomena. (Gottlieb, *Ann. Pharm.* 77, 274.)

Citraconamic acid. — C¹⁰NH⁷O⁶. — Citraconimide dissolves in boiling aqueous ammonia and does not separate out on cooling. The solution doubtless contains citraconamic acid in combination with ammonia; the process does not however yield the acid in a state of purity, as its salts do not crystallise, and the conversion of the citraconimide into the ammoniacal salt does not appear to be complete. — The *baryta-salt* of citraconamic acid is soluble in water, and is precipitated from the aqueous solution in yellow flakes by alcohol. While moist, it fuses readily at a gentle heat, but in the dry state it remains solid at 100°. — The *lead* and *silver* salts have the consistence of plaster while moist, and likewise melt when hot, but in the dry state they are as infusible as the baryta-salt. All these three salts have a yellow colour. (Gottlieb.)

Itaconic acid does not appear to form a compound analogous to citraconimide. When itaconate of ammonia is heated to 170°, a brownish mass is obtained resembling caramel in appearance, having a sour and bitter taste, more soluble in water than citraconimide, and forming a very soluble salt with ammonia. This compound is probably itaconamic acid; but its salts are extremely difficult to purify. (Gottlieb.)

¶ Chloropyrocitryl. $C^{10}H^4O^4,Cl^2$.

Obtained by the action of pentachloride of phosphorus on anhydrous citraconic acid :



When the rectified liquid product of the dry distillation of citric acid is poured upon pentachloride of phosphorus, a brisk effervescence is produced; and the mixture, when distilled, yields, first oxychloride of phosphorus, then at about 175°, chloropyrocitryl, mixed, however, with anhydrous citraconic acid, which raises its boiling point. It may be purified by distilling it two or three times with pentachloride of phosphorus, collecting only the portion which passes over between 175° and 190°, and rectifying the product thus obtained.

Transparent, colourless, strongly refracting, mobile liquid, which fumes in the air, and has an odour like that of damp straw. Sp. gr. about 1.4 at 15°. Boils at 175°, with slight decomposition. (Gerhardt & Chiozza.)

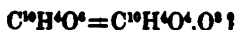
Calculation.

10 C	60.0	35.97
4 H	4.0	2.40
2 Cl	70.8	42.45
4 O	32.0	19.18

$C^{10}H^4O^4, Cl^2$ 166.8 100.00

When exposed to a moist atmosphere, it is converted into hydrochloric and hydrated citraconic acid. — Becomes strongly heated by contact with absolute alcohol; and water added to the mixture, separates a heavy liquid, having a fruity odour, and exhibiting the characters of citraconic ether. — It also becomes heated by contact with aniline, yielding micaceous laminae of itaconanilide. (Gerhardt & Chiozza, *Compt. rend.* 36, 1050; *Ann. Pharm.* 87, 294.) ¶

Pyromeconic Acid.



SERTÜRNER. *Gilb.* 57, 153.

RONIQUET. *Ann. Chim. Phys.* 5, 282; also *Gilb.* 57, 173. — *Ann. Chim. Phys.* 51, 236; also *J. Pharm.* 19, 61; also *Schw.* 67, 382; also *Ann. Pharm.* 5, 90.

CHOULANT. *Gilb.* 56, 349.

JOHN. *Berl. Jahrb.* 1819, 156.

STENHOUSE. *Phil. Mag. J.* 24, 128; also *Mem. Chem. Soc.* 2, 1; also *Ann. Pharm.* 49, 18; also *J. pr. Chem.* 82, 257.

Chem. Soc. J. 3, 18; *J. pr. Chem.* 38, 280; *Pharm. Centr.* 1852, 945; *N. Ann. Chim. Phys.* 38, 115; *Jahresber.* 1852, 489. — Further: *Ed. Phil. Trans.* 21, i, 49; *Phil. Mag. J.* [4], 8, 201; *Ann. Pharm.* 92, 321; *J. pr. Chem.* 63, 370; *Pharm. centr.* 1854, 797; *Jahresber.* 1854, 424.

Discovered by Sertürner in 1817, but regarded as identical with meconic acid, till Robiquet, in 1833, pointed out the difference.

Formation. Given off as vapour, when meconic acid (Sertürner) or comenic acid (Robiquet) is heated to 265°—288° (Stenhouse), or when acid meconate of copper is heated *per se* (Stenhouse), or when meconate of baryta is heated with excess of vitrified boracic acid. (Choulant.)

Preparation. By distilling any of the above-mentioned substances. The acid partly sublimes, partly distils over as an oil, which solidifies on cooling; towards the end of the distillation, parameconic acid passes over. (Stenhouse.) — The meconic acid must be thoroughly dried before sublimation, because the watery vapours carry over a large quantity of pyromeconic acid; and it must not be heated sufficiently to produce empyreumatic oil. (Robiquet.) — The sublimed and distilled pyromeconic acid must be freed from empyreumatic oil and acetic acid, by a second sublimation at the lowest possible temperature, pressure between paper, and repeated crystallisation from hot water or alcohol (Robiquet, Stenhouse), after which the crystals must be quickly dried, because while moist they turn red on exposure to the air. (Stenhouse.) Choulant sublimes a finely divided mixture of impure meconate of baryta and an equal quantity of vitrified boracic acid. Brown prepared the acid by distilling impure meconic acid (obtained by twice treating crude meconate of lime with hydrochloric acid) at 260° to 315°, and purified the resulting oily semifluid sublimate by pressure between paper and sublimation at a comparatively low temperature, in a glass cylinder provided with transverse partitions of filtering paper.

Properties. As obtained by sublimation: Long slender, transparent colourless needles (Sertürner), and four-sided laminae, or ramifications made up of elongated octohedrons (Robiquet); large transparent tables. (Brown.) Crystallised from alcohol: large colourless crystals (Stenhouse); tolerably large four-sided prisms, which are also obtained from the aqueous solution. (Brown.) The acid melts at 120° to 125°, forming an oil, and by careful heating (at a temperature but little above the melting point, according to Wackenroder, *N. Br. Arch.* 25, 170), may be volatilised without residue, and sublimes in crystals aggregated together by incipient fusion. (Robiquet.) Volatilizes gradually but completely at 100°, provided it is free from parameconic acid. Tastes sour (Sertürner, John, Choulant), then disagreeably bitter. (Choulant.) Reddens litmus (Robiquet), pretty strongly (Wackenroder), almost imperceptibly, so that a very small quantity of potash gives it an alkaline reaction. (Stenhouse.) Has a slight acid reaction, even after being thrice recrystallised from water. (Brown.)

	<i>Crystals.</i>		<i>Robiquet.</i>	<i>Brown.</i>	
10 C	60	53·57 53·42 53·23
4 H	4	3·57 3·64 3·71
6 O	48	42·86 42·94 43·06
<hr/>					
C ¹⁰ H ⁴ O ⁶	112	100·00 100·00 100·00

meconic acid as an aldid $C^{10}H^4O^4, O^2$. This view is supported by the fact that pyromeconic acid scarcely reddens litmus and does not combine with ammonia or potash, whereas pyromucic acid behaves like a strong acid.] — The crystals analysed by Brown were once sublimed and dried in vacuo.

Decompositions. 1. Pyromeconate of potash behaves with bromine like pyromucate of potash. (Cahours, p. 384.) ¶. Bromine-water is quickly absorbed by an excess of the strong aqueous solution of pyromeconic acid, and the resulting solution yields, after a while, crystals of *bromopyromeconic acid*, $C^{10}H^3BrO^6$. If the bromine-water is in excess, this acid is not formed, and the liquid, when evaporated, turns black, and is found to contain oxalic acid. (Brown.) — 2. *Chlorine* does not form any substitution-product with pyromeconic acid, but decomposes it completely, with formation of oxalic acid and other products. — 3. The acid is not acted upon by tincture of *Iodine*; but with protobromide or protochloride of iodine, it yields *iodopyromeconic acid* (p. 443):



It appears that the iodine, though capable of taking the place of an atom of hydrogen in the acid, has not a sufficiently powerful affinity for the hydrogen to abstract it in the form of hydriodic acid; but by combining the iodine with bromine or chlorine, whose affinity for hydrogen is stronger, the removal of an atom of hydrogen is effected, and the iodine takes its place. — With excess of chloride of iodine, pyromeconic acid forms *iodomecone* $C^8H^4I^2O^8$ (Brown.):



4. Crystallised pyromeconic acid, moistened with strong *Nitric acid*, becomes white and gelatinous, with evolution of nitrous fumes; and on gently heating the mixture, a brisk action takes place, with formation of oxalic and hydrocyanic acid. (Brown.) ¶.

Combinations. The acid dissolves readily in water.

Sulphuric acid has no action upon it in the cold, but dissolves it when gently heated, forming a solution from which the pyromeconic acid crystallises out unaltered on cooling. (Brown.)

Pyromeconic acid does not combine with ammonia, potash, or soda. The pale yellow mixture which it forms with excess of ammonia, yields, when evaporated in vacuo, crystals of the unaltered acid, free from ammonia. A solution of the acid in hot alcohol assumes a pale yellow colour when mixed with alcoholic potash, and on cooling deposits crystals of the acid, which contain but very little potash, and may be freed even from this, all but a trace, by repeated crystallisation. (Stenhouse.) The acid requires very little potash to neutralise it, and crystallises from the mixture nearly pure. (Robiquet.) A hot aqueous solution of pyromeconic acid, mixed with excess of strong potash-solution, deposits, after a while, crystals of the unaltered acid; and similarly with ammonia; in both cases the liquid turns black. (Brown.) On the other hand, Choullant and John describe crystallisable pyromeconates of ammonia, potash, and soda.

The acid does not precipitate the salts of baryta, strontia, or lime. (Stenhouse.) It forms no precipitate with chloride of barium, chloride of calcium, chloride of manganese, or sulphate of magnesia, even on addition of a small quantity of ammonia. (Brown.)

meconic acid, mixed with acetate of baryta, soon deposits pyromeconate of baryta in small, colourless, silky needles. In dilute solutions, these crystals do not appear till after some time, but increase rapidly when they have once begun to form. When the solution is evaporated in vacuo, the salt is deposited in short prisms of a yellowish colour. It is strongly alkaline, like all the pyromeconates, and exhibits, with sesquichloride of iron, a faint red colour, which becomes more distinct on using the crystals instead of the solution. The salt sustains a temperature of 100° without loss of weight, but burns at a higher temperature, with a slight appearance of fire, and without previous fusion. Dissolves in 40 pts. of water at 15.5°, and is the most soluble of all the earthy salts of pyromeconic acid. Slightly soluble in alcohol. (Brown.)

Washed with alcohol and dried at 100°.				Brown.
BaO	76.6	40.59	40.55	
10 C	60.0	31.82	31.46	
4 H	4.0	2.12	2.43	
6 O	48.0	25.47	25.56	
<hr/>				
C ¹⁰ H ³ PbO ⁶ , Aq.	188.6	100.00	100.00	

Pyromeconate of Strontia.—When an alcoholic solution of nitrate of strontia is mixed with an alcoholic and ammoniacal solution of pyromeconic acid, a precipitate is immediately formed, consisting of small silky needles, which, by solution in water, are obtained in stellate groups having a yellowish colour. The salt obtained by precipitation is colourless, slightly soluble in water and alcohol in the cold, more easily at higher temperatures, and has a strong alkaline reaction. Dissolves in 76.9 pts. of water at 20°. Does not lose weight at 100°: does not melt at higher temperatures, but burns with a slight explosion. (Brown.)

Dried at 100°.				Brown.
SrO	52	31.64	31.49	
10 C	60	36.62	36.16	
4 H	4	2.44	2.74	
6 O	48	29.30	29.61	
<hr/>				
C ¹⁰ H ³ SrO ⁶ , Aq.	164	100.00	100.00	

Pyromeconate of Lime.—The solution of hydrate of lime in the warm aqueous acid, deposits the lime-salt as it cools in white hard crystals. (Stenhouse.)—The salt is obtained in small, colourless, silky needles, by adding an excess of a solution of acetate of lime to an ammoniacal solution of pyromeconic acid. Sparingly soluble in boiling alcohol, somewhat more readily in water, from which it separates on cooling in crystals of considerable size. Dissolves in 322.6 pts. of water at 15.5°. (Brown.)

Dried at 100°.				Brown.
CaO	28	20.00	20.44	
10 C	60	42.85	42.94	
4 H	4	2.85	2.60	
6 O	48	34.30	34.02	
<hr/>				
C ¹⁰ H ³ CaO ⁶ + Aq.	140	100.00	100.00	

Pyromeconate of Magnesia.—A warm aqueous solution of pyromeconic acid forms, with acetate of magnesia, a white amorphous precipitate.

pitate insoluble in water and alcohol. Resembles the other pyromeconates. (Brown.)

		Dried at 100°.		Brown.	
MgO	20	16.26	16.53		
10 C	60	48.78	48.37		
3 H	3	2.44	2.76		
5 O	40	32.52	32.34		
$C^{10}H^3MgO^6$	123	100.00	100.00		†.

Pyromeconate of Lead. — The acid does not precipitate neutral acetate of lead (Robiquet), or the basic acetate. (Stenhouse). On digesting the aqueous acid with hydrated oxide of lead, the pyromeconate separates as the liquid becomes saturated. (Robiquet.) A warm concentrated ammoniacal solution of pyromeconic acid, added to neutral acetate of lead, instantly throws down a dense crystalline powder, which increases rapidly on stirring the liquid. The salt is colourless when first precipitated, but soon turns yellow when exposed to bright daylight. Does not diminish in weight at 100°, even in three or four hours. The crystals require a rather large quantity of hot water to dissolve them; in alcohol, whether warm or cold, they are still less soluble. (Brown.) The salt is nearly insoluble in water, but dissolves in pyromeconic and acetic acid. (Robiquet.)

		Robiquet.		Brown.	
PbO	112	52.09	51.70	52.02	
10 C	60	27.90	28.62	28.12	
3 H	3	1.40	1.36	1.65	
5 O	40	18.61	18.32	18.21	
$C^{10}H^3PbO^6$	215	100.00	100.00	100.00	

Ferric Pyromeconate. — Pyromeconic acid imparts a cherry-red colour to ferric salts. (Sertürner.) The colour is not destroyed by boiling, and but slowly by chloride of soda. (Wackenroder.) Ferric hydrate, boiled with the aqueous acid, combines with it, and forms a brown-red powder, which dissolves very sparingly in pure water, but easily in hot water slightly acidulated, forming a dark red liquid, which deposits small scarlet crystals on cooling. The finest crystals are obtained by mixing a boiling and rather dilute solution of pyromeconic acid with ferric sulphate, and leaving it to cool very slowly. The crystals are brittle, yield a scarlet powder, and dissolve very sparingly in water, either cold or hot, forming a reddish yellow solution. (Stenhouse.) The salt may be also, and perhaps more conveniently, prepared by adding sesquichloride of iron to a hot concentrated aqueous solution of the acid; vermilion-coloured crystals are then gradually deposited, which adhere closely to the bottom and sides of the vessel. (Brown.)

		Crystals.		Stenhouse.		Brown.	
Fe^2O^3	80	20.57	20.06	20.21			
30 C	180	46.27	46.80				
9 H	9	2.31	2.43				
15 O	120	30.85	30.71				
$C^{10}H^9Fe^2O^{18}$	389	100.00	100.00				

Cupric Pyromeconate. — The aqueous acid boiled for a short time with excess of hydrated cupric oxide, yields a pale green filtrate, which, on cooling, deposits long, slender, emerald-green, very fragile needles,

water, or in alcohol either hot or cold. (Stenhouse.) — Brown prepared the salt by mixing ammonio-cupric sulphate with a warm aqueous solution of pyromeconic acid.

	Crystals.		Stenhouse.		Brown.	
CaO.....	40	27·97	27·40	27·66		
10 C.....	60	41·96	42·22			
3 H.....	3	2·10	2·21			
5 O.....	40	27·97	28·17			
<hr/>						
C ¹⁰ H ³ CuO ⁸	143	100·00	100·00			

With mercuric chloride, pyromeconic acid forms, after a while, a white, amorphous precipitate, which redissolves on boiling. (Brown.)

Pyromeconate of Silver. — Pyromeconic acid does not precipitate nitrate of silver, but reduces part of the metal on boiling. When a few drops of ammonia are added to a cold mixture of the acid and the silver-solution, a pale yellow gelatinous precipitate is immediately formed, which contains 51·8 p. c. (1 At.) silver-oxide; assumes a dark brown colour, even in vacuo; burns faintly when heated; and dissolves to a certain extent in cold water and alcohol. — Oxide of silver, immersed in a cold aqueous solution of the acid, combines with it, and forms a heavy salt, which dissolves very sparingly in cold water; decomposes with black colouring, even in the cold; and when boiled with water, coats the sides of the test-tube with silver, without giving off any gas. (Stenhouse.)

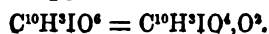
Pyromeconic acid dissolves in alcohol still more readily than in water. (Robiquet, Stenhouse.)

It dissolves in ether (John), and in rock-oil. (Choulant.)

It does not form a compound ether when heated with alcohol and sulphuric acid. (Stenhouse.)

¶ c. Iodine-nucleus. C¹⁰H³IO⁴.

Iodopyromeconic Acid.



J. F. BROWN. *Ed. Phil. Trans.* 21, i. 49; *Phil. Mag. J.* 8, 201; *Ann. Pharm.* 92, 321.

Formation and Preparation. By the action of protobromide or protochloride of iodine on pyromeconic acid (p. 440). A recently prepared solution of protochloride of iodine* is mixed with a solution of pyromeconic acid saturated in the cold, whereupon the liquid immediately becomes decolorised, and deposits a considerable quantity of iodopyromeconic acid in the form of thin plates. — If the solution of pyromeconic acid has been saturated while hot, or if the chloride of iodine is in excess, the action goes too far.—

* The protochloride of iodine is obtained by the action of chlorine gas on iodine suspended in a small quantity of water, the liquid being kept cold and the action being stopped before the iodine is completely dissolved. — The protobromide is obtained by agitating bromine-water with excess of iodine, and decanting the reddish-brown liquid. (Brown.)

These crystals are collected after a while on a filter, washed with cold water, and then dissolved in boiling alcohol, from which solution the acid separates on cooling in colourless shining plates; from boiling water it crystallises in long thin needles, having a slight acid reaction.

<i>Dried at 100°.</i>				Brown.
10 C	60	25.32	25.50	
3 H	3	1.26	1.48	
I	126	53.17	52.91	
6 O	48	20.25	20.11	
<hr/>				
$C^{10}H^2IO^4$	237	100.00	100.00	

The crystals do not lose weight at 100°, but melt at a higher temperature, forming a black liquid, which then suddenly decomposes, giving off a large quantity of iodine-vapour. The acid is decomposed by strong nitric acid, with separation of iodine.

It dissolves sparingly in cold, abundantly in boiling water. Alkalies and acids increase its solubility in water, but boiling with strong potash-solution decomposes it. The aqueous solution imparts a deep purple colour to sesquichloride of iron, and forms with nitrate of silver a yellowish white precipitate, soluble in ammonia.

Baryta-salt. — On mixing an alcoholic solution of the acid, rendered slightly alkaline by ammonia, with an alcoholic solution of acetate of baryta, iodopyromeconate of baryta quickly separates in delicate crystals, which have an alkaline reaction, do not lose weight at 100°, and dissolve but sparingly in water and alcohol, either hot or cold.

<i>Crystals dried at 100°.</i>				Brown.
BaO	76.6	24.42	23.84	
10 C	60.0	19.13		
3 H	3.0	0.96		
I	126.0	40.18		
6 O	48.0	15.31		
<hr/>				
$C^{10}H^2BaIO^4 + Aq.$	313.6	100.00		

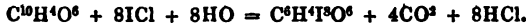
Lead-salt. — A mixture of the alcoholic solutions of iodopyromeconic acid and neutral acetate of lead, yields this salt on addition of a small quantity of ammonia, in the form of a colourless amorphous precipitate, which may be freed from excess of oxide of lead by digestion in warm acetic acid.

<i>Air-dried.</i>				Brown.
PbO	112	32.94	33.03	
10 C	60	17.65		
2 H	2	0.59		
I	126	37.06		
5 O	40	11.76		
<hr/>				
$C^{10}H^2PbIO^5$	340	100.00		

Iodopyromeconic acid dissolves sparingly in cold, readily in boiling alcohol. (Brown.)

Iodomecone. $C^6H^4I^2O^6$.J. F. BROWN. *Ann. Pharm.* 92, 324.

Formed by the action of an excess of chloride of iodine on pyromeconic acid (p. 440), or on meconic or comenic acid, which differ in composition from pyromeconic acid, only by the elements of carbonic acid :



When pyromeconic acid is acted upon by a quantity of chloride of iodine larger than is required to form iodopyromeconic acid, the liquid turns yellow and iodomecone is produced; and if, after separation of the undecomposed iodopyromeconic acid, potash be gradually added to the liquid, a black precipitate is formed which redissolves on agitation; on adding more potash, a point is attained, at which the precipitate exhibits a lighter colour, no longer redissolves on agitation, and is no longer increased by further addition of potash. The precipitate is then to be separated from the liquid by filtration, washed with cold water, and purified by repeated crystallisation from boiling alcohol.

Iodomecone crystallises in shining, yellow, six-sided tables; smells like saffron; is neutral to vegetable colours; sublimes without decomposition considerably below 100° . Altogether, its properties resemble those of iodoform.

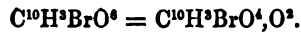
					Brown.
6 C	36	3.29	3.34
4 H	4	0.36	0.44
8 I	1008	91.97	91.97
6 O	48	4.38	4.25
<hr/>					
$C^6H^4I^2O^6$	1096	100.00	100.00

Iodomecone is decomposed with violence by strong nitric acid. Oil of vitriol does not act upon it in the cold, but decomposes it when heated, with separation of iodine. Caustic potash boiled with it for some time extracts a small quantity of iodine.

It is insoluble in water and in hydrochloric acid, and is not decomposed by the latter, even at a boiling heat. Dissolves in *alcohol* and *ether*. (Brown.)

7. *d.* Bromine-nucleus. $C^{10}H^2BrO^4$.

Bromopyromeconic Acid.

J. F. BROWN. *Ann. Pharm.* 84, 41.

Formed by the action of bromine on pyromeconic acid (p. 440).—When bromine-water is added to a strong aqueous solution of pyromeconic acid, the latter being in excess, the bromine is quickly absorbed, and there remains a colourless liquid, which, after standing for an hour or less, deposits bromopyromeconic acid in beautiful small colourless

prisms. If the bromine water is in excess, this acid is not produced. From boiling alcohol the acid crystallises in fibrous plates, or if the solution be slowly cooled, in short prisms. It reddens litmus slightly.

10 C	60	31.41	Brown.
3 H	3	1.57	31.93
Br	80	41.89	2.05
6 O	48	25.13	41.34
<hr/>			
$C^{10}H^3BrO^6$	191	100.00	100.00

The acid, when subjected to dry distillation, melts, blackens, and gives off a large quantity of hydrobromic acid; and if the heat be long continued, a white crystalline substance begins to collect in the cold part of the tube. Nitric acid decomposes bromopyromeconic acid with effervescence; sulphuric acid dissolves it without visible decomposition.

The acid dissolves sparingly in cold, somewhat more readily in hot water. — The solution does not precipitate chloride of barium, chloride of calcium, or sulphate of magnesia, even in presence of ammonia. — With ferric salts it yields a deep purple-red colour, quite different from the red tint produced by pyromeconic acid. — With ammonio-cupric sulphate it forms no precipitate in the cold, but on heating the liquid, a bluish precipitate is formed. — The acid does not form any precipitate with nitrate of silver; neither does it reduce the oxide to metallic silver at a boiling heat.

Lead-salt. A warm alcoholic solution of the acid forms with an alcoholic solution of acetate of lead, a white precipitate, consisting of small, closely aggregated crystalline needles, which quickly settle down to the bottom of the vessel. The salt may also be obtained by mixing the aqueous solutions of the acid and of acetate of lead, with addition of ammonia; but it is then strongly coloured.

PbO	112	36.97	Brown.
10 C	60	19.80	36.48
3 H	3	0.99	20.57
Br	80	26.40	0.85
6 O	48	15.84	
<hr/>			
$C^{10}H^3PbBrO^6, Aq.$	303	100.00	

The salt could not be purified by recrystallisation, on account of its insolubility in water and alcohol: it was therefore carefully washed with alcohol. (Brown.) ¶

c. Amidogen-nuclei.

¶. a. Amidogen-nucleus. $C^{10}AdH^7$.

Piperidine.



- ANDERSON. *Report of the Twentieth Meeting of the Brit. Assoc.*, 1850, *Notic. and Abstr.* 47; *Ann. Pharm.* 84, 345; *Jahresber.* 1852, 545.
 CAHOURS. *Ann. Chim. Phys.* 38, 76; *Chem. Soc. Qu. J.* 6, 175; *abstr. Ann. Pharm.* 84, 342; *Jahresber.* 1852, 546.

treated first with nitric acid and then with potash, yield volatile bases; afterwards, in 1852, he examined more particularly the base obtained in this manner from piperine, and determined its composition by the analysis of the platinum-salt. — Cahours showed, somewhat later, but independently of Anderson, that the same base is obtained by heating piperine with potash-lime. Rochleder & Wertheim had previously shown that piperine yields a volatile oily base when heated with soda-lime; but they found this base to possess the properties of picoline, and regarded it as a pseudo-salt containing the elements of picoline united with a quaternary group of atoms.

Preparation. 1. When 1 pt. of piperine is distilled with 2½ to 3 pts. of potash-lime in a retort connected with a cooled receiver, a distillate is obtained, consisting of water, two distinct volatile bases, and a neutral substance having an agreeable aromatic odour. When this crude liquid is treated with fragments of caustic potash, a light oily substance separates, having a strong ammoniacal odour, and dissolving in water in all proportions. This oil, when distilled, passes over almost wholly between 105° and 108°; but towards the end of the distillation, the thermometer rises quickly to 210°, and there remains stationary. The more volatile product, which forms more than ⅔ of the crude liquid, distils over entirely at 106°, when rectified. This liquid is piperidine. (Cahours.) — 2. Piperine, treated with nitric acid, evolves red fumes, and forms a substance having an odour of bitter almond oil, and a brown resin, which dissolves with blood-red colour in potash, and when boiled with that substance, yields piperidine, in the form of a volatile liquid. (Anderson.)

Properties. Colourless, very limpid liquid, having a strong ammoniacal odour, but recalling also that of pepper, and a very caustic taste (Cahours); peculiar aromatic odour. (Anderson.) Blues reddened litmus strongly. Boils at 106°. Vapour density 2·958. (Cahours.)

Cahours.					
10 C	60	...	70·58	70·41
N	14	...	16·48	16·60
11 H	11	...	12·94	13·01
C ¹⁰ NH ¹¹	85	...	100·00	100·02

	Vol.	Density.
C-vapour	10	4·1600
N-gas	1	0·9706
H-gas	11	0·7623
Vapour	2	5·8929
	1	2·9464

[Cahours regards this compound as an imidogen-base of the formula $N \left\{ \begin{array}{l} H \\ C^xH^y \\ C^{10-x}H^{10-y} \end{array} \right\}$

in other words, he supposes it to contain only 1 At. H. replaceable by an organic radical. This view appears to be supported by the action of iodide of methyl on methylopipe-ridine (p. 448).

Decompositions. — 1. *Nitrous acid* acts violently on piperidine, forming a heavy aromatic liquid, which however was not obtained in sufficient quantity for analysis. From the results obtained by the action of nitrous acid on aniline (see next vol.), it is probable that the compound

C¹⁰H¹⁰O² is first formed, and afterwards C¹⁰XH⁹O². — 2. Vapour of cyanic acid passed into piperidine forms piperidic urea :

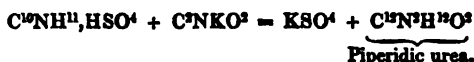


Cyanate of methyl and cyanate of ethyl form similar compounds, with 1 H replaced by 1 At. methyl or ethyl. — 3. Iodide of methyl added to piperidine forms the hydriodate of methylpiperidine, C¹⁰NH¹⁰(C²H³). Similar substitution-compounds are formed by the iodides of ethyl and amyl; also by chloride of benzoyl, chloride of cumyl; and apparently also by chloride of acetyl. (Cahours.)

Combinations. Piperidine dissolves in all proportions in Water, forming a strongly alkaline liquid, which behaves with saline solutions like ammonia, excepting that it does not redissolve the oxides of zinc and copper.

Piperidine saturates the strongest acids, and forms crystalline salts with sulphuric, hydriodic, hydrobromic, hydrochloric, nitric, and oxalic acids. (Cahours.)

Sulphate of Piperidine. C¹⁰NH¹¹.HO.SO³ is obtained by saturating piperidine with sulphuric acid. It is crystallisable, deliquescent, and very soluble in water. A solution of 1 At. of this salt, boiled with 1 At. cyanate of potash, yields sulphate of potash and a compound analogous to urea :



Sulphocarbonate of Piperidine. When bisulphide of carbon is added drop by drop to piperidine, a violent action takes place, and the mixture becomes very hot; and on dissolving the resulting solid mass (after the sulphide of carbon has been added in excess, and the action is terminated) in alcohol, and leaving the solution to evaporate, the salt separates, sometimes in slender needles, sometimes in symmetrical oblique prisms of considerable size. (Cahours.)

				Cahours.
11 C	66	...	53.65 53.61
N	14	...	11.38	
11 H	11	...	8.94 8.90
2 S	32	...	26.03 25.90
<hr/>				
C ¹⁰ NH ¹¹ .CS ²	123	...	100.00	

Hydriodate of Piperidine. — Crystallises in long needles resembling the hydrochlorate. (Cahours.)

				Cahours.
10 C	60	...	28.30 28.18
N	14	...	6.62 6.69
12 H	12	...	5.65 5.72
I	126	...	59.43	
<hr/>				
C ¹⁰ NH ¹¹ .HI	212	...	100.00	

Hydrochlorate of Piperidine. — Long colourless needles, easily soluble in water and alcohol. From the alcoholic solution the salt separates in long prisms (Cahours); in needles an inch long. (Anderson.) The crystals volatilise when moderately heated, and are not altered by exposure to the air.

10 C	60.0	49.58	49.65
N	14.0	11.53	11.65
12 H	12.0	9.87	10.00
Cl	35.4	29.23	29.00
<hr/>			
C ¹⁰ NH ¹¹ ,HCl	121.4	100.00	99.70

Nitrate of Piperidine. — Obtained by saturating the base with weak nitric acid, and evaporating in vacuo. Small crystalline needles. Decomposes when heated, giving off vapours which have an aromatic odour. Very soluble in alcohol. (Cahours.)

			Cahours.
10 C	60	40.54	40.68
2 N	28	18.90	
12 H	12	8.11	8.24
6 O	48	32.45	
<hr/>			
C ¹⁰ NH ¹¹ O,NO ⁵	148	100.00	

Chloroplatinate of Piperidine. — Long orange-coloured needles, very soluble in water, less soluble in alcohol. (Cahours.)

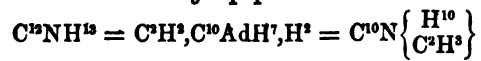
			Cahours.
10 C	60.0	20.60	20.45
N	14.0	4.81	4.93
12 H	12.0	4.12	4.22
Pt	99.0	34.00	33.81
3 Cl	106.2	36.47	36.45
<hr/>			
C ¹⁰ NH ¹¹ ,HCl,PtCl ²	291.2	100.00	99.86

Oxalate of Piperidine. — Formed by saturating piperidine with a solution of oxalic acid. Separates by evaporation in delicate needles, which may be obtained pure by a second crystallisation.

			Cahours.
12 C	72	55.38	55.58
N	14	10.77	10.84
12 H	12	9.23	9.39
4 O	32	24.62	24.19
<hr/>			
C ¹⁰ NH ¹¹ ,C ² HO ⁴	130	100.00	100.00

Conjugated Compounds of Piperidine.

Methylpiperidine.



CAHOUS. *N. Ann. Chim. Phys.* 38, 92; *Chem. Soc. Qu. J.* 6, 179.

Formed by the action of iodide of methyl on piperidine. The action is very violent, so that it is necessary to add the iodide of methyl drop by drop, and keep the tube cool; otherwise the contents will be thrown out. When the liquids are mixed in equal volumes, hydriodate of methylpiperidine is obtained in a beautifully white, crystalline mass,

which is soluble in water, and when treated with potash yields methylpiperidine in the form of an oily liquid, having an ammoniacal odour like that of piperidine, but more aromatic. The product is purified by digestion with fragments of caustic potash and subsequent rectification.

Colourless, very mobile liquid, having an ammoniacal and aromatic odour. Boils at 118° . Vapour-density = 3.544.

		Cahours.	
12 C 72 72.72 72.83
N 14 14.15 14.35
13 H 13 13.13 13.74
<hr/>			
$C^{12}NH^{13}$ 99 100.00 100.92
<hr/>			
		Vol.	Density.
C-vapour	12	4.9920
N-gas	1	0.9706
H-gas	13	0.9009
<hr/>			
Vapour of Methylpiperidine		2	6.8635
		1	3.4317

Methylpiperidine dissolves in *Water*, and forms crystallisable compounds with *Acids*.

Hydrochlorate. — Crystallises in beautiful colourless needles.

		Cahours.	
12 C 72.0 53.13 52.91
N 14.0 10.33
14 H 14.0 10.33 10.43
Cl 35.4 26.21 26.31
<hr/>			
$C^{12}NH^{13}, HCl$ 135.4 100.00

Chloroplatinate. — Hydrochlorate of methylpiperidine forms with bichloride of platinum, a double salt, which is soluble in water and still more in alcohol, and separates, by spontaneous evaporation of the alcoholic solution, sometimes in needles, sometimes in tables of a fine orange-colour.

		Cahours.	
12 C 72.0 23.59 23.77
N 14.0 4.59
14 H 14.0 4.59 4.63
Pt 99.0 32.43 32.40
3 Cl 106.2 34.80
<hr/>			
$C^{12}NH^{13}, HCl, PtCl^2$ 305.2 100.00

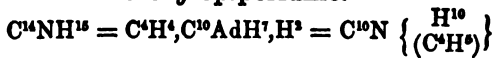
Methylpiperidine with Iodide of Methyl. — Methylpiperidine mixed with iodide of methyl, becomes slightly heated, and on heating the mixture in a sealed tube placed in the water-bath, it finally solidifies in a crystalline mass. On breaking the tube after a few days, heating to expel the excess of iodide of methyl, dissolving the crystals in alcohol, and leaving the solution to evaporate, it yields splendid crystals, which acquire a high lustre by drying between bibulous paper. These crystals when distilled in a retort, partly volatilise, and are partly resolved into methylpiperidine and iodide of methyl. The same decomposition takes place when the crystals are distilled with fragments of potash.

14 C	84	35.00	34.90
N	14	5.83	5.92
16 H	16	6.67	6.75
I	126	52.50	

C¹²NH¹², C²H²I 240 100.00

As the crystals, when distilled with potash, do not yield any distinct organic base, it does not appear possible to replace more than 1 At. H. in piperidine by methyl (see p. 447).

Ethylpiperidine.



CAHOURS. *N. Ann. Chim. Phys.* 38, 95; *Chem. Soc. Qu. J.* 6, 179.

Formation and Preparation. — By the action of iodide of ethyl on piperidine. The mixing of the two liquids is attended with considerable rise of temperature, though not so great as with iodide of methyl. The mixture must however be made with caution, and the vessel kept cool, to avoid projection of the liquid. On heating the mixture in sealed tubes placed in the water-bath, it solidifies in a mass of beautiful white crystals of hydriodate of ethylpiperidine, which, when decomposed by potash, yields the base.

Properties. Colourless, very mobile, oily liquid, lighter than water; has an odour like that of piperidine, but less ammoniacal and more aromatic. Boils at 128°. Vapour-density = 3.986.

				Calours.
14 C	84	74.33	74.16	
N	14	12.40	12.59	
15 H	15	13.27	13.19	
<hr/>				
C ¹⁴ NH ¹⁶	113	100.00	99.94	

	Vol.	Density.
C-vapour	14	5.8240
N-gas	1	0.9706
H-gas	15	1.0395

Vapour of Ethylpiperidine....	2	7.8341
	1	3.9170

Ethylpiperidine dissolves in *Water*, but less abundantly than piperidine; potash in fragments added to the solution separates the base completely. It dissolves readily in *Alcohol* and *Ether*.

Hydrochlorate. C¹⁴NH¹⁶, HCl, PtCl². — Forms beautiful needles, having considerable lustre.

Chloroplatinate. — A concentrated solution of the hydrochlorate, mixed with a concentrated solution of bichloride of platinum, forms an abundant precipitate, which dissolves in a larger quantity of water, especially when hot. If this precipitate be redissolved in a mixture of

equal parts of water and alcohol, and the solution left to evaporate spontaneously; the double salt separates in large orange-coloured prisms of great beauty.

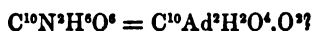
				Cahours.
14 C	84.0	...	26.31	26.23
N	14.0	...	4.39	4.28
16 H	16.0	...	5.01	5.16
Pt	99.0	...	31.02	30.86
3 Cl	106.2	...	33.27	
C ¹⁶ NH ¹⁶ ,HCl,PtCl ³				319.2 ... 100.00

Ethylo-piperidine scarcely exhibits any rise of temperature when mixed with iodide of ethyl. When placed together with excess of iodide of ethyl in sealed tubes, and heated in the water-bath for several days, it yields a viscous mass, which floats upon the hydriodic ether. Water dissolves this product in all proportions, forming a solution which does not crystallise in vacuo. The solution treated with excess of recently precipitated oxide of silver, yields a deposit of iodide of silver, and a liquid which, when evaporated in vacuo, yields very deliquescent crystals, having a bitter taste and a strong alkaline reaction. These crystals decompose when strongly heated, yielding ethylo-piperidine and an inflammable gas. They dissolve with rise of temperature in hydrochloric acid, forming a solution which, when concentrated by heat, or better by evaporation in vacuo, yields a slightly deliquescent salt, which crystallises in scales. — The solution of this hydrochlorate forms a copious precipitate with a concentrated solution of bichloride of platinum; but if the liquids be mixed in a state of greater dilution, and at a boiling heat, the mixture on cooling deposits the platinum-salt of [biethylo-piperidine] in small orange-coloured prisms, bearing a strong resemblance to chloroplatinate of potassium.

				Cahours.
18 C	108.0	...	31.10	31.01
N	14.0	...	4.03	
20 H	20.0	...	5.76	5.82
Pt	99.0	...	28.51	28.26
3 Cl	106.2	...	30.60	
C ¹⁸ NH ¹⁹ ,HCl,PtCl ³				347.2 ... 100.00

The formula of this salt may also, and with greater probability, be written in the form C¹⁸NH²⁰Cl,PtCl³, representing it as the chloroplatinate of biethylo-piperidammonium, C¹⁸NH²⁰ = C¹⁰N { $\begin{matrix} \text{H}^{10} \\ (\text{C}^4\text{H}^5)_3 \end{matrix} \}$ of which the viscous substance obtained by treating the product of the action of iodide of ethyl on ethylo-piperidine with oxide of silver, is the hydrated oxide = C¹⁸NH²⁰O,H₂O. (Cahours.) The salts of ethylo-piperidine, methylo-piperidine, and piperidine itself may of course be likewise represented as analogous to ammonium-salts, e. g. the hydrochlorate of piperidine = C¹⁰NH¹³,Cl. It would be interesting to know, whether the action of oxide of silver on the iodides of these bases would also give rise to the formation of crystallisable hydrates. ¶

Nitrothein.



STENHOUSE (1843). *Phil. Mag. J.* 23, 426; also *Mem. Chem. Soc.* 1, 219, and 239; also *Ann. Pharm.* 45, 371; 46, 229.
ROCHLEDER. *Ann. Pharm.* 73, 56.

Rochleder's *Cholestrophane*.

Formation. By the action of nitric acid or chlorine-water on coffein.

Preparation. 1. Coffein is boiled for some hours with strong nitric acid, till a sample of the liquid leaves, on evaporation, no longer a yellow but a white residue; the liquid is then evaporated to a syrup and cooled, and the resulting crystals purified by recrystallisation from water, and pressure between paper. 100 pts. of coffein yield from 5 to 6 pts. of nitrothein. (Stenhouse.)—2. Chlorine gas is passed through water in which coffein is suspended, till the amelic acid at first produced is decomposed; the solution is then left to crystallise. (Rochleder.)

Properties. Crystallises from water in large white nacreous laminæ; from ether by evaporation in very regular octohedrons; and by sublimation, which takes place readily and without decomposition, in delicate shining laminæ, like naphthalin. The crystals grate between the teeth, have a sweetish taste, and redden litmus very slightly, or not at all. (Stenhouse.)

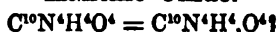
	<i>Crystals dried at 100°.</i>			Stenhouse.	Rochleder.
10 C	60	42·25	42·01	42·00
2 N	28	19·72	19·47	20·00
6 H	6	4 23	4·26	4·25
6 O	48	33·80	34·26	33·75
$C^{10}N^2H^2O^8$	142	100·00	100·00	100·00

Decompositions. 1. Nitrothein is easily set on fire, and burns with a bright flame. (Stenhouse.)—2. When boiled with potash-ley, it gives off a large quantity of ammonia (Stenhouse), and perhaps also ethylamine, and forms carbonate and oxalate of potash. (Rochleder.) If ethylamine is produced in this reaction, the equation may perhaps be :



Combinations. Nitrothein dissolves in 3 pts. of cold, and in a much smaller quantity of hot water. The solution produces no reaction with acetate of lead, ferrous sulphate, or nitrate of silver. (Stenhouse.)

Nitrothein dissolves readily in alcohol and ether. (Stenhouse.)

f. *Nitrogen-nucleus.* $C^{10}N^4H^4$.**Xanthic Oxide.**

MARCEZ. In his *Essay on the Chemical History and Medical Treatment of Calculous Disorders*. Lond. 1819. Translated into German by HEINEKER, Bremen; abstr. *Schw.* 26, 29.

WÖHLER & LIEBIG. *Pogg.* 41, 393; also *Ann. Pharm.* 26, 340.

Xanthin (which name would be preferable, if it did not also belong to madder-yellow.)—Discovered by MarceZ in 1819; (first analysed by Wöhler & Liebig). Very rarely forms human calculi. (MarceZ, Wöhler & Liebig, Langier, *J. Chim. méd.* 5, 513); occurs in the urine of spiders, (J. Davy, *N. Ed. Phil. J.* 40, 355.) According to Gorup-Besanez, this substance contains, not xanthic oxide, but guanine.

Properties. The calculus consisting of xanthic oxide is brown, smooth, hard, of laminar structure, and when dissolved in water reddens litmus slightly (MarceZ); it is globular, smooth, and of dark brownish yellow colour (Langier); its surface is sometimes light brown, smooth, and shining, sometimes whitish and earthy; on the fracture, it exhibits a brownish flesh-red colour; it acquires a waxy lustre by friction; consists of concentric layers without fibrous or crystalline structure; and has the hardness of the denser uric acid calculi. (Wöhler & Liebig.)—By dissolving the calculus in potash, precipitating the filtrate with carbonic acid, and washing and drying the white pulverulent precipitate, the xanthic oxide is obtained in very hard yellowish lumps, which acquire a waxy lustre by friction, and are free from potash. (Wöhler & Liebig.)

<i>Dried at 100°.</i>		Wöhler & Liebig.	
10 C	50	39·48	39·86
4 N	56	36·84	36·72
4 H	4	2·63	2·60
4 O	32	21·05	20·82
$C^{10}N^4H^4O^4$ 152 100·00 100·00			

[According to the formula $C^{10}N^4H^4, O^4$, xanthic oxide would be the monobasic acid of the nucleus whose bibasic acid is uric acid.]

Decompositions. 1. The xanthic oxide calculus yields by dry distillation, an aqueous solution of carbonate of ammonia which crystallises on cooling, and a thick yellow oil (MarceZ); it gives off a large quantity of hydrocyanic acid, and yields a sublimate of carbonate of ammonia, not of urea. (Wöhler & Liebig.)—2. Before the blow-pipe, the calculus flies to pieces, blackens, emits a faint, peculiar, empyreumatic, animal odour, (different from that of heated uric acid, and more like that of burnt horn. W. & L.) and consumes down to a small quantity of ash. (MarceZ.)—3. Its solution in nitric acid leaves on evaporation a dry lemon-yellow residue, which dissolves partially in water. The solution thus formed is yellow; loses its colour when mixed with acids, but is coloured bright red by potash; and yields by evaporation, a carmine-coloured mass which dissolves with yellow colour in water. (MarceZ.) The residue left on evaporating the solution in strong nitric acid, forms with water a yellow

yellow colour in water. (Laugier.) Xanthic oxide dissolves in nitric acid without evolution of gas, but much less quickly than uric acid, and the solution leaves on evaporation a bright lemon-yellow mass, which dissolves in water with light yellow, and in potash-ley with deep reddish yellow colour. The latter solution forms a yellow precipitate with sal-ammoniac, and, when mixed with chloride of soda, gives off nitrogen gas, and becomes dark-coloured at first, but afterwards colourless. (Wöhler & Liebig.) — As gelatin, chondrin, &c. likewise yield with nitric acid a yellow residue, which turns red when treated with potash, this behaviour of xanthic oxide with nitric acid is not characteristic. (E. Barruel, *J. Chim. méd.* 16, 13.)

Combinations. Xanthic oxide dissolves to a slight extent in boiling water, and as the solution cools, a white film forms on the surface, and gradually sinks to the bottom. (Marcet.)

It dissolves in *oil of vitriol*, and is not precipitated from the solution by water. (Wöhler & Liebig.)

It dissolves very sparingly in dilute acids, perhaps through the medium of the water contained in them. (Marcet.) It is insoluble, or very sparingly soluble, in hydrochloric acid. (Wöhler & Liebig.)

It dissolves in *ammonia* (Marcet), more readily than uric acid, and the solution leaves on evaporation a yellowish laminated mass, still containing a small quantity of ammonia. (Wöhler & Liebig.)

It dissolves very readily in *potash-ley*, whence it is precipitated by acids (Marcet); the solution has a dark greenish brown-yellow colour, like bile; immediately deposits the xanthic oxide when carbonic acid is passed through it; and when mixed with sal-ammoniac, deposits the xanthic oxide on evaporation, and with evolution of ammonia. (Wöhler & Liebig.)

Xanthic oxide likewise dissolves in aqueous *mono-carbonate of potash*, but not in bicarbonate of ammonia, potash, or soda. (Marcet.)

It dissolves sparingly in *acetic acid*. (Marcet.)

It is insoluble, or but very sparingly soluble, in *oxalic acid*. (Marcet, Wöhler & Liebig.)

It is insoluble in alcohol and ether. (Marcet.)

Uric Acid.



SCHÉELE. *Opusc.* 2, 73; also *Croll. N. Entdeck.* 3, 227.

BERGMAN. *Opusc.* 4, 387; also *Croll. N. Entdeck.* 3, 232.

PEARSON. *Scher. J.* 1, 48.

FOURCROY. *Ann. Chim.* 16, 116; 27, 225.

VAUQUELIN. *J. Phys.* 88, 456. — *Ann. du Mus.* 1, 96; 7, 253.

WILLIAM HENRY. *Ann. Phil.* 2, 57.

GAY-LUSSAC. *Ann. Chim.* 96, 53; also *Schw.* 16, 84.

CHEVALLIER & LASSAIGNE. *Ann. Chim. Phys.* 13, 155; also *Schw.* 29, 257.

GASP. BRUGNATELLI. *Brugn. Giorn.* 11, 38 and 117; 12, 133; 13, 464.

PROUT. *Schw.* 28, 182. — *Ann. Chim. Phys.* 11, 48. — *Ann. Phil.* 14, 363.

- BRACONNOT. *Ann. Chim.* Pogg. 7, 302; *ibid.* 8, 200.
 WETZLAR. *Beiträge zur Kenntniss des menschlichen Harns.* Frankf. 1821, 69; *abstr. Schw.* 33, 264.
 LIEBIG. *Pogg.* 15, 569. — *Ann. Pharm.* 5, 288.
 WÖHLER & LIEBIG. *Ann. Pharm.* 26, 241.
 LIPOWITZ. *Ann. Pharm.* 38, 348.
 AUG. BENSCH. *Ann. Pharm.* 54, 189.
 JAM. ALLAN & AUG. BENSCH. *Ann. Pharm.* 65, 181.
 HEINTE. *Ann. Pharm.* 55, 62.

Lithic acid, Harnsäure, Urinsäure, Blasensteinsäure, Acide urique, Ac. lithique, Pearson's lithic oxide, or animal oxide. — Discovered by Scheele in 1776. — Occurs in the urine of man, of the lion, tiger, leopard, hyæna, dog (Marchand, *J. pr. Chem.* 14, 496), of the ox (Bödeker, *J. pr. Chem.* 25, 254), also in the allantoic liquid (Jacobsen; *Meckel Archiv.* 8, 332; Prevost & Le Royer, *Bull. d. Sc. méd.* 7, 25); in the urine of birds, especially of the carnivorous and graminivorous kinds; therefore also in the dung of sea-birds, which accumulates in deep layers in the form of *guano* on the islands of South America and Africa; in the urine of serpents, crocodiles, lizards, and tortoises; in the urine of the silkworm-butterfly (Brugnattelli), and of other butterflies and moths (J. Davy); of several caterpillars, of horse-dung-beetles, grasshoppers, crickets, scolopendra, wasps (also, according to Audouin), and of several flies (J. Davy, *N. Ed. Phil. J.* 40, 231 and 335; 45, 17); in cantharides (Robiquet), in many species of *Meloë* (Lavini & Sobrero, *N. J. Pharm.* 7, 469); in the so-called biliary ducts (which, according to Audouin, *N. Ann. Sc. Nat. Zoologie*, 5, 130, should be regarded as urinary organs, or, according to Meckel, as urinary and biliary organs), of the *Lucanus Capreolus* (Aubé); in the urinary organ of several species of *Helix* (Mylius, *J. pr. Chem.* 20, 509), and in the urine of those animals (J. Davy, *N. Ed. Phil. J.* 45, 385) — Very many urinary concretions and deposits of man, fewer of the dog, and many of birds, serpents, lizards, and tortoises, consist of uric acid or urate of ammonia.

To determine the quantity of uric acid in a liquid urine, the urine is to be mixed with hydrochloric acid (or with acetic or phosphoric acid, if albumin is present), and the uric acid which settles down after some time collected. (Heintz, *Pogg.* 70, 122.) Scratching the sides of the vessel with a glass rod accelerates the deposition. (Wetzlar.) — Or the urine may be evaporated to an extract; this extract exhausted with 93 per cent. alcohol; the undissolved portion treated with dilute potash; the uric acid precipitated from the filtrate by acetic acid with the aid of heat (hydrochloric acid would likewise precipitate mucus); and the precipitate washed with water containing acetic acid. (Lehmann, *J. pr. Chem.* 25, 13.) — If a urinary calculus contains so small a quantity of uric acid, that it merely exhibits the red colouring when evaporated with nitric acid, but gives no precipitate with hydrochloric acid when exhausted with potash, it may be boiled with water and carbonate of lithia; the filtrate treated with hydrochloric acid will then yield a precipitate of uric acid. (Lipowitz, *Ann Pharm.* 38, 352.)

Preparation. a. *From urinary calculi containing uric acid or urate of ammonia, — or from the sediment deposited from human urine, especially after addition of hydrochloric acid, — or from the urine of carnivorous and graminivorous birds (Braconnot), — or from the urine of the Boa-constrictor,*

of these materials, which may be previously freed from phosphate of lime and a portion of the brown colouring matter, &c., by boiling (Kodweiss), or by a day's maceration (Wöhler) with dilute hydrochloric acid, is dissolved in warm potash-ley; the uric acid precipitated from the filtrate by hydrochloric acid; warm potash-ley saturated with the precipitate and washed uric acid; the solution evaporated to a pulp; the pulp consisting of granules of acid urate of potash, spread out upon linen, washed by stirring it up several times with a small quantity of cold water, and then strongly pressed; and the residue dissolved in boiling water. The liquid on cooling deposits the salt in white but still rather impure crystals; the purest salt is deposited, after a few days, from the mother-liquor decanted from the first crystals, this liquid then retaining nothing but brown colouring matter and carbonate of potash. This purest salt, dissolved in potash-ley, yields, on addition of hydrochloric acid, a white precipitate of pure uric acid, gelatinous at first, but afterwards aggregating in scales. (Braconnot.) — 2. Serpents' urine, poultry-dung, or a urinary calculus, is boiled with a solution of 1 pt. hydrate of potash in 20 pts. water as long as ammonia is given off; carbonic acid gas passed through the filtrate, till the precipitate, which is at first gelatinous, becomes heavy and granular, and sinks to the bottom — or, which comes to the same thing, till the liquid becomes nearly neutral; — the precipitate of acid urate of potash, washed till the wash-water shows turbidity on being mixed with the first filtrate; then dissolved in dilute potash and the solution poured while hot, into dilute hydrochloric acid. (Bensch.) — Delffs heats pulverised serpents' urine with 1 pt. of caustic potash and 14 pts. of water to the boiling point; allows the hot solution to run directly from the filter into a mixture of 2 pts. oil of vitriol and 8 pts. water, stirring all the while; and purifies the uric acid (which settles down in a less bulky form, in proportion as the mixture was hotter) by decantation and washing. (*Pogg.* 81, 311.) — 3. The substances containing uric acid, especially those from which potash would extract a large quantity of foreign matters, colouring the liquid and impeding the filtration — the dung of birds for example — may also be boiled with a solution of borax in 120 pts. of water, and the filtrate precipitated by hydrochloric acid (Wetzlar, Böttger, *N. Br. Arch.* 9, 132; see also Landerer, *N. J. Pharm.* 19, 439; and Arppe, *Ann. Pharm.* 87, 287). — 4. Serpents' urine may also be dissolved in warm oil of vitriol; the [decanted?] solution gradually diluted with water (if it be too much diluted, the colouring matter will be precipitated as well as the uric acid); and the precipitated uric acid washed on the filter with more water. (Fritzsche, *J. pr. Chem.* 14, 245.)

Various methods of Purification. — 1. The uric acid is dissolved in oil of vitriol, and precipitated therefrom by water. (Döbereiner.) — 2. It is boiled with dilute hydrochloric acid, which removes colouring matter and a peculiar flocculent substance. (Gasp. Brugnatelli.) — 3. W. Henry endeavours to free the uric acid from mucus by digestion with carbonate of ammonia, but converts it thereby into carbonate of ammonia, as Wetzlar and Döbereiner have shown. — 4. Luigi Brugnatelli (*Brugn. Giorn.* 12, 155) dissolves the uric acid in lime-water, and reprecipitates it therefrom by hydrochloric acid. — 5. O. Henry (*J. Pharm.* 15, 165) boils the precipitate obtained from human urine by basic acetate of lead with carbonate of potash, and precipitates the uric acid from the filtrate with hydrochloric acid.

potash, slaked lime, and water, the solution strained through a conical cloth filter, and evaporated to a thick pulp; this mass strongly pressed between linen; the residue suspended in water and decomposed with hydrochloric acid; the crude uric acid thus separated, washed with water and dissolved in weak potash-ley; the solution evaporated till it solidifies to a pulp, which is then strongly squeezed in the press-bags; the urate of potash thus obtained boiled with a double quantity of water, stirring constantly, and the liquid strongly pressed out; and this boiling and pressing three or four times repeated, till a sample of the residue treated with hydrochloric acid yields perfectly white uric acid. Lastly, the perfectly white urate of potash is dissolved in hot water containing potash; and the clear solution poured into excess of hydrochloric acid. The mother-liquors obtained in these processes yield, by further treatment, a little more uric acid, amounting altogether to 2½ per cent. of the guano. (Bensch, *Ann. Pharm.* 58, 206.) — 2. Guano is exhausted, first with water, then with potash-ley; the latter brown solution mixed with chloride of calcium to separate a mouldy substance; and pale yellow uric acid obtained from the pale yellow filtrate by precipitation with hydrochloric acid. (Bibra, *Ann. Pharm.* 53, 111.)

Properties. Delicate, white, nacreous scales (in the impure state, yellowish or brownish). The crystals obtained by evaporation from the hot aqueous solution, often appear, when examined by the microscope, to be four-sided prisms, acuminated with octohedral faces resting on the terminal edges. (Bensch.) Fritzsche observed under the microscope transparent, colourless, smooth, thin, square tables. — Tasteless and inodorous; the aqueous solution reddens litmus (Scheele, W. Henry); it does not redden litmus. (Pearson.)

	<i>Air-dried crystals.</i>			Liebig.	Mitscherlich.	Heints.	Var. & Will.
10 H	60	35·72	36·08	35·82	35·65		
4 N	56	33·33	33·36	34·60		33·18	
4 H	4	2·38	2·44	2·38		2·46	
6 O	48	28·57	28·12	27·20			
<hr/>							
C ¹⁰ N ⁴ H ⁴ O ⁶	168	100·00	100·00	100·00			

Liebig (*Ann. Pharm.* 10, 47); Mitscherlich (*Pogg.* 33, 335); Heints (*Pogg.* 70, 123); Varrentrapp & Will (*Ann. Pharm.* 39, 279.)

	Prout.		Bérard.	Kodweiss.	Göbel.
	<i>earlier.</i>	<i>later.</i>			
C	34·25	39·87	33·62	39·79	36·57
N	40·25	31·13	39·23	37·40	28·28
H	2·75	2·23	7·06	2·00	2·39
O	22·75	26·77	20·09	20·81	32·51
<hr/>					
	100·00	100·00	100·00	100·00	99·75

Kodweiss (*Pogg.* 19, 1); Göbel (*Schw.* 58, 475).

The crystallised acid contains no water of crystallisation (Bérard [*comp.* however p. 465]).

Decompositions. 1. Perfectly dry uric acid subjected to *dry distillation* neither melts nor gives off any liquid distillate, but yields a copious brownish yellow sublimate of cyanuric acid, urea, and hydrocyanate of ammonia, together with a large quantity of free hydrocyanic

urea is volatile, these bodies must be formed from other products of decomposition, e. g., urea from ammonia and cyanic acid. (Wöhler.) — At the commencement of the process, carbonate and hydrocyanate of ammonia sublime, and a brown empyreumatic oil passes over, together with free hydrocyanic acid; afterwards cyanuric containing ammonia sublimes, and is ultimately carried forward by the water loaded with empyreumatic oil. (Chevallier & Lassaigne.) The cyanuric acid thus formed amounts, according to Scheele, to $\frac{1}{15}$, according to Pearson, to $\frac{1}{17}$; the residual charcoal, which burns to ashes with difficulty, amounts, according to Scheele, to $\frac{1}{4}$, according to Pearson, to $\frac{1}{10}$, according to W. Henry, to $\frac{1}{4}$; according to Pearson, the dry distillation of 20 grains of uric acid produces 5 cubic inches of carbonic acid and 5 cubic inches of nitrogen gas; according to W. Henry, the gases evolved are carbonic acid and carburetted hydrogen.

2. Uric acid heated in contact with the air becomes carbonised, and gives off an odour of burnt bones. (Pearson.) — For the conversion of urate of ammonia into oxalate by the action of air and light, see page 467. — Mixed with carbonate of soda and fermented with beer-yeast, it is converted at 32° C. into oxalic acid, urea, and carbonate of ammonia. (Ranke, *J. pr. Chem.* 56, 1.)

3. Perfectly dry Chlorine gas does not act at ordinary temperatures on perfectly dry uric acid; but at higher temperatures, it produces a very large quantity of cyanic and hydrochloric acid, the uric acid disappearing altogether, with the exception of a small carbonaceous residue. (Liebig, *Pogg.* 15, 567.) If the uric acid be strongly heated from the very beginning of the action, solid chloride of cyanogen is likewise obtained. (Kodweiss.) — Moist uric acid swells up at ordinary temperatures in chlorine gas, giving off carbonic and cyanic acid, and leaving a residue which is perfectly soluble in water, and contains ammonia, hydrochloric acid, and a large quantity of oxalic acid. (Liebig.) Chevreul (*N. Gehl.* 7, 530), who states that the uric acid is converted into oxalic acid in five minutes, had probably used moist uric acid. — When uric acid is suspended in a large quantity of cold water, chlorine gas, not in excess, passed through the liquid, and the whole agitated, the uric acid dissolves, forming free hydrochloric acid, sal-ammoniac (which then, by the further partial action of the chlorine, produces a small quantity of chloride of nitrogen), a large quantity of acid oxalate of ammonia, a very small quantity of alloxantin or alloxan (inasmuch as the liquid, when evaporated to dryness, leaves a pale purple residue), parabanic acid, a substance rich in nitrogen and very sparingly soluble in water, and, according to Pelouze, also allanturic acid.

Uric acid suspended in 20 pts. of water, dissolves, when chlorine gas is passed through the liquid, with slight effervescence [of nitrogen gas, proceeding from the chloride of nitrogen], and separation of yellowish white flakes, which are a compound of chlorine with animal matter. The strongly acid solution, which continues for a very long time to give off gas bubbles, even without heating, contains hydrochlorate and oxalate of ammonia, hydrochloric acid, malic acid [?], oxuric acid (p. 169), and purpuric acid [?], which last three acids are decomposed when the passage of the chlorine is continued, so that only hydrochloric acid, oxalic acid, and ammonia, remain. (Vauquelin.) — When uric acid is heated with a quantity of chlorine-water not quite sufficient to dissolve it, a liquid is formed, which is reddened by evaporation, and still more

and retains nothing but nitrate of ammonia. Probably the aëria formed from the uric acid is converted by the nitrous acid at the beginning of the action, into nitrite of ammonia and cyanic acid :



The cyanic acid is converted, in the known manner, with water, into ammonia and carbonic acid, so that at first only the latter is evolved, and afterwards the nitrate of ammonia is resolved by heat into water and nitrogen gas, which is therefore given off in the pure state. But as the nitric acid is at first in very large excess, the nitrite of ammonia is partly resolved therewith into nitrate of ammonia and nitrous acid, which escapes in red vapours. (Liebig & Wöhler.) [As the mixture contains an excess of nitric acid up to the end of the reaction, it is not very easy to see how nitrite of ammonia can be formed.] — Cold nitric acid of sp. gr. 1.55 likewise yields alloxan, but at the same time produces a brown substance, by the formation of which the aggregated lumps of uric acid acquire a black-brown colour, and the resulting alloxan also becomes brown and difficult to decolorise. (Liebig & Wöhler.)

Uric acid boiled with strong nitric acid does not yield a trace of alloxan, but is converted into parabanic acid, which separates on cooling in long narrow prisms, and in scales. (Liebig & Wöhler.) — [On the supposition that alloxan is at first produced and then further oxidised, the equation is :



When 1 pt. of uric acid is gradually added to 2 pts. of cold nitric acid, of sp. gr. 1.25, and the mixture, after the completion of the action, cooled to 20°, till it solidifies to a thin pulp, and this product thrown on a filter, it yields a filtrate containing hydruilic acid, a large quantity of parabanic acid, oxalic acid, and ammoniacal salts, — and a residue, which when dissolved in a small quantity of hot water, is resolved into a large quantity of undecomposed uric acid (because the nitric acid was not in sufficient quantity), and a syrupy solution. This solution does not crystallise on cooling; when gently heated it becomes turbid, and deposits alloxantin, together with a *white sparingly soluble powder*; when heated with nitric acid, it gives off carbonic acid, with strong effervescence, and then solidifies on cooling to crystals of alloxan. (Schlieper.) — The *white sparingly soluble powder* mixed with the alloxantin, remains behind when the alloxantin is dissolved in dilute nitric acid. It is not altered by strong nitric acid; dissolves in oil of vitriol, whence it is but slightly precipitated by water; is insoluble in cold water; sparingly soluble in hot water, whence it is deposited by cooling and evaporation; and dissolves in ammonia, forming a liquid, which dries up to a gum, and forms, with nitrate of silver, a white precipitate which turns black on boiling; in potash it dissolves with evolution of ammonia, and is precipitated therefrom by acetic but not by hydrochloric acid, and may be regarded as the ammonia-salt of a peculiar acid. (Schlieper.) — To obtain this acid, the white powder is boiled with potash-ley, till it no longer gives off ammonia (whereby, however, an alteration appears to be produced, as hydrochloric acid then produces a precipitate); the solution, mixed with acetic acid and alcohol, whereby granular crystals are precipitated, still containing potash; these crystals redissolved in potash; and the acid obtained in the form of a soft white crystalline powder by super-

saturation the hot solution with hydrochloric acid and cooling. It contains 35.97 p. c. C, 16.98 N, 3.21 H, and 43.84 O, and is therefore $= C^{10}N^4H^8O^8$. It is insoluble in cold water, but dissolves with tolerable facility in hot water, whence it separates on cooling. It dissolves in oil of vitriol, is insoluble in nitric acid, and even in boiling ammonia; but dissolves readily in potash, whence it is precipitated by ammonia. (Schlieper, *Ann. Pharm.* 56, 10.)—When 2 pts. of nitric acid of sp. gr. 1.25 and 1 pt. of uric acid are mixed together all at once, the mixture becomes heated and froths in the course of a minute or two; and the heat continually increases, till at length the liquid suddenly boils and froths over, giving off an abundance of red vapours. There is thus formed, in a few minutes, a clear yellow solution, which still continues to give off carbonic acid with effervescence, in consequence of the decomposition of alloxan. If this solution be suddenly cooled, the greater part of the alloxan remains undecomposed; but if left to cool spontaneously, it solidifies, after long-continued evolution of carbonic acid, to a crystalline magma, which contains nitrate of urea together with alloxan, inasmuch as the nitric acid converts part of the alloxan into parabanic acid, and subsequently the parabanic acid into urea. (Schlieper, *Ann. Pharm.* 55, 254.)

In warm dilute nitric acid, uric acid dissolves with intumescence, proceeding from the escape of carbonic, nitrogen, and a small quantity of nitric oxide gas, and forms a yellow liquid, containing urea, nitrate of ammonia, and alloxantin. If the heat be continued, the last-mentioned substance is converted into alloxan and parabanic acid; and the latter, on saturation with ammonia, into oxaluric acid, which may then split up into oxalic acid and urea. (Wöhler & Liebig.) Allanturic acid is also formed. (Pelouze.)—The solution forms, after a while, a purple spot on the skin, and when gently evaporated to dryness, leaves a purple-red residue.—When uric acid is gradually added to warm and very dilute nitric acid, till the latter no longer acts upon it, carbonic acid and nitrogen gases are evolved in equal volumes, together with a trace of nitric oxide, and there is formed a colourless or pale yellow solution, which, when mixed with excess of ammonia, acquires a transient purple tint if still hot, but remains colourless if it has been previously cooled, and, after cooling, deposits gelatinous flakes of yellowish or reddish tufts of needles of oxalurate of ammonia.—The solution, when gently evaporated, exhibits effervescence at isolated spots, assumes an onion-red colour, becomes less acid in its reaction, and then deposits alloxantin on cooling. The remaining mother-liquor becomes redder and more acid by further evaporation, and leaves a syrup, from which parabanic acid, nitrate and oxalate of ammonia, and nitrate of urea, crystallise, while the mother-liquor still contains free urea precipitable by nitric acid. The solution evaporated till it exhibits an onion-red colour, and in which part of the alloxantin at first produced, is oxidised to alloxan by the nitric acid, assumes a deep purple-red colour when mixed with a very slight excess of ammonia, and on cooling deposits gold-green crystals of purpurate of ammonia, usually mixed with a reddish yellow powder of uramil. If the quantity of the alloxan be increased by further evaporation, an excess of ammonia imparts a transient purple colour to the hot liquid, which then, on cooling, frequently deposits, instead of the green crystals, a flesh coloured granular powder of mycomelate of ammonia. (Wöhler & Liebig.)—A solution of uric acid in dilute nitric acid, neutralized with ammonia and evaporated, gives off pure carbonic acid gas, recovers its acid reaction,

oxalate and nitrate of ammonia. (Wöhler & Liebig.) — Hot dilute nitric acid saturated with uric acid, forms with ammonia, yellow or yellowish red flakes, which partly aggregate into yellowish-white crystalline grains containing oxalate and purpurate of ammonia; the solution also contains urea. (Kodweiss, *Pogg.* 19, 1.) — When uric acid is dissolved in warm dilute nitric acid, carbonic and nitrous acids are evolved; the yellow saturated solution colours the skin deep red in half an hour; becomes blood-red when evaporated; and forms with lime-water, a white precipitate which chars when ignited. (Scheele.) — The deep red residue obtained by gentle evaporation, is nearly neutral, somewhat deliquescent, soluble with red colour in water, and may be decolorised by any acid; when too strongly heated, it swells up like a sponge. (Bergman.) — The red aqueous solution of the residue loses its colour when heated, but again leaves a red residue when evaporated. (Eug. Marchand, *J. Chim. méd.* 17, 178.)

6. The solution of perfectly pure uric acid in cold *oil of vitriol*, gives off at 180° with violent effervescence, sulphurous acid, carbonic acid, and carbonic oxide, and leaves sulphate of ammonia, the quantity of ammonia in which corresponds to 30.54 per cent. of nitrogen in the uric acid. (Heintz, *Pogg.* 66, 137.) Scheele and Bergman, in making the experiment with impure uric acid, likewise observed a separation of charcoal.

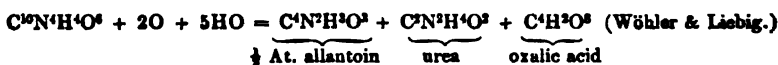
7. Uric acid, boiled with aqueous *Bichromate of potash*, gives off carbonic acid and ammonia, and forms a green liquid, from which alcohol throws down a green substance, and the transparent colourless filtrate leaves pure urea when evaporated. (Liebig.)

8. When a small quantity of *Permanganate of potash* is gradually added to uric acid suspended in water, a brisk effervescence is produced, and the filtered yellowish liquid contains in solution a large quantity of manganous oxide. But if the addition of the permanganate of potash to the uric acid be continued till the precipitate consisting of hydrated manganic oxide becomes black-brown, and the liquid colourless, the filtrate then no longer contains manganese, and yields on evaporation nothing but small, white, opaque prisms. (Gregory, *Ann. Pharm.* 33, 336.) [May not these crystals be alloxanate of potash? The following description of them by Gregory seems to favour such a view.] The crystals, when heated, give off hydrocyanic acid and ammonia, and leave a large quantity of cyanide of potassium. Their aqueous solution forms white precipitates with baryta-, lime-, lead-, and silver-salts; the baryta-precipitate dissolves in a large quantity of water; the lime-precipitate not; the silver-precipitate turns yellowish when boiled; by decomposing the lead-precipitate with sulphuretted hydrogen water, and evaporating, the free acid is obtained in transparent prisms, which have a very sour taste, and form an easily crystallisable salt with ammonia. — According to another statement of Gregory's (*J. pr. Chem.* 22, 273), manganate of potash produces urea and oxalic acid, besides the peculiar acid.

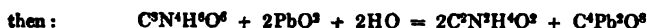
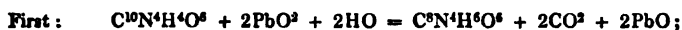
9. When 90 pts. of uric acid are heated in a capacious vessel with 132 pts. of *peroxide of manganese* and 294 pts. of *oil of vitriol*, ammonio-manganous sulphate is formed, and cyanic acid evolved. (Döbereiner, *Gülb.* 74, 418.) The mixture of these three bodies gives off nitric acid when distilled. (Liebig, *Pogg.* 14, 466.) — When uric acid is boiled with water and peroxide of manganese, a peculiar crystalline substance is formed. (Wöhler & Liebig.)

10. Uric acid heated with water and *peroxide of lead*, is converted

into allantoin, urea, oxalic acid, and carbonic acid. (Wöhler & Liebig.) — When uric acid is stirred up with water to a thin pulp, and finely pulverised peroxide of lead added at 100° , carbonic acid is evolved, the peroxide loses its colour, and the mass becomes thick, unless there is a deficiency of water. After peroxide of lead has been added to the heated mass, till fresh portions retain their colour, the liquid, if filtered hot, yields crystals of allantoin on cooling, while urea remains in the mother-liquor, and oxalate of lead is left on the filter. The carbonic acid is formed, as a secondary product, by the action of the peroxide of lead on the oxalate, after which the still remaining uric acid expels the carbonic acid from the carbonate of lead; hence the equation is :

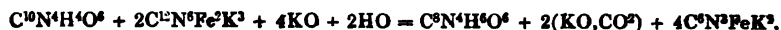


Allanturic acid is also formed in this reaction; the quantity of the urea produced varies considerably, and is often very small; and as peroxide of lead converts allantoin into allanturic acid and urea, even in the cold, the urea appears to arise from the allantoin, merely as a secondary product, so that in the first stage of the decomposition of the uric acid, allantoin is obtained without any urea. (Pelouze, *N. Ann. Chim. Phys.* 6, 71; also *Ann. Pharm.* 44, 108.) — It may, therefore, be probably assumed, that the uric acid is first converted into carbonic acid and allantoin, and the latter, by the further action of the peroxide, into urea and oxalic acid :



(Gerhardt, *Précis.* 1, 246.) — [168 pts. (1 At.) of uric acid in boiling water, mixed by degrees with 240 pts. (2 At.) peroxide of lead, and ultimately boiled for some time, give off at first carbonic acid, yield a filtrate containing urea as well as allantoin, and leave on the filter oxalate of lead, together with undecomposed uric acid. If, therefore, Gerhardt's view is correct, it must at least be supposed that the peroxide, in consequence of its insolubility, exerts a further partial decomposing action on the allantoin at first produced, before it has decomposed the whole of the uric acid.]

11. Uric acid boiled with water, *ferricyanide of potassium*, and potash, yields carbonate of potash and allantoin, part of which is then further transformed into lantanuric acid (ix. 445) and urea (Schlieper). — The first products are carbonate of potash and allantoin :



The allantoin thus formed is then resolved by the action of the excess of potash (to 1 At. urea there were used, not 4 At. but 6 At. potash), into lantanuric acid and urea :



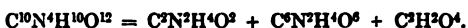
being perhaps first converted into hydantonic acid, $C^8N^4H^6O^6$. (Schlieper.)

12. With *tarchloride of gold*, uric acid forms a violet precipitate. (Proust.) — *Mercuroso-mercuric nitrate* colours it yellow. (Lassaigne.)

leaves a carbonaceous mass containing carbonate and cyanate of potash and cyanide of potassium, whereas, when the same mixture is ignited in an open crucible, the residue consists entirely of carbonate of potash. (Liebig & Lipowitz, *Ann. Pharm.* 38, 356.)—When fused at a gentle heat with hydrate of potash, uric acid does not blacken, but gives off ammonia, and leaves cyanide of potassium together with oxalate and carbonate of potash. (Gay-Lussac, *Ann. Chim. Phys.* 41, 398.)—By continued boiling with solution of potash, it gives off ammonia and forms oxalate of potash. (Kodweiss.)—¶. When a solution of uric acid in excess of a tolerably strong solution of potash was heated, for several days, nearly to the boiling point, the water being renewed from time to time as it evaporated, a slight evolution of ammonia took place, but the greater part of the uric acid remained unaltered even after eight days. The solution being left to stand in an open vessel, soon absorbed carbonic acid from the air, and deposited a white powder, consisting of acid urate of potash, which, however, after about four weeks, gradually disappeared, and was very slowly replaced by shining tabular crystals, consisting of the potash-salt of a new acid, *Uroxanic acid* $C^{10}H^{10}N^4O^{12}$. The mother-liquor contained oxalic acid, formic acid, lantanuric acid, and urea, together with the potash-salt of another peculiar acid, which, separated as a white powder, on addition of sulphuric acid; dissolved in nitric acid with evolution of gas, like uric acid; but did not exhibit any red colouring when the solution was evaporated, or the residue moistened with carbonate of ammonia; it likewise differed from uric acid in being soluble in ammonia. The formation of uroxanic from uric acid is expressed by the equation :



and that of the secondary products by the equation :



The oxalic acid [and the peculiar acid above mentioned?] may be regarded as the product of a further decomposition. (G. Städeler, *Ann. Pharm.* 78, 286.) ¶.

14. Uric acid heated, with *potassium* is decomposed, with emission of light, yielding charcoal and alkali. A similar reaction with *sodium*, but unattended with emission of light. (Gay-Lussac & Thénard.)

Combinations. With *Water*.—*a. Hydrate of Uric acid?*—1. Uric acid precipitated from the potash-solution by hydrochloric acid, forms at first a tumefied jelly, probably consisting of hydrate, which, however, soon sinks together in the liquid, in the form of the anhydrous crystallised acid. (Prout.)—2. The crystalline uric acid, precipitated from its cold solution in dilute potash by hydrochloric acid, always retains water, part of which, however escapes on exposure to the cold air, and the more quickly as the crystals are smaller; hence this water has always been overlooked. When pigeons' dung is exhausted with aqueous borax, as in Böttger's process, the filtrate, on being mixed with hydrochloric acid, deposits the greater part of the uric acid in small crystals; but the decanted liquid, when left to stand quietly, deposits much larger arborescent crystals, which have a light brown colouring, arising from the presence of other organic substances, do not effloresce in the air, give off 21.52 p. c. water (4 At. [or rather 5 At.]), at 100°, and likewise in sunshine, or

under a bell-jar over oil of vitriol, or when boiled with water, becoming opaque at the same time. The smaller crystals exhibit this effloresced appearance only under the microscope, the previously transparent, smooth square tables then appearing rough. (Fritzsche, *J. pr. Chem.* 17, 56.)

b. Aqueous Uric acid. — Uric acid dissolves in 1720 pts. (W. Henry), in 2800 (Göbel), in 10,000 (Prout), in 15,000 pts. (Bensch) of cold water, and in 300 pts. (Scheele), in 500 (Pearson), in 760 (Göbel, in 1400 (W. Henry), in 1800 (Bensch) of boiling water, from which it separates in small crystals on cooling. The solution does not putrefy. (Pearson.) Even in cold water it forms a cloud with lead and silver-salts. (Bensch.) The cold solution does not redden litmus-paper, but the hot solution reddens it quickly and strongly. (Göbel, *Schw.* 58, 475.)

Sulphate of Uric acid? — Uric acid dissolves with brown colour in cold oil of vitriol, and is precipitated therefrom, with milky turbidity, by water. (Wetzlar.) Warm oil of vitriol saturated with serpents' urine, yields on cooling, rather large crystals of sulphate of uric acid, which may be freed from adhering sulphate of ammonia by washing with cold oil of vitriol, solution in warm oil of vitriol, and crystallisation by cooling. Tolerably large, transparent, colourless crystals, which melt at 70° without decomposing, and solidify in a crystalline mass on cooling; they decompose at 170° ; absorb moisture greedily from the air, and become opaque from separation of uric acid; and are decomposed by water, even in small quantity, into dilute sulphuric and a precipitate of uric acid. (Fritzsche, *J. pr. Chem.* 14, 243.)

	Crystals.		Fritzsche.	
$C^{10}N^4H^4O^6$	168 30.00	28.65
8 SO^3	320 57.14	57.08
8 Aq.	72 12.86	14.27
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$C^{10}N^4H^4O^6, 8SO^3 + 8Aq.$	560 100.00	100.00

Or: according to Dessaignes (*N. J. Pharm.* 25, 31.)

			Dessaignes.	
$C^{10}N^4H^4O^6$	168 36.37	36.99
6 SO^3	240 51.96	}	62.88
6 Aq.	54 11.67		
<hr/>				
$C^{10}N^4H^4O^6, 6SO^3 + 6Aq.$	462 100.00	99.87

The crystals analysed by Dessaignes were purified by draining between porous plates.

Urates or Lithates. — Uric acid is one of the weakest of all acids in its affinity for salifiable bases, especially for the alkalis; nevertheless, it decomposes soaps and the sulphides of the alkali-metals with the aid of heat (W. Henry), and withdraws half the alkali from the aqueous solutions of the alkaline monocarbonates, thereby converting them into bicarbonates, which in closed vessels it does not decompose any further. (Wetzlar.) It likewise dissolves in aqueous borax, and in ordinary phosphate of soda (Al. Ure), in the form of acid urate of soda. — The urates are partly *basic* or *neutral* = $C^{10}N^4H^2M^2O^6$, partly *monobasic* or *acid* = $C^{10}N^4H^3MO^6$. From the neutral alkaline urates, even carbonic acid abstracts half the alkali. (Bensch & Allan.) Nearly all the urates are insoluble or sparingly soluble in water.

any way (Bensch & Anau.)—The acid salt occurs in many human urinary calculi; it forms the principal part of birds' and serpents' urine.—Uric acid abstracts ammonia from the aqueous solution of sesquicarbonate of ammonia, till that salt is converted into the bicarbonate. (Wetzlar.) When immersed in aqueous acetate of ammonia, which thereby acquires the power of reddening litmus slightly, it is converted into urate of ammonia, part of which dissolves. Similarly, in a solution of diphosphate of ammonia, only in this case the liquid does not acquire any acid reaction, and holds in solution a larger quantity of urate of ammonia. In solution of sal-ammoniac, on the contrary, it remains unaltered. (Gm.)—Uric acid dried at 100°, does not absorb ammoniacal gas at any temperature between 0° and 170°. (Bensch.)—1. Uric acid heated with excess of aqueous ammoniac, swells up to a mass, which, after washing and drying over lime, appears white and amorphous, and amounts to 110·18 pts. for every 100 pts. of acid used. (Bensch.)—2. Uric acid suspended in water, and mixed with excess of ammonia while the liquid is boiled, yields the salt in needles, which must be dried over lime. (Bensch.)—3. If a large quantity of water be used in this process, and the liquid filtered boiling hot, it yields on cooling a white curdy mass of the same salt, which may be dried over lime in an atmosphere of ammonia. (Bensch.)—4. The hot aqueous solution of acid urate of potash forms, with sal-ammoniac, a white precipitate, which is to be washed with water, then boiled with it, whereupon it swells up strongly; and lastly, dried over lime. (Bensch, Lehmann, *J. pr. Chem.* 25, 15.)—5. An aqueous solution of neutral urate of potash is precipitated by neutral oxalate of ammonia. (Coindet.)

Colourless amorphous mass or needles.

		Bensch.					
				(1) at 100°. (2) at 140°.		(3) dried over lime.	
10 C	60	32·43	32·60	32·43	32·26		
5 N	70	37·84	37·65	37·89	38·14		
7 H	7	3·78	3·92	3·85	3·91		
6 O	48	25·95	25·83	25·83	25·69		
<hr/>							
C ¹⁰ N ⁴ H ³ (NH ⁴)O ⁶	185	100·00	100·00	100·00	100·00		

Or:

		Bensch.		Lehmann.	Coindet.	
		(2)	(4)	(4)	a.	b.
NH ³	17	9·19	8·97	9·39	16·04	8·68
C ¹⁰ N ⁴ H ⁴ O ⁶	168	90·81		86·46		
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	185	100·00				

The salt (a) analysed by Coindet (*Bibl. Univ.* 30, 490) is that obtained by (5); b is found, according to that chemist, in the urine of birds. But the existence of the former salt, which would be neutral urate of ammonia, is, according to Allan & Bensch, extremely doubtful.—Liebig, by burning the ammonia-salt with oxide of copper, obtained 2 vol. carbonic acid gas to 1 vol. nitrogen = 10 : 5.

The salt, when heated, first gives off its ammonia. (Fourcroy.)—Pure urate of ammonia, in the moist state, does not undergo any alteration by exposure for months to light and air; but if it contains other animal substances, which appear to act as ferments, it is converted into acid oxalate of ammonia, a certain quantity of oxygen being at the same

time transformed into carbonic acid. (J. Davy.) — The moist urine of the white-headed sea-eagle, which, in addition to urate of ammonia, contains a certain quantity of animal matter, changes, when kept for two months in a loosely closed glass vessel, into a mass which smells of ammonia and guano; and, like the latter substance, is white and composed of microscopic crystals on the outside, while the interior is coloured brown by a substance soluble in water. The same decomposition takes place, even in the dark; but the quantity of oxalate of ammonia then produced is not so great. In well closed vessels containing but little air (which, under these circumstances, is converted into a mixture of 36 pts. nitrogen gas and 64 pts. carbonic acid), the urine undergoes but little change, not acquiring any ammoniacal odour, and containing only traces of oxalic acid, resulting from the decomposition; no oxalic acid is formed when the moist urine is heated for some time to 100° in a closed vessel, but a large quantity, if it be mixed with pulverised peroxide of manganese. (J. Davy, *N. Ed. Phil. J.* 36, 294; 38, 226.) — Before the other products formed in this reaction are known, it is perhaps premature to calculate the results stoichiometrically, as attempted by Denham Smith (*Phil. Mag. J.* 26, 138.)

Urate of ammonia immersed in hydrochloric acid swells up, and after a while yields free uric acid in the form of a crystalline powder (Bensch); but for the complete removal of the ammonia, the salt must be digested with the hydrochloric acid for 24 hours; acetic acid acts still more slowly. (Lehmann.) Common salt or phosphate of soda converts urate of ammonia dissolved in water into urate of soda. (Heintz.) Urate of ammonia dissolves, according to Prout, in 480 pts., and according to Bensch, in 1608 pts. of water at 15° , more abundantly in hot water. From a mixture of uric acid and urate of ammonia, the latter salt, being the more soluble, is extracted in greater quantity by boiling for a short time with water. (Eug. Marchand.) The solution, when boiled for a longer time, gives off all its ammonia, and deposits crystalline uric acid. (Bensch.) Acetate or hydrochlorate of ammonia precipitates the urate of ammonia from it in the amorphous state. (Bence Jones.) Urate of ammonia dissolves but sparingly in aqueous ammonia; consequently, carbonate of ammonia added to a solution of uric acid in excess of potash or soda, throws down the greater part of the uric acid in the form of the ammonia-salt, although a considerable quantity of ammonia is at the same time set free. (W. Henry.)

Urate of Ammonia with Glycocol. — A solution of 1 At. glycocol and 1 At. urate of ammonia in hot water, yields on cooling, a quantity of flakes, which increase on addition of alcohol, and appear, when examined by the microscope, to consist of small prisms. (Horsford, *Ann. Pharm.* 60, 38.)

<i>Crystals dried over oil of vitriol.</i>		<i>Horsford.</i>	
14 C	84	32.31	32.46
6 N	84	32.31	
12 H	12	4.61	4.40
10 O	80	30.77	
$C^6N^4H^4(NH^4)O^6 + C^4NH^4O^4$		260	100.00

URATE OF POTASH. — *a. Basic.* — Uric acid dissolves readily in excess of potash, forming a liquid which has a sweetish taste, froths like soap-water, and is precipitated even by carbonic acid. (Scheele.) The precipitate formed by carbonic acid is acid urate of potash, which at first

of it remains dissolved in the bicarbonate of potash. (Wöhler & Liebig, *Ann. Pharm.* 26, 342.) Basic urate of potash forms, with carbonate of ammonia, a precipitate of urate of ammonia, and precipitates all salts of the earthy alkalis, earths, and heavy metallic oxides. (W. Henry.)

b. Neutral. — 1. Uric acid is added to a cold dilute solution of potash free from carbonic acid, as long as it remains clear; the solution, boiled in a retort till delicate needles separate out; then taken off the fire, and decanted after a few minutes; and the needles washed, first with weak and then with strong alcohol. (Allan & Bensch.) — 2. A solution of 1 pt. of hydrate of potash free from carbonic acid, in 15 pts. water, is saturated, at ordinary temperatures, with uric acid suspended in water and added in successive portions; the clear solution heated in a flask and mixed with twice its bulk of boiling 80 per cent. alcohol; strong potash-ley dropt into the mixture, which remains clear and deposits bundles of needles; and the mother-liquor decanted from those after cooling; and the needles washed several times with alcohol by decantation, then on the filter with ether, freed from the ether by evaporation in vacuo, and dried completely in a current of air free from carbonic acid. During the whole operation, the air must be completely excluded, because the carbonic acid contained in it would exert a decomposing action. (Bensch.)

Colourless needles, or soft white crystalline powder, having a strong caustic taste. (Allan & Bensch.)

	<i>Crystals at 120°.</i>		Allan & Bensch	
			(1)	(2)
2 KO	94.4	38.62	38.23	37.94
10 C	60.0	24.55	24.22	24.25
4 N	56.0	22.92		22.78
2 H	2.0	0.82	0.94	0.91
4 O	32.0	13.09		14.12
<hr/>				
C ¹⁰ N ⁴ H ² K ² O ⁶	244.4	100.00		100.00

The crystals are anhydrous, and, after drying at ordinary temperatures in a stream of hydrogen or of air free from carbonic acid, do not undergo any further diminution of weight at 120°. (Allan & Bensch.)

The crystals turn yellow at 150°, black at higher temperatures, then melt, and slowly burn to a white residue. The moist or dissolved salt, when brought in contact with carbonic acid, rapidly absorbs that gas, and is converted into acid urate of potash. 100 pts. of the dry crystals, moistened and introduced into an atmosphere containing carbonic acid, then dried again at 100°, exhibit an increase of weight amounting to 13.425 pts., because 1 CO² and 1 HO have been added to them, the products being 1 At. acid urate of potash and 1 At. carbonate of potash, easily removable by water. (Bensch.) 244.4 (neutral salt) : 22 + 9 = 100 : 12.68. — The salt is gradually resolved by boiling with water into the acid urate and free potash. It dissolves in 26 pts. of water at 15°, the dissolved portion, however, appearing richer in potash than the residue, — very sparingly in alcohol, and not at all in ether. (Allan & Bensch.)

c. Acid. — Formation. 1. By the action of carbonic acid on the basic or neutral salt. — 2. By the action of uric acid on aqueous car-

bonate of potash. Uric acid, immersed in a concentrated solution of neutral carbonate of potash, swells up to a jelly consisting of this salt, which does not perceptibly dissolve; as the bicarbonate of potash formed at the same time gradually gives off carbonic acid in open vessels, the decomposition goes on slowly, if sufficient uric acid is present, till the whole of the carbonic acid is expelled. The solution of carbonate of potash in 8 pts. of water dissolves a small quantity of uric acid, which, in a short time, is almost wholly precipitated as acid urate of potash; the solution in 24 pts. of water takes up a large quantity of uric acid, then quickly becomes turbid, and deposits thick flakes of acid urate of potash; and the filtrate exhibits the same reaction with fresh uric acid, till the whole of the potash is converted into urate, a large quantity of which then remains dissolved in the water. The solution in 100 to 200 pts. of water dissolves uric acid quickly and abundantly; the undissolved portion is free from potash, and the solution contains acid urate and bicarbonate of potash. (Wetzlar.)—[Hence it may be concluded that acid urate of potash is much more soluble in pure water than in water containing carbonate of potash.]—When uric acid is gradually added to a boiling solution of 1 pt. neutral carbonate of potash in 90 pts. water, 2 pts. of the uric acid are taken up, with evolution of carbonic acid, and the solution on cooling deposits crystalline nodules of acid urate of potash; at a lower temperature it takes up much less. (Lipowitz.)—A perfectly neutral solution of acetate of potash boiled with uric acid, acquires the property of reddening litmus, doubtless from liberation of acetic acid; but on cooling, the uric acid is deposited almost free from potash, and the liquid retains but a slight acid reaction. (Lipowitz.)

Preparation.—A solution of uric acid in potash-ley, or of the neutral salt in water, is precipitated by passing carbonic acid through it; the granular salt thereby precipitated washed with cold water and dissolved in boiling water; and the solution cooled, whereupon it deposits flakes, which dry up on the filter to an amorphous mass. (Bensch.)—2. A warm solution of potash saturated with uric acid, is evaporated to the consistence of a pulp: this mass washed by stirring with a small quantity of cold water; and the residue strongly pressed between paper and crystallised from solution in hot water. (Braconnot.) [If this process were conducted without contact of air, the neutral salt would be obtained; but as the carbonic acid in the air partly converts this salt into the acid salt, Braconnot's product must be regarded as a mixture of the neutral and acid salts, a view which is indeed corroborated by Braconnot's description.]

Properties. White, granular or aggregated amorphous mass, tasteless and neutral. (Bensch.) White, crystalline, alkaline, and sweet. (Braconnot.)

	At 100°.		Bensch. Kodweiss. Bérard. Braconnot.			
KO	47·2	22·89	22·30	23·65	29·89	33·6
10 C.....	60·0	29·10	28·58			
4 N.....	56·0	27·16				
3 H.....	3·0	1·45	1·63			
5 O.....	40·0	19·40				

$C^{10}N^4H^4KO^6$... 206·2 ... 100·00

The salt yields cyanide of potassium when ignited alone, and sulphocyanide when ignited with sulphur. (Döbereiner.) It absorbs carbonic acid from the air. (Braconnot.) [Because his salt was partly neutral.] It dissolves in 790 pts. of water at 20°, and in 79 pts. of boiling water. (Bensch.)

out again almost completely when left to stand for some time. (Braconnot.) The hot solution solidifies by slow cooling, to a transparent gelatinous lump. (Wetzlar.) The aqueous solution is precipitated by sal-ammoniac, bicarbonate of potash, or soda, and by salts of barium, lead, and silver, but not by sulphate of magnesia. (Bensch.) The salt does not dissolve in alcohol or ether. (Bensch.)

URATE OF SODA. — *a. Basic.* — Like the potash-salt.

b. Neutral. — Prepared by the same two methods as neutral urate of potash. The first of these succeeds better with the soda than with the potash salt; in applying the second in this case, only one volume of alcohol must be added instead of two, and the nodules thereby separated washed as above with alcohol and ether. — The solution, concentrated by boiling, deposits the salt in hard nodules, which have a very strong alkaline reaction, and dry up to a tolerably hard white powder. (Bensch.)

	<i>Crystals.</i>		Bensch.		Allan & Rensch.	
2 NaO.....	62.4	27.08	27.09	27.34		
10 C.....	60.0	26.04	26.39			
4 N.....	56.0	24.30	25.15			
4 H.....	4.0	1.74	1.79			
6 O.....	48.0	20.84	19.58			
<hr/>						
$C^{10}N^4H^3Na^2O^6 + 2Aq.$	230.4	100.00	100.00			

The crystals analysed by Bensch were previously dried at 120° in a stream of air free from carbonic acid; those analysed by Allan & Bensch, in a stream of hydrogen at 100°.

The crystals, after drying at 100°, give off 2 At. water at 140°. They decompose at 150°, melt at a stronger heat, and leave a black residue, which ultimately burns white. The moist crystals are decomposed, even by the carbonic acid in the air, into acid urate and carbonate of soda. 100 pts. of the crystals dried at 100° and introduced into carbonic acid gas, after being moistened with water, exhibit, after drying at 100°, an increase of weight amounting to 9.942 pts., arising from 1 At. carbonic acid, the product being $C^{10}N^4H^3NaO^6 + NaO,CO^2$. $230.4 : 22 = 100 : 9.55$. (Bensch.) — The crystals dissolve in 62 pts. of water at 15°, the soda being, however, taken up in rather larger proportion, and the undissolved portion containing therefore a certain quantity of the acid salt. (Allan & Bensch.)

c. Acid. — Occurs in gouty concretions. (Wollaston.) — *Formation.* By the action of carbonic acid on the neutral salt. — 2. By treating uric acid with aqueous carbonate, borate, phosphate, or acetate of soda. — Uric acid exhibits, with neutral *carbonate of soda*, nearly the same reaction as with carbonate of potash, excepting that a lower degree of concentration is sufficient to prevent the solution of the resulting acid urate of soda. (Wetzlar.) The reaction with a boiling solution of carbonate of soda, is also similar, in every respect, to that already described with boiling carbonate of potash. (Lipowitz.) — Uric acid dissolves in aqueous *borax*, even when sufficient boracic acid is added to redden litmus, only more slowly in that case, — forming acid urate of soda, which is precipitated if the solution is strong, the liquid then taking up

a fresh quantity of uric acid. (Wetzlar.) A concentrated solution of borax takes up less uric acid than a dilute solution. (Böttger.) A solution of borax in 20 pts. of water (if less water is present, the urate of soda which coats the uric acid prevents the solution) takes up a large quantity of uric acid, and on cooling deposits acid urate of soda, amounting, when dried at 100°, to 17.02 per cent. (Kodweiss.) A solution of 1 pt. borax in 90 pts. water dissolves, even at a moderate heat, rather more than 1 pt. of uric acid, and on cooling deposits gelatinous urate of soda, part of which however remains in solution. A solution of borax of the above strength, mixed with excess of boracic acid, dissolves the same quantity of uric acid, but on cooling deposits the whole of the resulting urate of soda. (Lipowitz.) — With ordinary *diphosphate of soda* (2NaO,HO,PO⁵) uric acid forms acid urate of soda, the phosphate of soda being also thereby rendered acid. (Alex. Ure, *Repert.* 75, 65.) When uric acid is boiled with this salt, a large quantity of it dissolves, so that, on cooling, a bulky precipitate of urate of soda is formed, although a large quantity still remains in solution; when uric acid is boiled with ordinary acid phosphate of soda (NaO,2HO,PO⁵), only a small quantity of it dissolves. (Lipowitz.) The solution of uric acid in ordinary diphosphate of soda yields, on cooling, tufts of needles of urate of soda. (Heintz.) Bird (*Lond. Med. Gaz.* 1844, Aug.) regarded these crystals as a compound of uric acid with phosphate of soda, inasmuch as they left the latter salt when ignited; but Heintz obtained carbonate of soda. The mother-liquor of these crystals boiled with fresh uric acid, yields on cooling a small deposit containing less soda; and by repeatedly boiling the mother-liquor with fresh acid and cooling, a deposit of uric acid is finally obtained, which contains only a trace of soda, and exhibits the form of long rhombic tables with truncated corners, like the uric acid which separates from urine. — With phosphate of soda and ammonia, uric acid behaves as with phosphate of soda, excepting that the precipitate which separates on cooling, consists of a large quantity of urate of ammonia with a small quantity of urate of soda. (Heintz, *Ann. Pharm.* 55, 62.) — Uric acid does not decompose a *solution of common salt*. (Gm.) — It dissolves abundantly in warm aqueous *acetate of soda*, and crystallises partially and free from soda on cooling, while the rest remains dissolved as soda-salt in the liquid, which becomes turbid on addition of acetic acid, hydrochloric acid, or sal-ammoniac, especially if the sides of the vessel be rubbed with a glass rod. (Gm. *Heidelb. Jahrb. d. Lit.* 1823, 767.) — 3. By decomposing urate of ammonia with chloride of sodium. — Acid urate of ammonia dissolves at a boiling heat, more abundantly in water containing common salt than in pure water, and the solution on cooling deposits an amorphous powder, consisting of acid urate of soda and a very small quantity of urate of ammonia, while sal-ammoniac remains in the mother-liquor. The ammonia in the precipitated powder amounts to only 0.06 to 0.09 per cent., the quantity being smaller as the solution of salt is more saturated. When uric acid is boiled with a solution of common salt containing ammonia, the filtrate on cooling yields needles, containing rather more than 1 At. urate of ammonia to 1 At. urate of soda. (Heintz.)

For experiments on the different degrees of solubility of uric acid in water containing small quantities of carbonate or borate of ammonia, potash, or soda, whence it appears that carbonate and borate of potash, and therefore also tartarised borax, are the best solvents for urinary calculi: *vid.* Alex. Ure. (*J. Chim. méd.* 18, 63.)

tion of the neutral or basic salt, and the small nodules thereby separated, washed on the filter with cold water and dried. (Bensch.) — 2. A boiling solution of uric acid in soda-ley is mixed with bicarbonate of soda, and the small needles which separate treated as above. (Bensch.)

The salt when dry is a white light powder, and its aqueous solution is neutral to vegetable colours. (Bensch.) After drying at 100° it gives off 4.54 p. c. (1 At.) water at 170°. (Bensch.) When heated, it carbonises quickly without fusing, emits an animal empyreumatic odour, and leaves a residue of charcoal, cyanide of sodium, and carbonate of soda. (Fourcroy.) By dry distillation, it yields carbonate of ammonia, hydrocyanic acid, pyro-uric acid, and empyreumatic oil. (Wollaston, *Phil. Trans.* 1797, 386.) — It dissolves in 1150 pts. of water at 15°, and in 124 pts. of boiling water, forming a solution which is precipitated by alkaline carbonates, and by baryta, lead, and silver salts. (Bensch.)

	At 100°.		Bensch.	
NaO	31.2	16.40	
10 C	60.0	31.55 31.34
4 N	56.0	29.44	
3 H	3.0	1.58 1.75
5 O	40.0	21.03	
<hr/>				
C ¹⁰ N ⁴ H ³ NaO ⁶	190.2	100.00	
	At 100°.		Bensch.	
NaO	31.2	15.66 15.41
10 C	60.0	30.12 29.99
4 N	56.0	28.11	
4 H	4.0	2.01 2.13
6 O	48.0	24.10	
<hr/>				
C ¹⁰ N ⁴ H ³ NaO ⁶ + Aq.	199.2	100.00	

NEUTRAL URATE OF LITHIA. — Obtained by dissolving uric acid and carbonate of lithia in warm water. — 1 pt. of uric acid and 1 pt. of carbonate of lithia form, with 90 pts. of water, at a temperature somewhat above 50°, a solution which remains clear after cooling. At a boiling heat, nearly 4 pts. of uric acid dissolve, with evolution of carbonic acid, in 1 pt. of carbonate of lithia and 90 pts. of water; the solution thus saturated solidifies on cooling to a jelly, which becomes liquid again when heated, and yields by evaporation white crystalline urate of lithia, free from carbonate. 1 pt. of hydrate of lithia dissolved in water, takes up 6 pts. of uric acid and yields the same salt. — The salt dried at 100°, contains 171.08 pts. (nearly 1 At.) uric acid to 28.8 pts. (2 At.) lithia. — The salt, if not too strongly dried, dissolves in 60 pts. of water at 50°, without separating out on cooling; but at higher temperatures, it becomes yellowish and sparingly soluble. In consequence of the easy solubility of urate of lithia, carbonate of lithia is well adapted for separating uric acid from serpents' urine, &c. (Lipowitz.)

URATE OF BARYTA. — *a. Neutral.* — 1. Obtained by precipitating an aqueous solution of neutral urate of potash with a small quantity of chloride of barium, to remove the carbonic acid, and treating the filtrate with an additional quantity of chloride of barium; the salt then separates in the form of a heavy granular precipitate. — 2. By adding uric acid to an excess of baryta-water saturated at a boiling heat. — The salt

is slowly and gradually, and the solution becomes strongly alkaline reaction. It gives off 5.69 p. c. (2 At.) water at 170°; begins to decompose at 180°; melts and blackens at a stronger heat, and very slowly burns to a white residue. It absorbs carbonic acid with avidity. Dissolves without decomposition in 7900 pts. of cold, and in 2700 pts. of boiling water. (Allan & Bensch.)

				Allan & Bensch.	
				At 170°.	
2 BaO	153.2	50.53 49.12
10 C	60.0	19.79 20.63
4 N	56.0	18.47	
2 H	2.0	0.66 0.83
4 O	32.0	10.55	
<hr/>					
$C^{10}N^4H^2Ba^2O^6$	303.2	100.00	

				Allan & Bensch.	
				At 100°.	
2 BaO	153.2	47.69 46.84
10 C	60.0	18.68	
4 N	56.0	17.44	
4 H	4.0	1.25	
6 O	48.0	14.94	
<hr/>					
$C^{10}N^4H^2Ba^2O^6 + 2Aq.$	321.2	100.00	

The salt was dried in a current of hydrogen at 170° and at 100°.

b. Acid. — Produced, with evolution of carbonic acid, when uric acid is boiled with water and carbonate of baryta. (Wetzlar, Bensch.) Hot solutions of acid urate of potash and excess of chloride of barium deposit the salt in the form of a white amorphous powder, which must be washed with hot water; it burns easily and without fusion, and is not soluble in water, alcohol, or ether. (Bensch.) According to Wetzlar and Kodweiss, the salt is sparingly soluble in water.

				At 100°.		
				Bensch.	Kodweiss.	Bérard.
BaO	76.6	30.21 30.08 33.29
10 C	60.0	23.66 23.74 38.36
4 N	56.0	22.08		
5 H	5.0	1.97 2.18	
7 O	56.0	22.08		
<hr/>						
$C^{10}N^4H^2BaO^6 + 2Aq.$	253.6	100.00		

Bérard (*Ann. Chim. Phys.* 5, 295.)

URATE OF STRONTIA. — *a. Neutral.* — Uric acid suspended in water and added to an excess of strontia-water saturated at a boiling heat, dissolves completely at first; but as the quantity of uric acid added increases, the strontia-salt separates in needles united in stellate groups. The aqueous solution has a strong alkaline reaction. The crystals dried at 100° give off at 165°, 11.3 pts. (not quite 4 At.) water; they begin to decompose at 170°, and easily burn white. They absorb carbonic acid with avidity. They dissolve in 4300 pts. of cold, and in 2297 pts. of hot water; when they are boiled with a quantity of water not sufficient to dissolve them completely, the undissolved portion retains its composition. (Allan & Bensch.)

2 SrO	104	...	35.86	36.22
4 N	56	...	19.31		
6 H	6	...	2.07		
8 O	64	...	22.07		

$C^{10}N^4H^2Sr^2O^6$ 290 100.00

b. Acid.— On mixing hot solutions of acid urate of potash and chloride of strontium, a white amorphous powder is obtained, which is somewhat soluble in boiling water, but does not dissolve in alcohol or ether. (Bensch.)

	At 100°.		Bensch.	
SrO	52	...	21.94 22.79
10 C	60	...	25.32 26.17
4 N	56	...	23.63	
5 H	5	...	2.11 2.36
8 O	64	...	27.00	

$C^{10}N^4H^3Sr^2O^6 + 3Aq$ 237 100.00

URATE OF LIME.— *a. Neutral.*— 1. Uric acid suspended in water, is added to one measure of boiling lime-water till the liquid begins to redden litmus, the hydrate of lime, which is at first precipitated then dissolving; another measure of lime-water is then added, and the mixture boiled, the air being constantly excluded till the salt separates as a heavy granular powder.— 2. A solution of acid urate of potash, completely freed from carbonic acid by a little chloride of calcium, and filtered, is gradually added to a solution of chloride of calcium, till the precipitate becomes permanent; the liquid then boiled for an hour, whereby the precipitate is suddenly converted into a heavy granular powder; and this powder washed on the filter with hot water out of contact of air.— The salt, when examined by the microscope, presents the appearance of opaque amorphous grains; the solution has an alkaline reaction. After drying at 100° in a stream of hydrogen, it gives off only 1.8 p. c. water at 170°; it turns brown at 190°, and readily burns white. It dissolves in 1500 pts. of cold, and 1440 pts. of boiling water. (Allan & Bensch.)

	At 100°.		Allan & Bensch.	
2 CaO	56	...	27.19 27.09
10 C	60	...	29.12 27.09
4 N	56	...	27.19	
2 H	2	...	0.97 1.47
4 O	32	...	15.53	

$C^{10}N^4H^2Ca^2O^6$ 206 100.00

b. Acid.— 1. By boiling an excess of uric acid with caustic lime or carbonate of lime.— 160 pts. of lime-water dissolve 1 pt. of uric acid.— (Scheele.) The solution of uric acid in boiling water, mixed with lime-water till it no longer reddens litmus, deposits the lime-salt on evaporation, in small shining needles and laminæ. (Laugier, *J. Chim. méd.* 1, 8.) By triturating uric acid with milk of lime, a filtrate is likewise obtained, from which hydrochloric acid throws down uric acid. (Pearson.) Uric acid dissolves when boiled with carbonate of lime and a sufficient quantity of water.— 2. By precipitating a hot solution of acid urate of potash with chloride of calcium, a white amorphous precipitate is obtained.

pitate is obtained, (or if the acid urate of potash is mixed with the neutral urate: needles united in warty masses, and perhaps consisting of a double salt,) which must be washed with hot water. (Bensch.)—The salt dissolves in 603 pts. of cold, and in 276 pts. of boiling water, and much more readily in water containing chloride of potassium. (Bensch.) From boiling water it crystallises partially on cooling. Dissolves in potash-ley, leaving a small quantity of [carbonate of?] lime; hydrochloric acid added to the filtrate, retains part of the potash and of the lime, and throws down an acid, litmus-reddening salt, which, when boiled with water, is resolved into a less acid lime-salt and crystallising uric acid. (Langier.)

		(2). At 100°.		Bensch.
CaO	28	13.66	13.70	
10 C	60	29.26	29.38	
4 N	56	27.32		
5 H	5	2.44	2.66	
7 O	56	27.32		
$C^{10}N^4H^4CaO^6 + 2Aq.$	205	100.00		

URATE OF MAGNESIA. — *a. Neutral.* — Cannot be prepared, because a dilute solution of neutral urate of potash mixed with the boiling solution of a magnesia-salt, throws down a gelatinous mixture of magnesia and acid urate of magnesia (which may be dissolved out by boiling water). (Allan & Bensch.)

b. Acid. — 1. Uric acid boiled with water and carbonate of magnesia, forms a salt which dissolves in a large quantity of water. (Wetzlar.) — 2. A hot-saturated solution of acid urate of potash, mixed with sulphate of magnesia, forms at first a clear solution, but after two or three hours, deposits silky needles united in nodules, which may be purified by washing with cold water, solution in boiling water, crystallisation by cooling, and again washing with cold water. (Bensch.) — The needles obtained by (2) dry up to a light powder, which, after drying at 100°, gives off 19.2 p. c. (6 At.) water at 170°, turns brownish at 180°, and burns away at a higher temperature, leaving white magnesia. It dissolves in 3750 pts. of cold and 160 pts. of boiling water. (Bensch.)

		At 100°.		Bensch.
MgO.....	20	8.58	8.66	
10 C	60	25.75	25.69	
4 N	56	24.04		
9 H	9	3.86	3.96	
11 O	88	37.77		
$C^{10}N^4H^4MgO^6 + 6Aq.$	233	100.00		

Double urates of magnesia and ammonia, potash, or soda cannot be prepared. (Allan & Bensch.)

Basic urate of potash forms white precipitates with the salts of alumina and zinc-oxide, and brown with salts of ferric oxide. (Scheele.)

URATE OF LEAD. — *a. Neutral.* — When a dilute solution of neutral urate of potash is dropt into a dilute solution of nitrate of lead, and the liquid, after filtration from the yellow precipitate, mixed with a fresh portion of urate of potash, a white heavy precipitate is obtained, which is easily washed. If acetate of lead were used, the precipitate would contain acetic acid. The salt remains unaltered at 160°. It is not soluble either in water or in alcohol. (Allan & Bensch.)

			At 150°.	At 100°.
2 PbO.....	224	...	59·89 58·81
10 C.....	60	16·05 14·43
4 N.....	56	14·97	
2 H.....	2	0·53 1·01
4 O.....	32	8·56 1·09

C¹⁰N⁴H²Pb²O⁶ 374 100·00

b. *Acid.* — A saturated solution of acid urate of potash forms, with excess of neutral acetate of lead, a white heavy precipitate, which, after washing with hot water, dries up to a loosely coherent powder. This precipitate, after drying at 100°, does not diminish in weight at 160°, is easily combustible, and does not dissolve in water, alcohol, or ether. (Bensch.)

	At 100°.		Bensch.	
PbO	112	39·16 40·13
10 C.....	60	20·98 21·39
4 N	56	19·58	
4 H	4	1·40 2·53
6 O	48	18·88	

C¹⁰N⁴H³PbO⁶ + Aq 280 100·00

Compare G übel's analysis. (*Schw.* 58, 475.)

Aqueous urate of potash forms, with *Cupric* sulphate, a green precipitate, which cannot be obtained free from potash, even by long washing with cold water, and turns brown when boiled with water, while free uric acid dissolves in the water. The brown residue when sufficiently boiled with water and dried over oil of vitriol, becomes violet-coloured, and easily friable, and appears amorphous under the microscope. If afterwards dried at 140°, it gives off 5·57 p. c. water, and contains 42·79 p. c. CuO, 21·51 C, and 1·53 H. (Bensch.) [May not the salt, after it has turned brown, contain cuprous oxide or metallic copper ?]

Acid Mercuric Urate. — The precipitate obtained by mixing corrosive sublimate with a boiling aqueous solution of acid urate of potash, gives off, when heated after drying, carbonic, hydrocyanic, and a large quantity of cyanic acid, but no free cyanogen. (Wöhler.)

Very dilute solutions of acid urate of potash and nitrate of silver, form a white, very bulky precipitate, which, during washing and drying gradually turns yellow, then brown, then black, and still contains a small quantity of potash. (Kodweiss.) If the silver-solution is in excess, the gelatinous precipitate becomes dark-coloured, and immediately turns black when the liquid is heated; in the contrary cases, the precipitate remains white, even when dry, but is decomposed by boiling water. The precipitate, after fourteen days' washing with cold water, which is difficult on account of its gelatinous consistence, and subsequent drying, contains 9·01 p. c. KO, and 23·78 AgO; it is therefore a double salt.

Uric acid does not dissolve in alcohol or in ether.

It dissolves somewhat abundantly in warm aqueous *Glycerine*, and separates again for the most part on cooling; it dissolves much less copiously in warm aqueous *Mannite*, *Gum-sugar*, *Grape-sugar*, and common *sugar*. (Lipowitz.)

Uroxanic Acid. $C^{10}N^4H^{10}O^{12}$.

G. STADELER. *Ann. Pharm.* 78, 286; 80, 119.

Formation. By the action of Potash on uric acid (p. 465.)

The free acid is obtained by decomposing the potash-salt with dilute sulphuric or hydrochloric acid. If a warm, moderately dilute solution of the potash-salt be used, the acid sometimes separates in very beautiful colourless, transparent crystals, which under the microscope exhibit the form of tetrahedrons. From a cold or concentrated solution of the salt, it is generally obtained in short ill-defined prisms, arranged in concentric groups.

<i>Dried in vacuo.</i>				Städeler.
10 C	60	27.03	26.89
4 N	56	25.23	
10 H	10	4.50	4.17
12 O	96	43.24	
$C^{10}N^4H^{10}O^{12}$				222
			 100.00

As the amount of hydrogen found by analysis is much too low for the formula, it is probable that the acid analysed was partially decomposed; the formula of the acid is however sufficiently established by the analysis of the salts. (*inf.*) In Städeler's first memoir, the formula of the acid was incorrectly given as $C^{10}N^3H^9O^{12}$, in consequence of an error of calculation; but in the second memoir, this error is corrected.

Decompositions. 1. The acid, after drying in vacuo, gives off at a temperature somewhat above 100° , a small quantity of water and likewise carbonic acid. When kept for some time at 130° , it diminishes in weight by 34.8 per cent., and leaves a slightly yellowish, hygroscopic substance, nearly agreeing in composition with anhydrous uroxanic acid, $C^{10}N^4H^8O^{10}$; but as the abstraction of 2HO from uroxanic acid would only diminish the weight by 8.11 per cent., the agreement appears to be merely accidental; and the acid when heated as above, doubtless also gives off carbon and nitrogen, probably in the form of hydrocyanate or carbonate of ammonia. — [Städeler, in his first memoir, assigned to the residue obtained at 130° , the formula $C^8N^3H^7O^8$, and called it *uroxil*]. — At a higher temperature, the acid melts to a brown liquid, gives off ammonia, an oily distillate which solidifies on cooling, and probably also cyanide of ammonium, and leaves a small carbonaceous residue. — 2. Strong nitric acid does not act on uroxanic acid at ordinary temperatures, but dissolves it when heated, without evolution of gas; and the liquid, on cooling, deposits crystals, probably a product of oxidation. — 3. The acid boiled with potash-ley is decomposed in the manner already mentioned (p. 465).

Combinations. Uroxanic acid dissolves sparingly in cold water; more abundantly in boiling water, but with decomposition and evolution of carbonic acid.

The formula of the *Uroxanates* is $C^{10}N^4H^8M^2O^{12}$.

Uroxanate of Ammonia. — Uroxanic acid dissolves readily in aqueous ammonia; and on mixing the solution with alcohol till it begins to show

Uroxanate of Potash. — Preparation (p. 465). — Crystallises in large, nacreous, oblique four-sided prisms, with truncated summits; angles of the acute lateral edges = 83° (nearly); of the obtuse = 97°.

At 100°, the salt dried over chloride of calcium gives off 14.79 p. c. water (6 At. = 14.95). At a higher temperature, it melts, gives off carbonate of ammonia, and leaves a residue coloured by charcoal. The aqueous solution is neutral, and is not decomposed by boiling.

<i>Dried over chloride of calcium.</i>		<i>Städeler.</i>	
2 KO	94.4	26.75	26.29
10 C	60.0	17.03	17.20
4 N	56.0	15.90	15.87
14 H	14.0	3.98	3.88
16 O	128.0	36.34	36.76
<hr/>		<hr/>	
$C^{10}N^4H^8K^2O^{12} + 6Aq$	352.4	100.00	100.00

The salt dissolves pretty readily in cold, very easily in hot water, but is insoluble in alcohol. On adding alcohol to the aqueous solution, a white crystalline precipitate is immediately formed, in such quantity as to reduce the solution to a pulp. If a gentle heat be then applied, the precipitate redissolves, and the salt separates on cooling in delicate laminæ, exhibiting under the microscope the form of the original salt. Hence no acid-salt appears to be produced.

Uroxanate of Baryta. — Obtained by mixing the solution of the ammonia-salt in excess of ammonia with chloride of barium, and adding alcohol; the salt then separates in flakes, which soon change to slender needles.

Uroxanate of Lime. — Prepared like the baryta-salt. Four-sided tables.

Uroxanate of Lead. — Separates on mixing the solution of the potash-salt with nitrate of lead, in delicate scales having the lustre of satin. The crystals, heated to 100°, give off 2.2 p. c. (1 At.) water. Insoluble in water.

<i>Dried at 100°.</i>		<i>Städeler.</i>	
2 PbO	224	52.24	52.05
$C^{10}N^4H^8O^{10}$	204	47.76	47.95
<hr/>		<hr/>	
$C^{10}N^4H^8Pb^2O^{12}$	428	100.00	100.00
<i>Crystals.</i>		<i>Städeler.</i>	
$C^{10}N^4H^8Pb^2O^{12}$	428	97.96	
HO	9	2.04	2.22
<hr/>		<hr/>	
$C^{10}N^4H^8Pb^2O^{12} + Aq$	437	100.00	

Uroxanate of Silver. — By decomposing the potash-salt with nitrate of silver. White flocculent precipitate, which soon aggregates into a heavy amorphous powder. Turns red in sunshine, and when heated, immediately becomes brown-black, and afterwards coal-black. (Städeler.) ¶.

c. Nitro-amidogen-nucleus. $C^{10}N^4AdH^2$.

Guanine.



BODO UNGER. *Poij.* 65, 222. — *Ann. Pharm.* 51, 395; 59, 58 and 69.

Discovered and investigated by Bodo Unger in 1845.

Sources. In all kinds of guano, abundantly in the Peruvian, sparingly in the African. (Unger.) In the excrements of the garden-spider, and apparently also in the green organ of the river-crab, and in the Bojanian organ of the pond-muscle. (Gorup-Besanez & Fr. Will, *Ann. Pharm.* 69, 117.)

Preparation. Guano is boiled with thin milk of lime, till a filtered sample no longer appears brown, but pale greenish yellow; the liquid is then filtered; the filtrate neutralised with hydrochloric acid; the reddish mixture of uric acid and guanine, which is completely precipitated after some hours, treated with boiling hydrochloric acid to extract the latter; the filtrate cooled till the hydrochlorate of guanine crystallises out; the crystals purified by several recrystallisations; and the guanine precipitated from its aqueous solution by ammonia: the washed and dried product amounts to $\frac{1}{4}$ p. c. of the guano. The lime at the boiling heat takes up the brown colouring matter of the guano; it likewise sets free the potash and soda present in the guano, by which chiefly the guanine and the uric acid are dissolved.

Purification. The still yellowish guano thus obtained, is treated with excess of concentrated hydrochloric with the aid of heat, and the liquid decanted before the whole is dissolved; the undissolved portion, already a purer salt, is collected and repeatedly treated in the same manner, till ammonia precipitates white guanine from it.

Properties. White powder. Neutral to vegetable colours.

	At 125°.		Unger.	
10 C	60 39.73	39.58
5 N	70 46.36	46.49
5 H	5 3.31	3.42
2 O	16 10.60	10.51
$C^{10}N^4H^2O^2$	151 100.00	100.00

[According to the formula, $C^{10}N^4AdH^2O^2$, guanine is the amide of xanthic oxide: $C^{10}N^4H^4O^4 + NH^3 = C^{10}N^5H^2O^2 + 2HO$].

Decomposition. Guanine digested with chlorate of potash and hydrochloric acid, generally yields nothing but oxalic acid and ammonia, but sometimes also peruric acid, when left to crystallise over night. — When enclosed with water in a sealed tube, it does not dissolve or decompose at 250°, excepting that a trace of ammonia is formed.

Combinations. With Water. *Hydrate of Guanine.* — Sulphate of guanine is decomposed by contact with a large quantity of water, and the

acid, which does not contain a certain portion of guanine. The hydrate resembles the anhydrous guanine. It retains its water at 100°, but gives up the whole of it, amounting to 7.1 p. c. at 125°. — Guanine does not dissolve in water.

Guanine combines both with acids and with alkalis. From the former compounds, water extracts the acid, which, if volatile, is likewise expelled by heat.

Phosphate of Guanine. — Deposits from the solution in crystalline grains, which unite into a crust, contain 58.50 p. c. guanine, 36.28 phosphoric acid, and 4.53 water (loss 0.69), and retain their water till heated to 125°.

Sulphate of Guanine. — Sulphuric acid is added to guanine till the latter is completely dissolved; the strongly acid liquid diluted with hot water; and the clear mixture cooled, whereupon it yields yellowish needles, often an inch long, which must be washed, not with water, but with weak alcohol. At 120°, they give off 8.12 p. c. (= 2 At.) water of crystallisation, and no more at higher temperatures, even above 200°. By a large quantity of water, they are resolved into hydrate of guanine and dilute sulphuric acid, which, however, still retains in solution a certain portion of the guanine.

	<i>At 120°.</i>		<i>Unger.</i>	
C ¹⁰ N ⁵ H ⁶ O ²	151	75.50	75.61	
SO ³	40	20.00	20.08	
HO	9	4.50	4.31	
<hr/>				
C ¹⁰ N ⁵ H ⁶ O ² , HO, SO ³	200	100.00	100.00	

Hydrochlorate of Guanine. — a. Mono-acid. — a. Anhydrous. — Obtained by exposing the compound β to a continuous current of air, or heating it to 100°. The residue gives off all its hydrochloric acid, amounting to 19.27 p. c., at 120°, while pure guanine remains behind.

β. Hydrated. — Crystallises from the solution of guanine in strong boiling hydrochloric acid, on addition of a large quantity of hot water, and cooling, in an abundance of slender, light yellow needles, which give off their water at 100° and their acid at 200°.

	<i>Anhydrous.</i>		<i>Unger.</i>	
C ¹⁰ N ⁵ H ⁶ O ²	151.0	80.58	80.70	
HCl	36.4	19.42	19.30	
<hr/>				
C ¹⁰ N ⁵ H ⁶ O ² , HCl	187.4	100.00	100.00	
	<i>Needles.</i>		<i>Unger.</i>	
C ¹⁰ N ⁵ H ⁶ O ²	151.0	73.51	72.69	
HCl	36.4	17.72	17.12	
2 HO	18.0	8.77	10.19	
<hr/>				
C ¹⁰ N ⁵ H ⁶ O ² , HCl + 2Aq	205.4	100.00	100.00	

[The needles analysed by Unger had probably some mother-liquor still adhering to them; he prefers representing them by the formula: 3(C¹⁰N⁵H⁶O², HCl + 7Aq.)]

b. Bi-acid. — Guanine swells up, and becomes slightly heated in hydrochloric acid, and at a winter-temperature, absorbs, when completely saturated, 48.14 p. c. hydrochloric acid (100 : 48.14 = 151 : 72.195).

Nitrate of Guanine. — a. Mono-acid. — Guanine dissolves easily and without decomposition in a boiling mixture of nitric acid of sp. gr. 1.2 and water; and the solution yields, on cooling, long, very fine, capillary, interlaced crystals, which taste sour at first and rough afterwards; reddened litmus strongly; effloresce in the air, with loss of a portion of their acid; dissolve in hot water much more abundantly than in cold; and are not altered by boiling the solution.

<i>Crystals.</i>		<i>Unger.</i>
10 C	60	24.89
6 N	84	34.85
9 H	9	3.74
11 O	88	36.52
<hr/>		
$C^{10}N^4H^4O^3, NO^3 + 4Aq$	241	100.00
<hr/>		
Or:		
		<i>Unger.</i>
$C^{10}N^4H^4O^3$	151	62.66
NO^3	54	22.40
4 Aq	36	14.94
<hr/>		
	241	100.00
		100.0

b. Bi-acid. — Crystallises on cooling from a solution of guanine in boiling nitric acid of sp. gr. 1.25, in short prisms, which effloresce in the air, with loss of part of their acid, and give off the whole of it when heated.

<i>Crystals.</i>		<i>Unger.</i>
$C^{10}N^4H^4O^3$	151	48.24
2 NO^3	108	34.51
6 HO	54	17.25
<hr/>		
$C^{10}N^4H^4O^3, 2NO^3 + 6Aq$	313 ...	100.00

Between these two compounds, *a* and *b*, there are two intermediate compounds, which crystallise out, when a nitric acid solution which would yield *a* on cooling, is mixed in a certain proportion with another which would yield *b*. One of these intermediate crystallised compounds may be regarded as $3C^{10}N^4H^4O^3, 4NO^3 + 12Aq$; the other as $3C^{10}N^4H^4O^3, 5NO^3 + 16Aq$.

Soda-compound. — Guanine dissolves in aqueous soda (also in potash,) more readily than in acids. The concentrated soda-solution, saturated with guanine, and then mixed with a large quantity of alcohol, yields the soda compound in confused laminæ, which, after drying in vacuo, give off 33.26 p. c. (12 At.) water when heated above 100° ; absorb carbonic acid rapidly from the air; and effloresce with separation of guanine; and when dissolved in water, even not containing carbonic acid, are decomposed with partial separation of guanine.

<i>Anhydrous.</i>		<i>Unger.</i>
2 NaO	62.4	29.24
$C^{10}N^4H^4O^3$	151.0	70.76
<hr/>		
$2NaO, C^{10}N^4H^4O^3$	213.4	100.00
<hr/>		
<i>Crystals.</i>		<i>Unger.</i>
2 NaO	62.4	19.41
$C^{10}N^4H^4O^3$	151.0	46.98
12 HO	108.0	33.61
<hr/>		
$2NaO, C^{10}N^4H^4O^3 + 12Aq$	321.4	100.00

acids, such as carbonic acid.

Nitrate of Mercurous-oxide and Guanine. — The compound of mercurous nitrate with nitrate of guanine forms crystals, which, when heated, deflagrate with emission of white fumes, but without perceptible noise, and dissolve sparingly in water.

Sulphate of Silver-oxide and Guanine. — A solution of sulphate of guanine diluted as much as possible, forms with nitrate of silver a very bulky translucent precipitate, which shrinks together very much in drying, and leaves a hard mass of a pale flesh-colour. This mass, when heated in a crucible, is converted, with partial projection, into a brown powder, which emits an odour of sulphurous acid and cyanogen when ignited, and ultimately leaves silver. The flesh-coloured mass is not altered by boiling with sulphuric acid or with potash. When decomposed with zinc, it yields silver, guanine, and sulphuric acid, but no nitric acid. The reduced silver is black, but as soon as all the zinc is used up, and hydrogen gas is no longer evolved, it becomes brownish green, insoluble in hot nitric acid, and at a red heat again gives off the odour of sulphurous acid and cyanogen.

Chloroplatinate of Guanine. — The hot-saturated solution of guanine in hydrochloric acid, is mixed with excess of hot concentrated bichloride of platinum; the mixture evaporated to one-half at 100°; and the crystals which form on cooling, washed with alcohol or water, and dried over oil of vitriol. Orange-yellow needles, and prisms of lemon-yellow colour. Over oil of vitriol, they become opaque and give off a trace of hydrochloric acid. In a current of dry air at 15°, they evolve traces of hydrochloric acid; then between 100° and 120°, they give off 6.51 p. c. (4 At.) water, with a trace of hydrochloric acid, and leave a pale lemon-yellow residue, which dissolves slowly in cold water, but perfectly in boiling water, and on cooling yields the original crystals; absolute alcohol does not extract any chloride of platinum from it. Zinc, with hydrochloric acid, separates platinum-black from the crystals, while guanine remains in the liquid. When the crystals are fused with carbonate of soda, cyanide of sodium is formed. They dissolve in water, and readily, without evolution of carbonic acid, in caustic potash, or soda, or their carbonates, whence they are precipitated by acids.

	<i>Crystals.</i>			<i>Unger.</i>
10 C	60	10.66 10.54
5 N	70	12.43 12.30
10 H	10	1.77 1.94
2 Pt	198	35.17 34.98
6 O	48	8.53 8.35
5 Cl	177	31.44 31.89
<hr/> $C^{10}N^5H^6O^2, HCl + PtCl^2 + 4Aq$		563 100.00 100.00

Oxalate of Guanine. — Separates from a mixture of the solution of hydrochlorate of guanine with a tolerably concentrated solution of oxalate of ammonia, in crystals, which do not give off anything at 120°.

	Crystals.		Unger.	
38 C.....	228 36.02	36.00
15 N	210 33.17	33.19
19 H	19 3.00	3.01
22 O	176 27.81	27.80
<hr/>				
$3C^{10}N^4H^3O^4, 2C^2H^2O^3$	633 100.00	100.00

Tartrate of Guanine. — Separates from a dilute and strongly acid solution, in yellowish radiated nodules, which may be dried at 100° , and do not give off anything even at 120° .

	Crystals.		Unger.	
46 C.....	276 34.98	34.78
15 N	210 26.62	26.43
31 H	31 3.93	3.98
34 O	272 34.47	34.81
<hr/>				
$3C^{10}N^4H^3O^4, 2C^2H^2O^3 + 4Aq.$	789 100.00	100.00

Appendix to Guanine.

Peruric Acid.

UNGER. *Ann. Pharm.* 59, 69.

Formation and Preparation. — An intimate mixture of 3 pts. guanine and 5 pts. chlorate of potash is set aside with 25 pts. water and 30 pts. hydrochloric acid. At first the mixture becomes solid, from formation of hydrochlorate of guanine, then dissolves gradually, with evolution of chlorous acid gas, and in the course of 24 hours, yields crystals of peruric acid. To free these crystals from an admixed amorphous substance, they are dissolved in hot, very dilute ammonia; the hot solution mixed with nitrate of silver, and quickly filtered from the precipitate of silver oxide and amorphous matter; the filtrate slightly supersaturated with nitric acid; and crystals of the pure acid obtained on cooling.

Properties. Colourless, shining, short, oblique rhombic prisms or plumose crystals, which are inodorous, tasteless, grate between the teeth, and redden moist litmus paper,

	At 100° .		Unger.	
10 C	60 31.09	31.12
4 N	56 29.01	
5 H	5 2.59	2.60
9 O	72 37.31	
<hr/>				
	193 100.00		

The acid subjected to dry distillation, gives off water and a large quantity of cyanic acid, and leaves a slowly combustible charcoal.

Combinations. The acid dissolves slowly in water. It dissolves easily and abundantly in caustic alkalis and their carbonates; its solution in ammonia does not precipitate chloride of barium or chloride of calcium, and when left to evaporate freely, leaves crystals of peruric acid free from ammonia.

of silver, the liquid becomes acid, and yields a curdy precipitate, which, after washing, dries up to a white, loosely coherent powder, which does not blacken when exposed to light, and after drying at 100°, contains 66·3 p. c. silver. If the acid liquid above the precipitate be exactly neutralised with ammonia, and then kept at a lukewarm temperature for 24 hours, during all which time it remains neutral, a precipitate is obtained, which, when washed and dried at 100°, exhibits the following composition:

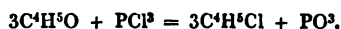
					Unger.
10 C	60	14·74	13·40
4 N	56	13·76	12·71
3 H	3	0·73	0·86
2 Ag.....	216	53·07	56·83
9 O	72	17·70	16·20
<hr/>					
	407	100·00	100·00

[Even if the difference between the analysis and the formula of this salt can be explained by the presence of an excess of oxide of silver, the improbability both of this formula and that of the free acid, nevertheless renders a repetition of the analysis desirable.]

ADDITIONS TO VOL. VII.

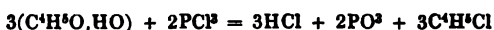
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Action of Terchloride of Phosphorus on Alcohols, Ethers, Acids, &c. —
 1. Terchloride of phosphorus decomposes *Vinic ether* at a temperature of 180° to 200°, with formation of chloride of ethyl and phosphorous acid:

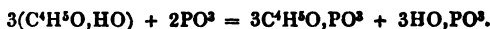


Anhydrous ether mixes with terchloride of phosphorus at ordinary temperatures, without sensible increase of heat; but the presence of water or alcohol, in quantities however small, causes an extremely violent reaction. When the anhydrous ether and the terchloride are heated together to the above temperature for 20 hours, in a sealed tube, the tube becomes covered with a thick crust of phosphorous acid, mixed however with phosphoric acid and red phosphorus, resulting from the decomposition of the phosphorous acid at the high temperature; and on opening the tube, a large quantity of hydrochloric ether escapes with rapidity. No hydrochloric acid appears to be formed.

2. With absolute *Alcohol*, terchloride of phosphorus forms hydrochloric acid, phosphorous acid, and chloride of ethyl, just as it would with a mixture of ether and water, and the phosphorous acid afterwards acts upon another portion of the alcohol, forming tribasic phosphite of ethyl (ix. 360) and hydrated phosphorous acid; thus:



and



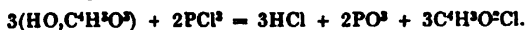
When the terchloride is dropt into absolute alcohol, a violent action takes place, even if the retort is immersed in a freezing mixture; hydrochloric acid is evolved at the first instant, but its evolution soon ceases, recommencing however on the application of heat. The residue in the retort yields the phosphorous ether by distillation, in the form of a very fetid liquid, having an alliaceous odour. The quantity of this ether produced is however but small.

3. *Anhydrous acetic acid* and terchloride of phosphorus, in the ratio of 3 At. $C^4H^3O^3$ to 1 At. PCl^3 , heated in a sealed tube placed in the water-bath, yield phosphorous acid and chloride of ethyl:



No action takes place at ordinary temperatures; but towards 65° the mixture suddenly becomes turbid, from separation of a white substance, which becomes yellow towards 80°. No gas is evolved on opening the tube. The liquid portion all distils over between 55° and 60°, yielding chloride of ethyl with only a trace of chloride of phosphorus.

4. *Hydrated acetic acid* acts with terchloride of phosphorus, just like a mixture of the anhydrous acid and water:



The action commences, even at ordinary temperatures, with evolution of hydrochloric acid. On heating the mixture in a sealed tube, it soon became turbid, and the decomposition was completed between 30° and 40°. On opening the tube, a torrent of hydrochloric acid was evolved, and the liquid yielded a distillate of chloride of ethyl, with a residue of hydrated phosphorous acid. Terchloride of phosphorus appears to act in a similar manner on all the monobasic acids.

5. *Acetate of Ethyl* and terchloride of phosphorus decompose each other between 160° and 180°, forming chloride of ethyl, chloride of ethyl, and phosphorous acid:



No action takes place in the cold or at 100°; but at the temperature above mentioned, the tube becomes coated with phosphorous acid, and the action is complete in about 24 hours. (A. Béchamp, *Compt. rend.* 40, 944; 41, 23.)

From these experiments, Béchamp concludes that alcohol and the ethers of the monobasic acids are compounds of the same order, and formed by the union of oxide of ethyl with water, or with the anhydrous acid; moreover, that the hydrated and anhydrous monobasic acids stand to one another in the same relation.

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Organic Bases containing Phosphorus.

A. CAHOURS & A. W. HOFMANN. *Compt. rend.* 41, 831; *Chem. Gaz.* 1855, 11.

P. Thénard (vii. 328), by acting upon phosphide of calcium with chloride of methyl, obtained certain compounds containing methyl and phosphorus, viz. P^2Me , PMe^3 , PH^2Me and PMe^2 . Cahours and Hofmann, by following a similar mode of proceeding, with phosphide of sodium and iodide of methyl, have also obtained the compounds PMe^3 and PMe^2 , and likewise PMe^2I , a beautifully crystallised substance, corresponding with iodide of tetramethylum. This mode of preparation however is difficult and dangerous, inflammable and detonating compounds being formed, and complex products obtained, which are very difficult to separate.

[F. Berlé (*J. pr. Chem.* 66, 78), by acting upon phosphide of sodium with iodide of ethyl, has obtained *triphosphethylamine* (or *triethylphosphine*), PAe^3 , in the form of a yellow, strongly fuming liquid, which, when heated with iodide of ethyl, forms a crystalline mass, consisting of PAe^2I , (iodine by analysis 45.5 and 47.8 p. c.; by calculation 46.3).—A better result was obtained by heating a mixture of phosphorus, sodium, and iodide of ethyl, in a sealed tube. The resulting crystalline mass, purified by recrystallisation, first from alcohol and ether, then from water, yielded needles containing 67.8 p. c. iodine; the formula $\text{PAe}^2\text{I}, \text{HI}$ requires 67.2 p. c. On trying the same experiment

with fumes of ethyl, dissolves in considerable quantity, but does not form any basic compound. (Berlé.)]

A better mode of preparation is furnished by the action of terchloride of phosphorus on zincmethyl, zincethyl, and zincamyl. When one of these substances is placed in a U-tube filled with carbonic acid, and vapour of terchloride of phosphorus passed through it, the mass becomes strongly heated, and a viscous substance is formed, which solidifies completely on cooling. This solid mass is a compound of chloride of zinc with triphosphomethylamine, triphosphethylamine, triphosphamylamine, &c., *e. g.*



These compounds, distilled with an excess of strong potash-solution, yield chloride of potassium and zincate of potash, which remain in the retort, and volatile oily distillates, having a peculiar odour something like that of the arsenic bases, possessing very decided alkaline properties, and consisting of triphosphomethylamine, &c. These bodies form with acids, crystallisable and very soluble salts. Their hydrochlorates form with bichloride of platinum, orange-coloured, very soluble compounds, which, by slow evaporation, may be obtained in beautiful crystals.

Triphosphomethylamine in contact with iodide of methyl, becomes strongly heated, and yields a concrete substance, a considerable portion of which dissolves in alcohol, and separates out on evaporation in long white needles of *iodide of tetraphosphomethylium*, $P(C^2H^3)_4I$. — Iodide of ethyl acts in the same manner, but less energetically, forming $P(C^2H^5)_3(C^4H^6)I$, which is isomorphous with the preceding. — In like manner, iodide of amyl forms $P(C^2H^3)_3(C^{10}H^{11})I$.

Triphosphethylamine, treated in a similar manner with the iodides of the alcohol-radicals, yields the compounds PAe^3MeI , PAe^3I , PAe^3AmI . The second of these compounds forms very fine crystals. — Triphosphamylamine also yields corresponding compounds.

All these iodides are easily decomposed by oxide of silver, yielding hydrated oxides, which neutralise hydrochloric acid, and form beautiful crystalline compounds with bichloride of platinum, *e. g.*, $P(C^2H^3)_4Cl$, $PtCl_2$.

The preceding iodides, treated with nitrate, sulphate, &c. of silver, yield iodide of silver, and the corresponding salts of the phosphorus-bases.

Terchloride of arsenic acts upon zinc-methyl, &c. in the same manner as terchloride of phosphorus, yielding *triarsenmethylamine*, *triarsenethylamine*, &c. Chloride of bismuth appears to act in the same manner. (Cahours & Hofmann.)

Oxide of Methyl. — Gaseous oxide of methyl (hydrate of methylene) liquefies when passed into a tube cooled to -36° by a mixture of snow and chloride of calcium. The resulting liquid distils at -21° , and disappears completely, reproducing the original gas. During the liquefaction, a few small bubbles of gas are evolved, consisting of oxide of carbon, formed in the preparation of the methylic ether by the action of sulphuric acid on wood-spirit. (Berthelot, *N. Ann. Chim. Phys.* 44, 348.)

Selenmethyl. C^2H^4Se .F. WÖHLER & J. DEAN. *Ann. Pharm.* 97, 5.

Preparation. By distilling a solution of sulphomethylate of baryta with selenide of potassium. Selenium was converted into selenious acid by oxidation with nitric acid; the solution evaporated to complete dryness, and till the selenious acid began to sublime; the acid dissolved in water, and neutralised with carbonate of potash; a sufficient quantity of fine charcoal-powder shaken into the liquid; and the whole evaporated to dryness. The mixture was then transferred to a glass retort, and gradually heated over a charcoal fire, till the selenite of potash was reduced to selenide of potassium, which reduction took place at a temperature considerably below redness, suddenly, and with bright incandescence and semi-fusion of the mass. After complete cooling, the retort was broken, the mass added to the solution of sulphomethylate of baryta, the mixture quickly distilled, and the product purified by redistillation.

Properties. Reddish yellow, very mobile liquid, heavier than water and insoluble therein. Its odour is as disagreeable as that of sulphethyl, tellurethyl, &c. It is very inflammable, and burns with bluish selenium-flame.

Methyloselenious acid. $C^2H^4Se^2O^6 = C^2H^4O^3, 2SeO^2$. — Selenmethyl is readily dissolved by nitric acid, with evolution of heat. The solution does not yield any precipitate with hydrochloric acid; sulphurous acid reduces selenmethyl from it, in the form of an oily liquid. On attempting to concentrate the solution by evaporation, nitric oxide is sometimes evolved, and a very violent action takes place, which may increase to such a degree as to set fire to the liquid, and decompose it completely, with evolution of vapours which are intolerably irritating to the eyes. But by very carefully regulating the heat, the solution may be concentrated to a syrup; it then on cooling yields beautiful groups of colourless prisms, and the entire mass suddenly solidifies in the crystalline form.

The crystalline body thus obtained is methyloselenious acid. It has a strong acid reaction, an unpleasant odour, and persistent metallic taste; deliquesces in the air; dissolves readily in water and alcohol; melts at 122° ; solidifies again in the crystalline form; and when heated in the air, burns with the blue flame of selenium. When heated in a tube, it gives off very irritating vapours, and yields a reddish yellow oil, together with fused selenium. Hydrochloric acid does not alter the solution; sulphurous acid throws down from it a very dark yellowish red fetid liquid, probably biselenide of methyl.

With *Ammonia* the acid forms a crystallisable salt, from whose solution chloride of barium throws down the *methyloselenite of baryta*, in the form of a white crystalline precipitate.

Silver-salt. $C^2H^4AgO^3, 2SeO^2$. — Obtained by saturating the acid with carbonate of silver. Sparingly soluble in cold water; from a solution prepared at the boiling heat, it separates in groups of beautiful prisms,

having a glassy lustre. When exposed to light or heated, it quickly blackens, and selenide of silver is reduced, even from its solution, by continued heating. Heated, even slightly in a glass tube, it yields selenium and selenide of silver. Two silver-determinations gave 45·8 and 45·9 p. c. silver, whereas the formula requires 43·2 p. c.; but the precipitated chloride of silver was always black after fusion, from the presence of selenide of silver, a selenium-compound being precipitated simultaneously with it.

Chloromethylselenious acid. — $C^2H^4ClO, 2SeO^2$. — A solution of methylselenious acid, mixed with hydrochloric acid and evaporated, yields beautiful transparent prisms of the chlorinated acid, which do not deliquesce on exposure to the air. The acid has a very unpleasant taste and odour. It melts between 88° and 90° into a brown oil, therefore with partial decomposition, and afterwards solidifies in the amorphous state. When heated in a tube, it yields reduced selenium and a yellow oil. Dissolves readily in water and alcohol. Sulphurous acid added to the solution, throws down a dark red oil. Has a strong acid reaction; but in contact with bases, it is decomposed, with formation of a chloride and a methylselenite; e. g. with oxide of silver :



		Wöhler & Dean.	
2 C	12·0	7·0	7·2
4 H	4·0	2·3	3·3
Cl	35·4	20·7	20·4
2 Se	80·0	46·7	45·7
5 O	40·0	23·3	

$C^2H^4ClO, 2SeO^2$ 171·4 100·0

(Selenide of ethyl, C^4H^6Se , probably forms a similar chlorinated acid. At all events, the crystals which Joy obtained (viii, 357) by leaving chloride of selenethyl in contact with a mixture of nitric and hydrochloric acid, exhibited a composition not differing greatly from the formula $C^4H^6ClO, 2SO^2$, which requires 12·9 p. c. C, 3·2 H and 19·1 Cl.)

Bromomethylselenious acid. — $C^4H^6BrO, 2SeO^2$. — Produced when a solution of the chlorinated acid is mixed with hydrobromic acid and evaporated. Crystallises in yellowish prisms, and fuses readily into a liquid having the appearance of bromine.

Iodomethylselenious acid. — $C^4H^6IO, 2SeO^2$. — Obtained by mixing the chlorine-compound with hydriodic acid or iodide of potassium. Forms a heavy black liquid, having a greenish metallic lustre, and solidifying after awhile in the crystalline form. Has a very unpleasant odour. Dissolves readily in hydriodic acid and in iodide of potassium. Dissolves also in alcohol; and when the alcoholic solution is left to evaporate, the compound volatilises completely without leaving any residue. (Wöhler & Dean.)

Formation and Preparation. By distilling telluride of potassium with sulphomethylate of baryta, the distillation being continued as long as drops of oily liquid pass over with the water, and the process conducted altogether as for the preparation of tellurethyl. (viii. 383.)

Properties. Pale yellow mobile liquid, which sinks in water, and does not mix with it. Boils at 82°, forming a yellow vapour like tellurium itself. Has an extremely disagreeable alliaceous odour, which is so intense and persistent, that even the breath is affected by it after some time.

Calculation.

2 C	12	15.19
3 H	3	3.80
Te.....	64	81.01
C ² H ³ Te			
	79	100.00

Decompositions. Telluromethyl fumes in the air from oxidation. When set on fire, it burns with a bright bluish-white flame, diffusing white fumes of tellurous acid. Strong nitric acid oxidises it, with evolution of nitric oxide.

Combinations. Telluromethyl behaves with oxygen, chlorine, &c. like a radical or a metal, forming a basic oxide and analogous haloïd-compounds.

Oxide of Telluromethyl. C²H³Te.O. — Obtained by decomposing the chloride or iodide with oxide of silver. Either of these compounds is moistened with water, and oxide of silver, recently precipitated by baryta-water and well washed, added in excess, whereupon decomposition begins immediately, and the mass becomes spontaneously heated. The filtrate contains the oxide in solution.

Oxide of telluromethyl is indistinctly crystalline when dry. Has an abominable taste, but is inodorous. Deliquesces in the air like potash, and absorbs carbonic acid. Its aqueous solution is strongly alkaline to test-paper; eliminates ammonia from sal-ammoniac, even at ordinary temperatures, and forms a blue precipitate with sulphate of copper. Sulphurous acid added to the solution immediately throws down telluromethyl, in the form of an oily stinking liquid; hydrochloric acid precipitates the white chloride; hydriodic acid the red iodide. On saturating the aqueous oxide with sulphuretted hydrogen, a slight milky turbidity is produced; and on distilling the liquid, white sulphur separates out, and a yellow oil passes over, which appears to be merely reduced telluromethyl.

Sulphate of Telluromethyl, formed by directly saturating the base with the acid, crystallises in very regular transparent cubes of considerable size. It dissolves readily in water, but is insoluble in alcohol.

Iodide. — When colourless hydriodic acid, or iodide of potassium, is dropt into a solution of nitrate of telluromethyl, a precipitate is formed of a bright lemon-yellow colour, but changing in a few seconds to vermillion-red. If the solutions are mixed warm, the precipitate exhibits

at once a red colour and crystalline structure. When dry, it forms a vermilion-coloured powder. — The compound dissolves sparingly in cold, much more freely in hot water, and abundantly in hot alcohol, forming a reddish yellow solution. From both solutions, it crystallises in small shining, vermilion-coloured prisms, which are largest when they separate from the alcoholic solution. They yield an orange-yellow powder. Under the microscope, they appear orange-yellow by transmitted light, but certain faces exhibit a fine blue surface-colour. — It appears to be dimorphous, like iodide of mercury; for, on mixing the cooled alcoholic solution with about an equal volume of water, the iodide is precipitated, of a lemon-yellow colour; but in a few minutes, a movement of the particles is observed throughout the liquid, and the precipitate soon assumes the character of vermilion-coloured, crystalline laminae. The yellow variety cannot, however, be obtained in a permanent form; for the alcoholic solution yields red crystals by evaporation, and the compound cannot be melted without decomposition. Even at 130°, it is converted into black iodide of tellurium.

				Wöhler & Dean.	
2 C	12	5·86 5·40
3 H	3	1·46 1·61
Te	64	31·22 31·24
I	126	61·46 61·54
<hr/>					
C^2H^3TeI	205	100·00 99·79

Bromide. C^2H^3TeBr . — Prepared like the chloride, which it closely resembles, and with which it is probably isomorphous. Forms shining, colourless prisms, which melt at 89°.

Chloride. C^2H^3TeCl . — Obtained as a thick white precipitate, resembling chloride of lead, on adding hydrochloric acid to a solution of the nitrate. Redissolves when heated, and crystallises on cooling in long thin prisms, like corrosive sublimate. When prepared from the amorphous nitrate (*inf.*), it contains tellurous acid, mixed or combined. Melts at 97·5°, but appears not to be volatile without decomposition. Solidifies from fusion in a mass having a highly crystalline structure. Does not distil over with water, but its heated aqueous solution has a faint alliaceous odour. Does not form any precipitate with bichloride of platinum. Dissolves readily in alcohol.

Oxychloride. C^2H^3TeCl, C^2H^3TeO . — Formed by dissolving the chloride in ammonia. On evaporating and digesting the residue of sal-ammoniac and oxychloride in alcohol, the latter dissolves and separates from the solution in short colourless prisms. Hydrochloric acid added to the solution precipitates the chloride.

Sulphochloride. C^2H^3TeS, C^2H^3TeCl ? — Sulphuretted hydrogen passed through a solution of the chloride, forms a white flocculent precipitate, which afterwards turns yellowish, the liquid at the same time acquiring an extremely repulsive odour. If it be then distilled, there passes over with the water, a heavy oily liquid, having a reddish yellow colour and extremely offensive odour, and yielding sulphuric acid when oxidised with aqua-regia.

Nitrate. C^2H^3TeO, NO^6 . — Telluromethyl, heated with moderately strong nitric acid, dissolves partially at first, with reddish yellow colour; but after a while, a violent reaction ensues, attended with evolution of nitric oxide, and a colourless solution of the nitrate is obtained, which by

on evaporation, not in crystals, but in the form of a transparent amorphous mass, containing tellurous acid, mixed or combined, and arising probably from decomposition of a portion of the telluromethyl. — The nitrate decomposes with explosion if heated. It dissolves readily in water and alcohol. The aqueous solution, mixed with hydriodic, hydrobromic, or hydrochloric acid, yields a precipitate of the iodide, bromide, or chloride of telluromethyl.

Oxide of telluromethyl dissolved in hydrocyanic acid does not form a cyanide of telluromethyl: on evaporating the solution, the base remains in its original state. (Wöhler & Dean.)

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Chloride of Methyl. — Gaseous chloride of methyl (or hydrochlorate of methylene) liquefies at -36° , without any evolution of gas. The resulting liquid boils at -22° , reproducing the gas; and by the time the temperature has risen to -20° , nearly the whole has distilled over. A small quantity of a liquid, however, generally remains, free from chlorine, insoluble in water, and probably arising from some impurity in the wood-spirit.

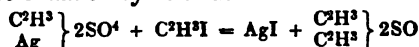
Chloride of methyl passed through a glass tube filled with pumice-stone and heated to dull redness, scarcely undergoes any decomposition; at a bright red heat, an abundant deposit of charcoal is formed on the pumice-stone, and a liquid condenses beyond the tube. The gaseous products are comparatively small in quantity (*compare vii*, 287.) The gases obtained both at the dull and at the bright red heat, were found, after being washed with a large quantity of water, to undergo scarcely any diminution by the action of bromine. — 100 pts. of the gas collected at a dull red heat, yielded 74 pts. of carbonic acid; the total absorption amounted to 229 pts. — 100 pts. of the gas collected at a bright red heat, yielded 73 pts. of carbonic acid; the total absorption amounted to 232 pts. This gas, treated with bromine and then analysed again, yielded the same results. Hence the gas contains 53 p. c. marsh-gas, 18 carbonic oxide, and 27 hydrogen. The oxide of carbon is probably due, either to a small quantity of moisture, or to the formation of a small quantity of oxide of methyl, together with the chloride. (Berthelot, *N. Ann. Chim. Phys.* 44, 349.)

Page 306.

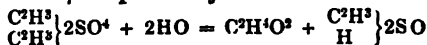
Spontaneous Decomposition of Sulphomethylates. — A mixture of the dry crystallised sulphomethylates of baryta and lime, set aside in a loosely stopped bottle and exposed to daylight for 22 months, was found to have diminished in bulk by one-third, the upper portion of the contents being a yellowish acid liquid of disagreeable odour, the lower a white apparently amorphous substance, surmounted by a crystalline crust, from which sprung numerous distinct crystals, having their summits turned towards the flight. — These crystals consist of sulphate of lime, $\text{CaO}, \text{SO}^3 + 2\text{Aq}$; they belong to the oblique prismatic system; their hardness is between 1.5° and 2° ; sp. gr. between 2.21 and 2.3525; lustre pearly in some aspects, vitreous in others. The crystalline crust, from which the prismatic crystals rose, also consisted of this salt. The white amorphous powder was sulphate of baryta, intermixed, however, with botryoidal masses of granular sulphate of lime, $2(\text{CaO}, \text{SO}^3) + \text{Aq}$.

The yellow liquid was a mixture of sulphovinic and sulphuric acids, with water and a small quantity of an oily odorous liquid. When neutralised with carbonate of baryta, it yielded, after separation of the sulphate of baryta, and subsequent evaporation and recrystallisation, crystals of sulphomethylate of baryta, which, when dried between paper, were found to contain 38.66 p. c. baryta, agreeing with the formula $C^2H^3BaO^2, 2SO^2 + 2Aq$, which requires 38.76 p. c. The same salt, dried at 100° , contained 42.60 p. c. baryta, agreeing with the formula $C^2H^3BaO^2, 2SO^2$, which requires 42.65. — The saturated solution of this sulphomethylate is not altered by prolonged ebullition, and the crystals may be heated to 100° without becoming acid or otherwise decomposing. In this respect, the salt differs remarkably from the ordinary sulphomethylate of baryta (vii, 306), although agreeing with it in constitution; it is, in fact, the homologue in the methyl-series of the stable sulphovinate (parathionate) which Gerhardt (*Compt. chim.* 1845, 176) obtained by repeatedly boiling and neutralising with carbonate of baryta, the aqueous solution of the ordinary sulphovinate, and which has more recently been identified by Berthelot (*N. Ann. Chim. Phys.* 45, 392) with the sulphovinate obtained by saturating with carbonate of baryta the mixture of 4 vol. sulphuric acid and 1 vol. alcohol used to prepare olefiant gas, or the solution of that gas in oil of vitriol. This view is further confirmed by the fact, that protonitrate of mercury, added to a strong solution of ordinary sulphovinate or sulphomethylate of baryta, forms a grey or slaty precipitate; whereas, with Gerhardt's parathionate, with the sulphomethylate obtained by the same method, and with the stable sulphomethylate above mentioned, the precipitate is white. The acid of the stable sulphomethylate may, for distinction, be called β -Sulphomethylic acid. (A. H. Church, *Phil. Mag.* [4], 10, 40.)

Action of Water on Sulphomethylates. — When sulphomethylate of silver, iodide of methyl, and absolute alcohol are placed together in a sealed tube, and somewhat strongly heated in an oil-bath, iodide of silver is formed, and on opening the tube, a certain quantity of sulphomethylate of methyl may be obtained by distillation:

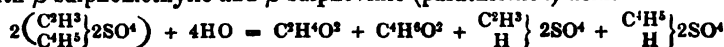


This sulphomethylate of methyl appears to be identical with the sulphate of methyl obtained by distilling wood-spirit with oil of vitriol. Both these products, when placed in water, are decomposed slowly at ordinary temperatures, but almost instantaneously at 100° , the products being methylic alcohol and β -sulphomethylic acid.

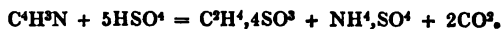


In whatever way the methylic sulphate may be prepared, and its transformation in contact with water effected, β -sulphomethylic acid appears to be invariably produced. Only in one instance was a small quantity of acid obtained which yielded a baryta-salt, decomposable at 100° . The modified sulphomethylic acid is obtained in the purest state when sulphate of methyl is decomposed by water at the ordinary summer temperature; at higher temperatures, secondary products are also formed.

Sulphomethylate of ethyl (or sulphethylate of methyl), treated with water in a similar manner, yields methylic and vinic alcohols, together with β -sulphomethylic and β -sulphovinic (parathionic?) acid:



Methylotetrasulphuric Acid. $C^2H^4,4SO^3$. — Formed by the action of fuming sulphuric acid on acetonitrile (cyanide of methyl):



When acetonitrile and fuming sulphuric acid are rapidly mixed, and the liquid rather strongly heated, carbonic acid is abundantly evolved; and the residual mass, which is tough and resinous, yields, when treated with water and boiled with an excess of carbonate of baryta, a magnificent crystallisation of *methylotetrasulphate of baryta*, $C^2(H^2Ba^2)4SO^3 + 4Aq$. This is a very stable salt. It does not lose weight at 100° , but gives off its 4 At. water at 170° . No further alteration takes place at 170° , but at a stronger heat, the salt is resolved into water, sulphide of barium, sulphurous acid, sulphur, and carbonic oxide.

The free acid is obtained by precipitating a solution of the barium-salt with sulphuric acid, or by decomposing the lead or silver salt with sulphuretted hydrogen. Crystallises in long needles, very soluble and deliquescent. Has a sharp taste, with somewhat of the flavour of tartaric acid.

Calculation.

2 C	12	6.82
4 H	4	2.27
4 SO ³	160	90.91

$C^2H^4,4SO^3$ 176 100.00

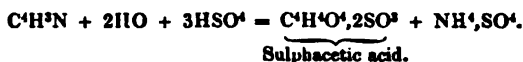
May be regarded as marsh-gas associated with 4 At. sulphuric acid. The change which the acetic molecule undergoes in the formation of this compound under the influence of sulphuric acid, is the same as that which it suffers under the influence of an alkali. In both cases, the molecule splits up into marsh-gas and carbonic acid (ix. 294); only in the latter case, it is the carbonic acid which is fixed, while in the former, the marsh-gas remains in combination.

Ammonia-salt. $C^2[H^2,(NH^4)^2],4SO^3$. — Obtained by neutralising the acid with ammonia, — or by the action of fuming sulphuric acid on acetamide (ix, 246), which differs from acetonitrile only by 2HO. Crystallises with great facility in colourless prisms, sometimes an inch long. They are anhydrous, and perfectly stable at 190° .

Silver-salt. $C^2(H^2Ag^2)4SO^3$. — Obtained by digesting oxide of silver with the aqueous acid. Forms large crystals, which dissolve readily in water, but are insoluble in alcohol and ether.

When fuming sulphuric acid, instead of being suddenly mixed with acetonitrile, is added to it in small quantities, and the mixture cooled after each addition, a different action takes place, the nascent acetic acid simply combining with 2 At. sulphuric acid, producing the *sulphacetic*

acid which Melsens obtained (viii, 436), by the action of anhydrous sulphuric acid on glacial acetic acid:



By addition of water and saturation with carbonate of baryta, crystals are obtained, consisting of sulphacetate of baryta. (G. B. Buckton & A. W. Hofmann, *Proc. Roy. Soc.* 7, 544.)

Page 321.

Penta-iodide of Tetramethylum. $(\text{C}^4\text{H}^4)^4\text{N}, \text{I}^5$. — An alcoholic solution of iodine added to a heated solution of proto-iodide of tetramethylum, throws down the penta-iodide in an abundant crop of needles, having a metallic lustre.

		Weltzien.			
8 C	48	6.82	6.89
N	14	1.99	
12 H	12	1.70	1.90
5 I	630	89.49	89.05
					88.32
$\text{C}^4\text{NH}^4\text{I}^5$	704	100.00		

This compound is decomposed by boiling with water, yielding a yellow liquid, from which white, opaque, well-formed crystals of proto-iodide of tetramethylum, $\text{C}^4\text{NH}^4\text{I}$, separate; and on the other hand, still higher iodides are probably formed. The crystals of the proto-iodide yielded by analysis 23.72 p. c. C, 6.28 H, and 61.38 I; the formula requiring 24 p. c. C, 6 H, and 63 I. (Weltzien.)

Deca-iodide of Tetramethylum. $(\text{C}^4\text{H}^4)^4\text{N}, \text{I}^{10}$. — On adding iodine to a boiling solution of the penta-iodide in dilute alcohol, there was formed at the bottom of the boiling liquid, a melted mass, which crystallised on cooling, and gave off iodine-vapours when exposed to the air.

		Weltzien.			
8 C	48	3.60
N	14	1.06	
12 H	12	0.90	
10 I	1260	94.44	95.35
$\text{C}^4\text{NH}^4\text{I}^{10}$	1334	100.00		

The compound ammoniums containing 4 At. Me, Ae, &c., whose compounds are not volatile, and whose hydrated oxides bear a close resemblance to potash, appear to be the only ones capable of forming these periodides. The solution of iodine in iodide of potassium may, perhaps, contain similar periodides of potassium. (Weltzien, *Ann. Pharm.* 91, 41.)

Bromoform. C^3HBr^3 . — In the preparation of bromine from the last portions of the mother-liquor obtained from the Schönebecksalt-spring, there distils over, together with the free bromine, an oily liquid, which, being less volatile than bromine itself, remains in the first of the series of receivers used to condense the products. This substance was formerly regarded by Hermann as a definite compound C^3HBr^3 , the variations in its boiling point being attributed to the facility with which it decomposes; but later experiments, performed with a larger quantity of material, have shown that this view is incorrect, and moreover that the liquid cannot be brought to a definite state by fractional distillation, even in an atmosphere of carbonic acid. By subjecting the liquid, however, to the following treatment, a definite compound is obtained from it.

The oily liquid cooled to $-20^\circ C$, by a mixture of ice and salt, solidifies for the most part in white shining crystalline laminae. To purify these, the mother-liquor is carefully decanted, the crystals melted, again crystallised and separated from the mother-liquor, and these operations several times repeated. The solidified mass, after being freed as completely as possible from the mother-liquor, is then introduced into a capacious funnel, in the apex of which is placed a small perforated filter. At first the principal part of the mother-liquor runs off, and the rest is displaced by the liquid proceeding from the gradually melting crystals. The product which last drips from the melting crystals may be regarded as perfectly pure. If the mother-liquor obtained as above be again treated in the same manner, a product is ultimately obtained which no longer crystallises at $-20^\circ C$.

The crystals consist of bromoform, the formation of which is due to the action of the free bromine on the highly carboniferous organic matters contained in the mother-liquor of the salt-spring.

The melting point of the crystals is $-9^\circ C$. : if they have previously been completely dehydrated by remaining some time over dry chloride of calcium, they form, in the melted state, a colourless, very mobile liquid, having a saccharine taste, with a very persistent burning after-taste:

				<i>Hermann (mean).</i>	
2 C	12	4.74	4.80
H	1	0.40	0.43
3 Br	240	94.86	94.77
C^3HBr^3	253	100.00	100.00

Bromoform exposed to the air decomposes to a certain extent, assuming a red colour, from the presence of free bromine. When distilled, even in a stream of carbonic acid, it is decomposed in the same manner as the crude liquid, a small quantity of bromide of carbon being ultimately formed. When exposed to the action of chlorine in sunshine, the liquid is gradually but completely converted into solid chloride of carbon.

Bromoform is not, like chloroform, converted by caustic potash into bromide of potassium and formiate of potash. Not a trace of formic acid is produced, and the reaction is different, according as the hydrate of potash is used in the free state, or dissolved in alcohol.

When hydrate of potash is brought in contact with bromoform, no action takes place at first, but after a while, the mass becomes so strongly heated that the bromoform begins to distil over, and at the same time

a gas is evolved, which, when freed by agitation with water from a small quantity of diffused bromoform, exhibits the characters and composition of pure carbonic oxide. The decomposition is expressed by the following equation:—



and is analogous to that which the corresponding oxygen-compound, viz. formic acid, undergoes under the influence of sulphuric acid.

With an alcoholic solution of potash, on the other hand, the evolved gas is a mixture of carbonic oxide and olefiant gas, the latter proceeding from the alcohol, which, under these circumstances, is resolved into olefiant gas and water, its decomposition being induced by that of the bromoform. The relative quantities of carbonic acid and olefiant gas thus produced, vary with the degree of concentration of the alcoholic solution of potash; but it is especially remarkable that the simultaneous decompositions of the bromoform and alcohol, though not connected by any mutual action, nevertheless take place in simple atomic proportions: so that, for example, 1 atom alcohol is decomposed for every 3 atoms bromoform; or, with a differently concentrated solution, 5 atoms bromoform to 3 atoms alcohol; thus affording an example of the remarkable law discovered by Bunsen relating to the coefficients of affinity.

The non-crystallisable portion of the original liquid appears to contain protobromide of carbon, C_1Br_2 . (M. Hermann, *Ann. Pharm.* 95, 211.)

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Action of Chlorine on the Sulphides of Methyl.

A. RICHE. *N. Ann. Chim. Phys.* 43, 284.

Monochlorinated Methylic Sulphide. $\text{C}^2\text{H}^2\text{ClS}$. — Formed by the action of chlorine on methyl sulphide, under the influence of diffused daylight and a low temperature. At ordinary temperatures, chlorine acts with great violence on methyl sulphide, each bubble of the gas, as it passes into the liquid, producing flame and a carbonaceous deposit. To obtain a definite result, it is necessary to place the sulphide in a retort, surrounded with ice, and to introduce perfectly dry chlorine very slowly by means of a tube, terminating a little above the surface of the liquid. In this manner, the yellow oil mentioned by Regnault (vii. 355) is produced; it is at first contaminated with hydrochloric acid and unaltered sulphide of methyl, which quickly induce its decomposition, even in stoppered vessels; but by heating it to 50° or 60° , and passing a rapid current of dry carbonic acid through it, these impurities are removed, and the compound may then be preserved without alteration.

Yellow oil, heavier than water, and having a strong, disagreeable odour. When heated in a retort, it partly distils; but a considerable portion is decomposed, and leaves a carbonaceous residus.

				Riche.
2 C.....	12.0	18.35 18.92
2 H	2.0	3.06 3.42
Cl	35.4	54.13 53.22
S	16.0	24.46	
<hr/>				
$\text{C}^2\text{H}^2\text{ClS}$	65.4	100.00	

passed by separate bubbles into the preceding compound, a rapid action takes place, which may even produce inflammation. To prevent this occurrence, the retort must be cooled at the commencement of the operation, and the delivery-tube made to terminate above the liquid; towards the end, however, the tube must be made to dip into the liquid, and the chlorine may be passed into it with considerable rapidity. As soon as the chlorine ceases to be absorbed, it must be replaced by a current of dry carbonic acid, to expel the excess of chlorine and hydrochloric acid. — The product is a heavy yellow liquid, sometimes of a very deep colour. It boils at a high temperature, and is partly decomposed by distillation.

				Riche.
2 C	12·0	... 12·03 12·70
H	1·0	... 1·00 1·17
2 Cl	70·8	... 70·94 70·35
S	16·0	... 16·03	
<hr/>				
C ² HCl ² S	99·8	... 100·00	

In diffused daylight, this compound may be kept for several days in an atmosphere of dry chlorine without sensible alteration; but in sunshine the chlorine is absorbed and a heavy liquid, of a light ruby-red colour is formed, consisting of Regnault's terchlorinated methylic sulphide (vii. 355), together with bichloride of carbon and protochloride of sulphur:



When this liquid is distilled, it begins to boil at 70°, but the boiling point soon rises to 170° — 175°. The first portions of the distillate exhibit a bright red colour, due to the presence of chloride of sulphur, the subsequent portions are of a light yellow colour. The greater portion of the liquid distils over between 155° and 163°, and if this portion be collected apart and repeatedly rectified, a very limpid, amber-coloured liquid is finally obtained, which boils without alteration between 156° and 160°. This liquid is *terchlorinated methylic sulphide*, C²Cl²S. It has a strong, penetrating odour, is insoluble in water, but dissolves easily in alcohol and ether. It is not decomposed by aqueous potash or ammonia. Vapour-density 5·68. — This same compound is also formed by the continued action of chlorine on bisulphide of methyl in sunshine (p. 503).

				Riche.	
				a.	b.
2 C	12·0	... 8·94 9·37 9·08
3 Cl	106·2	... 79·14 79·16 79·16
S	16·0	... 11·92		
H			0·09	

C²Cl²S 134·2 ... 100·00

				Vol.	Density.
C-vapour	2	... 0·8320		
Cl-gas	3	... 7·3629		
S-vapour	½	... 1·1093		
<hr/>					
Vapour of C ² Cl ² S	2	... 9·3042		
		1	... 4·6521		

a, from monosulphide; *b*, from bisulphide of methyl. The calculated vapour-density differs considerably from the experimental; but the difference would be much greater if the vapour were regarded as monatomic. It appears probable therefore that the compound C^2Cl^2S is resolved by heat, like C^2Cl^2O (vii, 355) into $CClS$ and CCl^2 ; and that the vapour whose density was actually determined was a mixture of these two vapours. The low boiling-point of the compound, as compared with the boiling-points of monochlorinated and bichlorinated methylic sulphide, appears to favour this view.

By carefully distilling the red liquid produced by the continued action of chlorine in sunshine or monosulphide of methyl (p. 500), a ruby-coloured distillate is obtained below 100° , which consists of chloride of sulphur mixed with *bichloride of carbon*. By treating this distillate with caustic potash, the chloride of sulphur is decomposed, and the bichloride of carbon separated; and by digesting the latter over fused chloride of calcium and rectifying, it is obtained in the form of a colourless liquid, of sp. gr. 1.567 at 12° , having a pleasant ethereal odour, and boiling at 77° . It gave by analysis 7.80 p. c. C and 91.88 Cl: the formula C^2Cl^4 requiring 7.69 C and 92.31 Cl. (*compare* vii. 356.) — When the sulphide of methyl and the chlorine are both very dry, and all necessary precautions are taken to preclude the entrance of moisture into the vessels, the quantities of chloride of sulphur and chloride of carbon obtained are but small; but if moisture is present, they are produced in great abundance.

Chloride of Methylic Bisulphide. $C^2H^2S^2, Cl$. — When a few drops of bisulphide of methyl are let fall into a flask containing dry chlorine, a number of sulphur-yellow crystals, having the form of rhomboïdal laminæ are immediately deposited on the sides of the vessel. These crystals are very instable, and are destroyed by an excess of chlorine. During the first stage of the reaction, that is to say, while the crystals are forming, no evolution of hydrochloric acid is observed; consequently the crystals contain all the hydrogen of the bisulphide of methyl, and their formation is due to a simple fixation of chlorine. They are very difficult to isolate, on account of their great volatility and their strong tendency to decompose. To obtain a sufficient quantity for analysis, it is necessary to drop bisulphide of methyl successively into several flasks containing chlorine, quickly remove the crystals with a thin glass plate, press them between bibulous paper, and enclose them in a glass bulb previously weighed.

	<i>Crystals.</i>			<i>Riche.</i>
2 C	12.0	14.56	14.81
3 H	3.0	3.64	3.62
Cl	35.4	42.98	42.37
2 S	32.0	38.82	
$C^2H^2S^2, Cl$ 82.4 100.00				

May also be regarded as C^2H^2S, ClS .

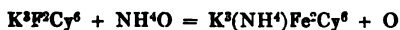
By the continued action of chlorine, this compound is decomposed, with formation of a liquid which is yellow at first, but alternately assumes a bright red colour, if the action of the chlorine be continued to the utmost, and in sunshine. On distilling this liquid, the first portion which passes over below 90° is found to contain a considerable quantity of chloride of sulphur; but the principal portion, which distils over between 150° and 160° , consists chiefly of terchlorinated methylic sul-

the chlorine, and monosulphide of methyl which is transformed by the chlorine in the same manner as if it were in the free state. The crude product is but very slowly altered by contact with water or with potash. (Riche.)

Double Ferrocyanides.

F. REINDEL. *J. pr. Chem.* 65, 450.

Ferrocyanide of Potassium and Ammonium. — $K^2(NH^4)Fe^2Cy^6 = (K^2NH^4)Cy^4, 2FeCy$. — Obtained by the action of ammonia on ferricyanide of potassium in presence of a reducing agent.



When ammonia is poured upon a mixture of ferricyanide of potassium and grape-sugar, (in the proportion of 20 : 1,) in a loosely stoppered bottle, and the liquid left to stand for several days, with frequent shaking, its colour gradually becomes paler, and in eight or ten days changes to a pure yellow. In most cases, when large quantities are taken, yellow crystals are soon deposited. The product is always the same, even when the ammonia is in excess. The pure solution of the yellow salt may be evaporated to the crystallising point without decomposition; but the presence of undecomposed grape sugar and ammonia, gives rise to other actions during the evaporation; hence it is best to precipitate the salt from the liquid by alcohol and recrystallise from water. — The alkaline sulphites effect the reduction more quickly than grape-sugar, but are less convenient, on account of the difficulty of separating the resulting sulphates.

Pale yellow square prisms, which are partially decomposed, even between 80° and 100°, and at higher temperatures give off hydrocyanic acid and cyanide of ammonium. Dissolve easily in cold, and still more in hot water. The solution behaves with metallic salts, like ordinary yellow prussiate of potash. When heated with a fixed alkali, it gives off ammonia, and yields a similar salt in which the ammonia is replaced by the alkali-metal used. (Reindel.)

	<i>Crystals.</i>		<i>Reindel.</i>	
3 K.....	117.6 29.28	29.58
NH ⁴	18.0 4.48	4.65
2 Fe	56.0 13.94	13.87
6 Cy	156.0 38.85	38.77
6 HO	54.0 13.45		



Ferrocyanide of Potassium and Sodium. $K^2NaFe^2Cy^6 = (K^2Na)Cy^4, 2FeCy$. — Obtained by treating a mixture of ferricyanide of potassium and grape sugar with caustic soda, or by boiling a solution of the preceding salt with caustic soda; the product may be purified by preci-

pitation with alcohol and recrystallisation. Forms rhombic or nearly square prisms, having a glassy lustre; they are not efflorescent, and do not give off their water below 200°. Dissolve readily in water, either hot or cold. (Reindel.)

	<i>Crystals.</i>		<i>Reindel.</i>	
3 K	117·6 28·29	28·18
Na.....	23·0 5·55	5·34
2 Fe.....	56·0 13·47	13·56
6 Cy.....	156·0 37·54	37·75
7 HO	63·0 15·15	15·14
<hr/>				
$K^2NaFe^2Cy^6 + 7Aq$	415·6 100·00	99·97

When chlorine gas is passed through a solution of this salt, chloride of potassium is separated and a salt is formed, which appears to be composed of $(K^2Na)Cy^2, Fe^2Cy^2 + xAq$. This and two other salts derived from it, viz., $(K^2Na^2)Cy^4, 2FeCy$ and $(K^2NaNH^4)Cy^4, 2FeCy$, are reserved for further investigation. (F. Reindel.)

ADDITIONS TO VOL. VIII.

Page 4.

Ammoniacal Cuprosocupric Cyanide. — $2\text{NH}^3, 2\text{Cu}^2\text{Cy}, \text{CuCy}$. — When an ammoniacal solution of hydrated cupric oxide is poured into aqueous hydrocyanic acid, till the odour of the ammonia becomes distinctly predominant, the clear, slightly yellow solution then heated to the boiling point, and an additional quantity of the ammoniacal copper-solution continually added, (while the heat is still continued,) till the dark blue colour becomes permanent, micaceous, crystalline laminæ make their appearance after a while; and the liquid, if then filtered, yields, on cooling, green rectangular laminæ of remarkable lustre; these, after complete cooling, may be purified by filtration and washing with cold water; they are then dried, first upon paper in the air, and afterwards over chloride of calcium. — When these green crystals are immersed in a mixture of equal volumes of moderately dilute solutions of caustic ammonia and carbonate of ammonia, and the liquid heated, they dissolve and form a blue solution. On boiling this solution for about an hour, and then leaving it to cool, it deposits blue shining laminæ, which may be collected on a filter, and completely purified by washing with cold water. — During the boiling, the blue ammoniacal liquid often becomes turbid, in consequence of the separation of a brown substance, but it may be rendered clear again by addition of ammonia. (L. Hilkenkamp, *Ann. Pharm.* 97, 218.)

<i>Blue crystals.</i>		Hilkenkamp.	
2 NH ³	34	12·59	12·66
5 Cu	158	58·52	58·22
3 Cy	78	28·89	28·73
<hr/>			
2NH ³ , 2Cu ² Cy, CuCy	270	100·00	99·61
<hr/>			
Or:		Hilkenkamp.	
2 NH ³	34·0	12·59	
2 Cu ² Cy	178·4	66·07	66·90
CuCy	57·6	21·34	
<hr/>			
	270·0	100·00	
 <i>Green crystals.</i>		 Hilkenkamp.	
2 NH ³	34	11·80	11·56
5 Cu	158	54·87	54·37
3 Cy	78	27·08	27·30
2 HO	18	6·25	
<hr/>			
2NH ³ , 2Cu ² Cy, CuCy + 2Aq	288	100·00	

The quantity of cuprous cyanide in the green crystals was found by analysis to be 60·85 p. c.; the formula requires 61·97.

The green compound is hydrated, perfectly insoluble in cold water, and is decomposed by boiling with water, a bulky brown precipitate being then formed. When dry, it may be heated to 100° without decomposition; but when heated to that temperature in the moist state, it is gradually decomposed as by boiling with water. It is decomposed by dilute acids, leaving a white residue of cuprous cyanide, [which dissolves, with evolution of hydrocyanic acid, when the liquor is heated. Solutions of caustic fixed alkalis, or alkaline carbonates, change the colour of the green crystals to blue, even at ordinary temperatures. Caustic fixed alkalis take up cuprous cyanide, which, on boiling, turns brown, and is converted into cupric oxide; in the solution formed by fixed alkaline carbonates, a small portion of the green compound is converted into the blue anhydrous crystals. This solution when boiled, likewise yields a brown precipitate, but the supernatant liquid, as it cools, deposits splendid blue laminae of the anhydrous salt. The green crystals dissolve in ammonia and carbonate of ammonia, and partly separate out unaltered as the liquid cools, but partly converted into the blue compound, especially after long boiling. (*Vid. sup.*)

The blue compound behaves like the green crystals with all reagents, excepting those which converted the latter into the former. (Hilkenkamp.)

Page 43—58.

Platinocyanides.

A. SCHAFARIK. *Wien. Akad. Ber.* 17, 57; *Chem. Gaz.* 1855, 441.

Protocyanide of Platinum. PtCy. — Schafarik prepares this compound by heating platinocyanide of ammonium for some time to 300° on the sand-bath. The yellow crystals first become pure white, but afterwards again assume a yellow colour, give off a light and very pungent vapour, and ultimately leave pseudomorphous crystals of protocyanide of platinum, which, when more strongly heated, smoulder away on access of air, leaving spongy platinum in distinct pseudomorphous crystals. — Hydroplatinocyanic acid boiled with nitric acid likewise yields a very pure protocyanide of platinum, together with other products not yet examined. In the products obtained by these two processes, and likewise in that prepared by Knop's method (viii, 43), Schafarik found 75.24, 75.59, 76.05, 76.36, and 77.18 p. c. platinum. Now the formula PtCy requires 79.20 p. c.; Schafarik, however, regards the several products which he analysed as the protocyanide contaminated with variable quantities of foreign matters, which could not be removed by washing.

Platinocyanide of Ammonium. $\text{NH}_4\text{PtCy}_2 + \text{Aq.}$ — Obtained by precipitating a solution of platinocyanide of barium with a mixture of caustic ammonia and carbonate of ammonia; the filtrate, when slowly evaporated, yields slender prisms of a deep lemon-yellow colour, and exhibiting a splendid blue fluorescence on the surface. These crystals, placed under a bell-jar with caustic lime on which ammonia is dropped, become

white crystals recover their yellow colour, though slowly, on exposure to the air; but if placed over sulphuric acid, they remain white. Colourless needles are likewise obtained by adding caustic ammonia to a very strong solution of the salt, and evaporating over the water-bath; these also, when exposed to air, take up water and turn yellow. (Knop attributed this change to loss of water, but analysis shows that the yellow crystals contain more water than the white. Both the white and the yellow salt give off their water, but not entirely, at 100°; at 150°, they part with the whole, amounting for the yellow salt, to 10.05 (2 At.), and become milk-white or pearly.) Any brown colour which they may exhibit after drying, when prepared by Quadrat's method, (viii. 46), is due to impurities in the ether or alcohol used in the preparation. When the anhydrous salt is dissolved in absolute alcohol, and the solution evaporated over sulphuric acid, crusts of colourless, radiating needles shoot out from the margin of the vessel, and at last coat the whole surface with a network exhibiting a beautiful violet fluorescence; on exposure to the air, they rapidly turn yellow. The yellow salt dissolves in about its own weight of water, and a smaller quantity of alcohol.

<i>Anhydrous.</i>			Schafarik.	
NH ⁴	18	10.65		
Pt	99	30.77		
2 Cy	52	58.58	58.05	58.88
<hr/>				
NH ⁴ Cy, PtCy	169	100.00		
<i>White, hydrated.</i>			Schafarik.	
NH ⁴	18	10.02		
Pt	99	55.62	55.88	
2 Cy	52	29.35		
HO	9	5.01	5.10	
<hr/>				
NH ⁴ PtCy ² + Aq.	178	100.00		
<i>Yellow.</i>			Schafarik.	
NH ⁴	18	9.63		
Pt	99	52.94	52.22	
2 Cy	52	27.80		
2 HO	18	9.63	10.05	
<hr/>				
NH ⁴ PtCy ² + 2Aq.	187	100.00		

Platinocyanide of Potassium. — Of the several methods given for the preparation of Gmelin's salt, Schafarik regards that of Knop (viii, 47, 2), as the most convenient. He finds, in accordance with the results of Gm., Laurent, Gerhardt, and others, that it has always the composition KCy, PtCy, not that assigned by Quadrat.

Platinocyanide of Sodium. — Platinocyanide of barium prepared by Quadrat's method (viii, 52), was dissolved in a little hot water, and mixed with excess of sulphate of soda; 10 times its volume of a mixture of alcohol and ether was then added; and the liquid filtered after standing for several hours. The clear solution, evaporated, first in the air and afterwards in vacuo over oil of vitriol, was entirely converted into beautiful, colourless, brilliant, glassy prisms of the sodium-salt, about 8 mm. long and 1 mm. thick.

<i>Crystals.</i>		<i>Schafarik.</i>	
Na	23	11·44	11·58
Pt	99	49·25	48·62
2 Cy	52	25·88	
3 HO	27	13·43	13·85
<hr/>		<hr/>	
NaCy, PtCy + 3Aq.....	201	100·00	

Platinocyanide of Barium. — Most easily obtained by dissolving platinocyanide of potassium in the smallest possible quantity of cold or moderately warm water; adding 1 At. of pure monohydrated sulphuric acid (23 pts. acid to 100 pts. of the potassium salt), taking care to avoid overheating, which would separate protocyanide of platinum; and afterwards adding 10 times the volume of alcohol, of sp. gr. 0·863: the addition of a little ether facilitates the precipitation of sulphate of potash. The mixture is then immersed in cold water for several hours to complete the deposition of the sulphate of potash; and the filtrate evaporated to one-third, mixed with water, and saturated at the boiling heat with carbonate of baryta. The barium-salt thus obtained is quite pure, as the traces of potassium-salt taken up by the alcohol remain in the mother-liquor. — Quadrat's method of preparing this salt from the platinocyanide of copper is troublesome, on account of the difficulty of washing the copper-salt.

Platinocyanide of Strontium. — Prepared by saturating platinocyanide of hydrogen with carbonate of strontia, or by Quadrat's method of decomposing the copper-salt with strontia-water. — Forms sometimes milk-white, sometimes transparent crystals, which, when exposed to the air, acquire a violet tint throughout. The white crystals obtained by the second method are also surrounded with a crust of indistinct yellow crystals, which, however, become white when laid on paper over night. — The white or transparent crystals, left over sulphuric acid for 24 hours, acquire a splendid purple-violet colour, like a solution of permanganate of potash, and at the same time a gold-green metallic surface-lustre; by exposure to the air for a few days, they completely regain their previous appearance. A solution of the salt swung round in a hot vessel, likewise coats it with a violet-purple crust, having a gold-green lustre: this purple tint appears to be due to a peculiar state of hydration. At 100°, the salt becomes turbid throughout, and acquires a deep orange colour, deeper than that of the dry barium-salt, the gold-green surface-lustre being at the same time converted into azure. At 150°, the salt becomes white and anhydrous, but is so sensitive to moisture that when breathed upon, it immediately acquires a blackish purple colour.

		<i>Schafarik</i> <i>(mean).</i>	
Sr	44	18·33	18·34
Pt	99	41·25	40·81
2 Cy	52	21·67	
5 HO	45	18·75	18·83
<hr/>		<hr/>	
SrCy, PtCy + 5Aq.....	240	100·00	

Of the 5 At. water, 7·71 p. c. (3 At.) are given off at 100°.

Platinocyanide of Calcium. CaCy, PtCy + 5Aq. — Resembles the strontium-salt, and also gives off 3 At. water at 100°.

carbonate of magnesia: the product obtained by this last method was darker in colour than that obtained by either of the former. If the salt, after being deprived of its water, be dissolved in hot absolute alcohol, of which it requires a considerable quantity, the whole liquid becomes filled, on cooling, with a tissue of delicate, white, satiny, filamentous crystals, which soon turn yellow on exposure to the air, and ultimately contract into crystalline crusts of a carmine-red colour with golden lustre. If the dry salt be dissolved in such a quantity of alcohol that no crystallisation takes place on cooling, and the solution left to evaporate in a shallow dish in a warm dry atmosphere, it yields thin rectangular tables, or rather laminæ, characteristically grouped in a fan-like form, and having a lemon-yellow colour, with a fine blue superficial fluorescence. These lemon-yellow crystals are evidently identical with the yellow masses into which the salt is converted between 30° and 45° (at 35°, according to Quadrat, viii, 54), while the asbestos-like needles are $MgPtCy^3 + 2HO$, the same salt into which the red-salt is converted at 100°.

	<i>Red crystals.</i>		<i>Schafarik.</i>			
Mg	12	5·31	5·79	5·53	5·36	
Pt	99	43·81	43·48	43·96	43·37	
2 Cy	52	23·01				
2 HO	18	7·96	7·05	6·45	8·29	
5 Aq	45	19·91	18·25	18·48	18·45	
		27·87	25·30	24·93	26·74	
$MgPtCy^2$, 2HO + 5Aq	226	100·00				

Of the 7 At. water, 5 At. (water of crystallization) go off at 100° and the rest at a higher temperature. — The determinations of platinum and magnesium in the above analysis agree with the formula, but the amount of water is too small. On the other hand, the formula $MgPtCy^2 + 6HO$ requires 5·53 p. c. Mg, 45·62 Pt and 24·89 water which does not agree so well with the platinum-determinations. The formula with 7HO is most probably correct. — Quadrat found in his salt 33·26 p. c. of water, of which 18·69 p. c. was given off at 100°. But he gives the formula $Mg^6Pt^8Cy^{11} + 8HO + 11Aq$, which represents only 16·70 p. c. water, but requires 48·34 p. c. platinum or about 5 p. c. more than the reality. To obtain 33 p. c. water, the formula should be $Mg^6Pt^8Cy^{11} + 47HO$, which gives 33·15 p. c. water, but only 38·8 p. c. platinum, which is 5 p. c. too little. The above quantities of platinum and magnesium calculated for the anhydrous salt, give, as a mean result, 60·45 p. c. Pt and 7·70 Mg, agreeing nearly with the formula $MgPtCy^2$, which requires 60·74 Pt and 7·36 Mg. [According to Schafarik's calculation, the amount of magnesium thus calculated for the anhydrous salt agrees with the formula $MgPtCy^2$, but that of the platinum is too small, agreeing more nearly with Quadrat's formula $Mg^6Pt^8Cy^{11}$; but in this there is evidently an error; the mere abstraction of the water cannot alter the relative quantities of the magnesium and platinum]. Baumert has also made two analyses of the anhydrous salt prepared according to Quadrat's method, and found 60·51 and 59·81 p. c. Pt and 7·38 to 7·28 Mg. These results, joined with the consideration that the salt is derived from the barium-salt, $BaPtCy^2$, sufficiently determine its constitution.

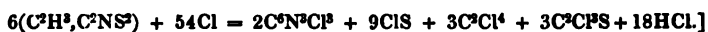
Platinocyanide of Copper. $CuPtCy^2$. — Produced whenever a soluble platinocyanide is mixed with the solution of a copper salt. Forms a bulky bluish or yellow green precipitate, which is completely deposited within 24 hours from a solution containing excess of the copper-salt, but remains for a long time suspended in pure water, and is very difficult to wash on the filter. When dried, it shrinks together remarkably, breaks up, and is converted into shining, sharp-edged fragments, of a deep grass-green or leek-green colour, which however yield a dull light green powder. The salt retains moisture very obstinately, not becoming com-

gen, which, as it goes off, burns with a beautiful purple flame bordered with yellow. The evolved gas has an extremely penetrating and powerful odour. The residue smoulders away in contact with air, leaving a black powder, probably platinum and oxide of copper. This powder, when boiled with nitric acid, yields copper to the acid, and leaves spongy platinum, but it is not possible to extract all the copper by this process. The best method of decomposing the salt for analysis is to spread it in fine powder, and in as thin a layer as possible, on a flat platinum dish; let it burn, first at a gentle heat; then calcine it strongly for a considerable time in a muffle; and, lastly, fuse with bisulphate of potash. A portion of the salt, prepared with platinocyanide of potassium which was obtained by Quadrat's method, and only once recrystallised (and, therefore, according to Quadrat = $K^6Pt^4Cy^{11}$) gave, when thus treated, 55.98 and 54.09 p. c. platinum, the last determination agreeing exactly with the formula $KPtCy^2$, which requires 54.10, whereas the formula $K^6Pt^4Cy^{11}$ requires only 50.87. — The salt suspended in water and treated with chlorine gas is very slowly attacked, yielding shining green crystals of platinidcyanide of copper. It is not attacked by sulphuric or by a mixture of sulphuric and nitric acids, even when boiled therewith for half an hour.

Platinocyanide of Mercury. — Platinocyanide of potassium forms with corrosive sublimate a white precipitate of platinocyanide of mercury, and with mercurous nitrate a precipitate, which is white at first, but as the quantity of mercurous nitrate is increased, becomes in succession yellow, green, and blue, the blue salt consisting of platinocyanide of mercury *plus* mercurous nitrate. (Döbereiner, viii. 57.) Rammelsberg found the blue salt to consist of $5HgPtCy^2 + Hg^2O, NO^2 + 10Aq$. This blue salt cannot be freed from mercurous nitrate by washing. If it be washed as much as possible, then pulverised, placed in a thin layer on a platinum dish covered with a glass plate, and heated to 200—250°, it gradually becomes snow-white, and the glass plate is seen to be coated with small globules of metallic mercury. If these be rubbed off after the salt has become white, it may then be heated for any time to the same temperature, without giving off more mercury; above 300°, it becomes slightly brown, but without change of composition. When slowly heated to redness in a covered vessel, it gives off mercury and cyanogen, and leaves yellow protocyanide of platinum, which, at a higher temperature, gives off more cyanogen and turns black; and this black mass burns quickly away when exposed to the air, leaving spongy platinum. (Schafarik.)

	<i>White salt.</i>		<i>Schafarik.</i>						
Hg	100	...	39.84	38.36	...	39.72	...	39.55
Pt.....	99	...	39.44						
2 C	52	...	20.72						
<hr/>									
HgPtCy ²	251	...	100.00						

Action of Chlorine on Sulphocyanide of Methyl. — Dry chlorine attacks sulphocyanide of methyl in the cold, even under the influence of mere diffused daylight; but the action soon comes to an end. The product is a liquid having a faint yellow colour, together with very beautiful colourless crystals of *solid chloride of cyanogen*. If the vessel be then exposed to direct sunshine, the quantity of these crystals continually increases, and a very mobile liquid (*a*) is finally obtained, having a fine red colour arising from *chloride of sulphur*, and containing a large quantity of crystals. This liquid begins to boil at 70°, but the last portions do not pass over below 200°. If the portion which distils over below 85° or 86° be shaken up with potash-ley, till the chloride of sulphur is completely decomposed, and the remaining liquid dried over fused chloride of calcium and distilled, a colourless aromatic distillate is obtained which boils at 80°, and exhibits the composition of *bichloride of carbon* C²Cl⁴ (analysis: 7.99 p. c. C and 92.3 Cl). This compound appears to be a constant product of the action of chlorine on the sulphuretted compounds of the methyl series (pp. 500°—504°). — The portion of the liquid (*a*) which passes over between 140° and 170°, shaken up with potash-ley, washed with pure water, then dried and carefully distilled, yields a very mobile amber-coloured liquid, which boils between 150° and 160°, and exhibits the composition and properties of perchlorinated methylic sulphide, C²Cl²S. — [The formation of these several products may be represented by the following equation :



(A. Riche, *N. Ann. Chim. Phys.* 43, 295.)

Formation of Alcohol from Olefiant Gas. — A large glass globe, capable of holding 31 or 32 litres, was exhausted of air and filled with olefiant gas; 900 grammes of pure and boiled sulphuric acid, poured into it in several separate portions; then a few kilogrammes of mercury; and the whole submitted to violent and long continued agitation: the gas was then gradually absorbed. After 53,000 agitations, the absorption became too slow, and the operation was discontinued; the quantity thus absorbed amounted to 30 litres. The acid was then mixed with 5 or 6 times its volume of distilled water; and, after repeated distillation, and subsequent separation by means of carbonate of potash, 52 grammes of hydrated alcohol were obtained, containing 45 grammes of absolute alcohol. This weight corresponds to $\frac{3}{4}$ of the olefiant gas absorbed, the rest was lost in the several manipulations.

The alcohol thus obtained exhibited all the characters of ordinary alcohol, having a spirituous taste and odour, distilling without residue at 79° to 81°, yielding olefiant gas when heated with oil of vitriol, and acetic ether when heated with a mixture of acetic and sulphuric acids.

To obtain further confirmation of the result, olefiant gas obtained by the action of hydrochloric acid and mercury on iodide of ethylene ($C^4H^4I^2 + 4Hg = C^4H^4 + 2Hg^2I$), was absorbed by oil of vitriol, and the liquid saturated with carbonate of baryta or lime; in this manner the sulphovinates of baryta and lime were obtained. The baryta-salt distilled with an acetate of soda, yielded acetic ether; with butyrate of potash, butyric ether; and with benzoate of potash, benzoic ether. This last product boiled at 210° , and when treated with potash, was resolved into benzoic acid and alcohol.

Lastly, to show that the same results may be obtained with olefiant gas not originally derived from alcohol, coal-gas was subjected to the action of iodine, and the resulting iodide of ethylene decomposed by heating it with potash. The pure olefiant gas thus obtained was absorbed by sulphuric acid as before, and by the series of operations just described, benzoic ether was obtained, which, when distilled with potash, yielded benzoic acid and alcohol. (Berthelot, *N. Ann. Chim. Phys.* 43, 385; compare Faraday and Hennel, viii. 416.)

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Action of Heat upon the Acetates of Iron.—A solution of pure ferric acetate, heated to 100° for four or five hours, becomes opaline, appears turbid by reflected, though it remains transparent by transmitted light, and changes in colour from that of venous blood to brick-red. The solution continues in this state after standing for several days. After standing for 25 to 30 hours (not consecutive), it completely loses the taste of iron-salt, and acquires that of vinegar; when boiled in a shallow open vessel, it gives off a large quantity of acetic acid, and remains limpid for a while, but in the course of $1\frac{1}{2}$ to 2 hours, deposits the whole of the iron in the form of ferric hydrate. The solution thus transformed no longer exhibits the usual characters of ferric salts; sulphocyanide of potassium does not heighten its tint; the ferrocyanide, like other potassium salts, forms in it a brown ochreous precipitate, which acquires a greenish tint by long contact. A trace of sulphuric acid or an alkaline salt precipitates all the iron in the form of a reddish brown deposit, which is insoluble in all cold acids, even when concentrated, is dissolved by boiling hydrochloric acid, but is not acted upon by nitric acid.

When the liquid is poured into hydrochloric or nitric acid, a brick-red granular precipitate is thrown down, which collects at the bottom of the vessel and cakes together very easily. This precipitate, which has no resemblance in its form to ordinary ferric hydrate, may be washed without alteration with the strongest hydrochloric or nitric acid, and even with aqua-regia; but if the mother-liquor be freed by one or two decantations with water from the greater part of the acid which it contains, the precipitate disappears entirely, and a brick-red opaline liquid is produced, exactly like that formed by the modified acetate. In this manner, an indefinite number of precipitations and solutions may be effected by the use of hydrochloric or nitric acid; but if any other acid (except acetic acid) be substituted, the deposit, when once formed, does not redissolve in pure water.—This substance is not precipitated by ordinary alcohol, by hydrochloric or nitric acid diluted with water, by acetic acid of any degree of concentration, or by the acetates of

acid; but it was found impossible to separate the latter acid completely, or to obtain a pure aqueous solution of the ferric compound. Nevertheless, by spreading the precipitate upon a plate of unglazed porcelain, the mother-liquor was almost entirely absorbed, and the substance was obtained in the form of a moist varnish, very slightly acid, entirely soluble in pure water, and having no appreciable taste; when dried in vacuo, it became insoluble in water. — The watery solution, when boiled, also deposits insoluble ferric hydrate; but the precipitation is prevented by the presence of acetic acid.

The opaque appearance presented by the acetate, when modified by heat and viewed by reflected light, appears to arise from the formation of a kind of pseudo-solution, like that of prussian blue in oxalic acid.

Hydrated ferric oxide, precipitated from the chloride by ammonia or bicarbonate of soda, and thoroughly washed, is also modified by boiling, acquiring the brick-red colour which characterises the modified acetate, and becoming insoluble in acids in the cold, and altogether indifferent in its chemical relations as compared with the ordinary hydrate. When heated however with acetic acid, and also with nitric or hydrochloric acid, it is taken up, and forms a liquid which exhibits all the characters of the modified acetate, being transparent by transmitted, but turbid and of a brick-red colour by reflected light. The acetic acid therefore is not an essential element of the action. (L. Péan de St.-Gilles, *Compt. rend.* 40, 568, and 1243.)

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Action of Chlorine on Sulphide of Ethyl.

A. RICHE. *N. Ann. Chim. Phys.* 43, 297

1. *Bichlorinated Ethylic Sulphide.* — When chlorine is cautiously passed into a vessel containing pure and dry sulphide of ethyl, care being taken to prevent rise of temperature and to keep the vessel in the shade, the gas rapidly disappears, and hydrochloric acid is disengaged in considerable quantity. At first the chlorine must not be passed directly into the liquid, because the action is very violent and the liquid might take fire; but afterwards the rapidity of the action diminishes, and the gas-delivery tube may be allowed to dip below the surface. If the quantity operated on be from 12 to 15 grammes, the action is complete in four hours.

To purify the product from dissolved chlorine and hydrochloric acid, it is heated to 75° or 80°, and a rapid current of carbonic acid gas passed through it. There is then obtained a yellowish liquid, heavier than water, which begins to boil at 150°; the greater portion, however, passes over between 163° and 173°, and the boiling point then rises to 230°; but the liquid no longer distils over unaltered, part of it being decomposed, hydrochloric acid being evolved, and a carbonaceous residue remaining in the retort.

The liquid which passes over between 163° and 173° is redistilled, the greater part then passing over between 167° and 172°; and this

portion, when again rectified, forms a light yellow liquid of sp. gr. 1.547 at 12°, and having a strong and disagreeable odour. An alcoholic solution of potash or monosulphide of potassium decomposes it, giving rise to viscid, fetid products not yet examined.

				Riche.
4 C	24.0	...	21.09 21.27
3 H	3.0	...	2.64 3.01
2 Cl	70.8	...	62.27	
S	16.0	...	14.00	
<hr/>				
C ⁴ H ³ Cl ² S	113.8	...	100.00	

2. *Terchlorinated Ethylic Sulphide.*—If the vessel containing the sulphide of ethyl be left at the temperature of the air, instead of being cooled, and the passage of the chlorine be continued by diffused daylight as long as it is absorbed, a liquid is obtained which is blackish at first, but ultimately acquires a deep yellow colour. It is freed from chlorine and hydrochloric acid by a stream of carbonic acid, and then fractionally distilled. The temperature rises rapidly to 185°, and a distillate is first obtained which boils between 185° and 200°, and when carefully re-distilled, assumes a decided yellow tint, and boils almost entirely between 189° and 192°.

				Riche.
4 C	24.0	...	16.19 15.37
2 H	2.0	...	1.35 1.35
3 Cl	106.2	...	71.66 72.40
S	16.0	...	10.80	
<hr/>				
C ⁴ H ² Cl ³ S	148.2	...	100.00	

3. *Tetrachlorinated Ethylic Sulphide.*—After the terchlorinated compound, which is the chief product of the preceding reaction, has distilled over, the boiling point rises to 240°, and a second distillate is then obtained, not however without decomposition and the evolution of a considerable quantity of hydrochloric acid. When this product is carefully fractionated, the greater part is found to boil at about 220°; and on once more redistilling this portion and collecting apart that which passes over between 217° and 220°, a liquid is obtained, having nearly the composition of the tetrachlorinated sulphide. — This product is however obtained more easily and in greater quantity, by passing chlorine in large excess and for a long time, through sulphide of ethyl heated to a temperature between 60° and 80°.

				Riche.
4 C	24.0	...	13.14 12.89
H	1.0	...	0.55 0.81
4 Cl	141.6	...	77.55 77.20
S	16.0	...	8.76	
<hr/>				
C ⁴ HCl ⁴ S	182.6	...	100.00	

The action of chlorine in diffused daylight does not yield any product containing a larger proportion of chlorine than the tetrachlorinated sulphide; but if the liquid be exposed for a considerable time to the sun, and the stream of chlorine kept up, that gas is again absorbed and hydrochloric acid evolved in abundance. By continuing this action as long as the atmosphere of chlorine in the vessel continues to lose colour, a light yellow liquid is obtained, which deposits very well defined

passed carbonic acid through it, it begins to boil at 175°; and if the product which passes over up to 185° be collected apart, it solidifies on cooling. — From 185° to about 200°, there passes over a second product, which remains liquid and has a deep yellow colour; and at 200°, nothing remains in the retort, there being no carbonaceous residue in this case.

The crystals which boiled at 180°, exhibited the composition of sesquichloride of carbon, C⁴Cl⁶, yielding by analysis 9·7 p. c. C, and 88·2 Cl, whereas the formula requires 10 C and 90 Cl. — The other crystalline product doubtless consisted of perchlorinated ethylic sulphide, C⁴Cl⁶S, being homologous with the compound C²Cl⁴S (vii. 355), formed under similar circumstances from sulphide of methyl; but the analysis was prevented by an accident. (Riche.)

Page 378.

Preparation of Chloride of Ethylene. — A tubulated retort is half filled with a mixture of 2 pts. peroxide of manganese, 3 pts. common salt, 4 pts. water, and 5 pts. oil of vitriol, and loosely connected with a flask, to serve as a receiver. Olfiant gas is then passed into the mixture by means of a tube passing through the cork of the tubulure and dipping half an inch below the surface of the liquid. So long as the gas is passing through the mixture, the retort must be only very gently heated, — as by placing a single red-hot coal under it, — and the resulting chloride of ethylene afterwards distilled off at a higher temperature. If this precaution be attended to, the operator will not be annoyed by escape of chlorine. — Coal-gas, if at hand, may be used as the source of the ethylene; if not the gas may be prepared from alcohol by Wöhler's method (ix. 517.) The crude product thus obtained in an hour and a half from 2 ounces of alcohol, yielded 1 ounce of pure chloride of ethylene. (H. Limpricht, *Ann. Pharm.* 94, 243; *Chem. Soc. Qu. J.* 8, 157.)

Pages 222 and 415.

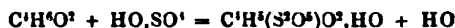
Action of Sulphuric Acid upon Alcohol. Constitution of Sulphovinic Acid.

C. BLONDEAU. *N. J. Pharm.* 28, 5.

Sulphovinic acid is usually represented by the formula C⁴H⁶O²,2SO³, or C⁴H⁶O,HO,2SO³, or $\left. \begin{array}{l} \text{C}^4\text{H}^6 \\ \text{H} \end{array} \right\} 2\text{SO}^4$. Gay-Lussac, however (viii. 417), regarded it as containing, not sulphuric, but hyposulphuric acid, supposing that, in its formation, 1 At. oxygen from 2 At. sulphuric acid combined with 1 At. hydrogen to form water. This view of the constitution of sulphovinic acid is in accordance with the solubility of its salts, and with its proneness to decompose and give off sulphurous acid when

beated. Gmelin (*loc. cit.*) objects to this view,—that, whereas hyposulphuric acid, both in the free state and in its salts, is in many reactions resolved into sulphurous and sulphuric acid, sulphovinic acid, under the same circumstances, yields sulphuric acid and alcohol. Blondeau, however, finds that sulphovinate of lead, calcined with hydrate of potash, yields sulphate and sulphite of potash in equal numbers of atoms, just as isethionate of potash does when similarly treated. Now sulphate of potash, as found by Liebig and Berzelius, is not reduced to sulphite by ignition with any organic substance (viii. 219). Blondeau, therefore, adopts Gay-Lussac's view of the constitution of sulphovinic acid, regarding it as $C^4H^6(S^2O^5)O^2,HO$, that is to say, as alcohol in which 1 At. H is replaced by hyposulphuric acid.

The formation of sulphovinic acid by the action of sulphuric acid upon alcohol may then be represented by the equation:



According to Blondeau, this change takes place only between the temperatures of 135° and 140° ; below 135° , nothing is formed but an instable compound of the acid with the alcohol, and the mixture, if distilled, yields nothing but alcohol and water; above 140° , the sulphovinic acid is resolved into ether and hydrated sulphuric acid, according to the equation:

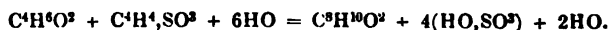


When vapour of alcohol is passed into a mixture of 2 pts. oil of vitriol and 1 pt. water, which boils at 140° , no formation of sulphovinic acid takes place, the alcohol-vapour passing through the boiling mixture quite unaltered; but if the tube which conveys the alcohol-vapour be removed, 10 grms. of sulphovinate of potash introduced into the retort, and the boiling continued, 2 grms. of ether condense in the receiver, a quantity corresponding exactly with that of the sulphovinate introduced. (Blondeau.)

[Robiquet (*N. J. Pharm.* 26, 161) takes a different view of the process of etherification. Regarding ether as alcohol + ethylene, he supposes the action of sulphuric acid upon alcohol to consist of two stages: 1. Oil of vitriol mixed with alcohol, at ordinary temperatures, forms water and sulphate of carbyl:



2. The water and sulphate of carbyl acting at higher temperatures, on a second atom of alcohol, produce ether and hydrated sulphuric acid, a portion of the water formed in the first stage being at the same time set free:



There is, however, no proof that oil of vitriol, mixed with alcohol at ordinary temperatures, forms sulphate of carbyl.]

Sulphovinates.—These salts are generally supposed to give off all their water when dried in vacuo over oil of vitriol (viii. 421–426); their composition, when thus dried, being represented by the general formula: $C^4H^6MO^2,2SO^2$, or $C^4H^6O,MO,2SO^2$. According to Blondeau's experiments, however, they retain, even at 100° , 1 At. HO more than is denoted by that formula: their true formula, when dried at that temperature, being $C^4H^6O^2,MO,2SO^2$; rather, $C^4H^6(S^2O^5)O^2,MO,HO$; and this last atom of

further decomposition. This statement is confirmed by the following analyses of the lead, barium, and calcium salts. To prepare these salts, 2 pts. of alcohol of 85 p. c. were mixed with 3 pts. of oil of vitriol, whereby a liquid was obtained which boiled at 140°, and gave off at that temperature a considerable quantity of ether. The liquid was removed from the fire, after boiling for a few seconds, then saturated with carbonate of lead, &c., and left to crystallise by cooling.

<i>Baryta-salt dried at 100°.</i>				Blondeau.
4 C	24.0	11.85	11.29	11.29
6 H	6.0	2.96	2.90	2.90
2 O	16.0	7.90	8.80	8.80
2 SO ³	80.0	39.50	39.39	39.39
BaO	76.6	37.79	37.62	37.62

$C^4H^6(S^2O^5)O^2, BaO, HO$ 202.6 100.00 100.00

<i>Lime-salt dried at 100° in vacuo.</i>				Blondeau.
4 C	24	15.58	15.41	15.41
6 H	6	3.89	3.92	3.92
2 O	16	10.38	11.14	11.14
2 SO ³	80	51.90	51.47	51.47
CaO	28	18.25	18.06	18.06

$C^4H^6(S^2O^5)O^2, CaO, HO$ 154 100.00 100.00

<i>Lead-salt dried at 100°.</i>				Blondeau.
4 C	24	10.10	10.08	10.08
6 H	6	2.52	2.39	2.39
2 O	16	6.74	6.73	6.73
2 SO ³	80	33.68	33.65	33.65
PbO	112	46.96	47.15	47.15

$C^4H^6(S^2O^5)O^2, PbO, HO$ 238 100.00 100.00

This salt, heated to 150° in a dry vacuum for about two hours, gives off 3 p. c. (1 At.) water, leaving the anhydrous sulphovinate $C^4H^6(S^2O^5)O^2, PbO$. (Blondeau.)

Stable Sulphovinates. (Parathionates). — Berthelot (*N. Ann. Chim. Phys.* 43, 391), by saturating with carbonate of baryta or lime, the sulphuric acid which had absorbed a quantity of olefiant gas (p. 511), has obtained stable sulphovinates similar to the β -sulphomethylates described by Church (p. 496.) The baryta-salt thus formed, yielded by analysis 55 p. c. sulphate of baryta, 10.3 C, 3.3 H (total), and 9.5 water of crystallisation, numbers which agree nearly with the formula $C^4H^6BaO^2, 2SO^3 + 2Aq$ (calculation: 55.1 BaSO⁴, 11.3 C, 3.3 H (total), and 8.5 water of crystallisation). This salt gives off its water in vacuo without becoming acid; its solution may be evaporated to dryness without decomposing. — The lime-salt is similar in properties and composition; it gave by analysis 41.8 CaSO⁴, and 12.0 Aq, the formula $C^4H^6CaO^2, 2SO^3 + 2Aq$, requiring 41.7 CaSO⁴ and 11.0 Aq. This lime-salt was obtained: 1. With olefiant gas and common sulphuric acid; 2. From the stable baryta-salt; 3. From the ordinary sulphovinate of lime, by repeated solution in water and ebullition. This is the process by which Gerhardt obtained the stable sulphovinate (parathionate) of baryta; it yielded, however, only traces of the corresponding lime-salt; 4. With a mixture of 3 or 4 vol. oil of vitriol and 1 vol. alcohol, which had given off nearly all its olefiant gas.

This is the process by which Regnault (viii. 431) obtained the althionates. Berthelot, however, by repeated fractional crystallisation of the baryta-salt pushed to the limit of complete evaporation, obtained nothing but the stable sulphovinate, agreeing with the ordinary sulphovinate in its form, and in the property of yielding benzoic ether when distilled with alcohol and benzoic acid.

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Action of Sulphuric Acid upon Ether.

BLONDEAU. *N. J. Pharm.* 28, 99.

The action of sulphuric acid upon ether is analogous to that which it exerts upon alcohol. The two bodies first enter into combination; then at 150°, decomposition takes place, and sulphetheric or isethionic acid $C^4H^4(S^2O^5)O$ is formed; and lastly, at 160°, this compound is resolved into olefiant gas and hydrated sulphuric acid.

Tribasic Sulphate of Ether. — When oil of vitriol is poured by degrees into ether, considerable rise of temperature takes place, and an oily liquid is formed, in which the properties of the acid are so far neutralised that chalk may be added to it without causing any evolution of carbonic acid. To ensure complete saturation, a slight excess of ether is added, which floats on the surface of the oily liquid, the density of the latter being 1.022. The compound is decomposed by water, the ether separating out.

				Blondeau.
3 C^4H^4O	111	73.51	
SO^3	40	26.49 26.23
<hr/>				
$3C^4H^4O, SO^3$	151	100.00	

The sulphuric acid was determined by decomposing the compound with water, decanting the ether, and precipitating with chloride of barium.

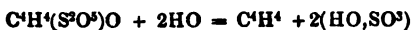
The compound, when heated, begins to boil at 45°, and gives off ether; but as the temperature rises, the affinity of the ether for the acid increases, and the boiling point soon rises to 150°; at 160°, the evolution of ether ceases. The quantity evolved amounts to $\frac{2}{3}$ of that which is contained in the compound, so that there remains a monobasic sulphate of ether C^4H^4O, SO^3 [identical, or at least isomeric, with Wetherill's compound (viii. 413).]

Sulphetheric or Isethionic acid. $C^4H^4(S^2O^5)O$. — Formed when the mixture of sulphuric acid and ether is heated to 150°—160°, 1 At. H from the ether then combining with 1 At. O of the sulphuric acid, and reducing it to hyposulphuric acid, which then takes the place of hydrogen removed:



At 160°, olefiant gas begins to escape; and if at the moment when this phenomenon is observed to commence, the liquid be removed from the

which may be crystallised. The lead salt thus prepared may be decomposed by sulphuretted hydrogen, and yields the acid in the form of a colourless liquid, which may be evaporated to a syrup, but does not crystallise. It has a very sour taste, and is much more stable than sulphovinic acid, undergoing no change when introduced into a mixture of sulphuric acid and water which boils at 150°. Above 160°, it is decomposed, olefiant gas being evolved, and hydrated sulphuric acid reproduced:



The production of olefiant gas by heating a mixture of oil of vitriol and alcohol or ether to 160° or upwards, takes place, therefore, in a manner precisely similar to that of the formation of ether from alcohol.

The *Sulphetherates* or *Isethionates* dried at 100° are isomeric with the sulphovinates dried at 150°, their formula being $C^4H^4MO^3, 2SO^3$, or rather $C^4H^4(S^2O^8)O, MO, HO$. They are less stable than the sulphovinates, and dissolve more readily in water. Heated to 200°, in contact with hydrate of lime, they give off ether, whereas the sulphovinates give off alcohol. The potash-salt fused with hydrate of potash, yields sulphite and sulphate of potash in equal numbers of atoms, which could not be the case if the rational formula of the salt were $C^4H^4O, KO, 2SO^3$ (p. 516); for sulphate of potash is not reduced to sulphite by ignition with organic matter (viii. 429). 100 pts. of the potash-salt fused with 100 pts. hydrate of potash, yield a product, which, when neutralised with hydrochloric acid and precipitated by chloride of barium, yields a quantity of sulphate of baryta corresponding to 52·60 pts. sulphate of potash, which is just half the quantity that should have been obtained if all the sulphur had been in the state of sulphuric acid.

Sulphetherate of Lead. — Obtained by heating the oily compound of sulphuric acid and ether (p. 518), till it begins to give off olefiant gas; removing the liquid from the fire after the ebullition has continued for a while; and saturating it when cold with carbonate of lead. The filtrate concentrated at a gentle heat, yields the lead-salt in transparent needles, which at 100°, give off their water of crystallisation, and become opaque.

<i>Dried at 100°.</i>		Blondeau.	
4 C.....	24	10·48	10·46
5 H	5	2·18	2·28
O	8	3·49	3·45
2 SO ³	80	34·94	35·30
PbO	112	48·91	48·51
$C^4H^4(S^2O^8)O, PbO, HO$		229	100·00
		100·00

If the salt thus dried at 100° be afterwards heated to 160° for an hour, it gives off 4 p. c. (1 At.) water, without further decomposition, and is reduced to $C^4H^4(S^2O^8)O, PbO$.

Sulphetherate of Baryta. — Prepared in a similar manner. The solution evaporated to a syrupy consistence, deposits, after a while, regular semi-transparent crystals. The solution decomposed by sulphuric acid, yields sulphetheric acid.

		Dried at 100°.		Blondeau.		
4 C	24.0	12.45	12.45
5 H	5.0	2.58	2.31
O	8.0	4.13	4.56
2 SO ²	80.0	41.34	41.29
BaO	76.6	39.50	39.39
C ⁴ H ⁵ (SO ²)O, BaO, HO		193.6	100.00	100.00

Sulphetherate of Lime. — Prepared like the preceding.

		Dried at 100°.		Blondeau.		
4 C	24	16.55	16.19
5 H	5	3.46	3.58
O	8	5.52	
2 SO ²	80	15.17	
CaO	28	19.30	19.15
C ⁴ H ⁴ (SO ²)O, BaO, HO		145	100.00	

Berthelot (*N. Ann. Chim. Phys.* 43, 397,) finds that sulphetheric, or an analogous acid, is produced in the action of anhydrous or of fuming sulphuric acid upon olefiant gas, ether, and alcohol, and likewise, though in small quantity, in the action of ordinary sulphuric acid on olefiant gas and on alcohol. — Sulphovinic acid is not converted into sulphetheric acid by the action of fuming sulphuric acid. The sulphetherates do not reproduce alcohol or the compound ethers, such as benzoic ether, under the same circumstances as the sulphovinates.

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Sulphocyanide of Ethylene. C⁴H⁴,2CyS².

H. L. BUFF. *Ann. Pharm.* 96, 302.

F. L. SONNENSCHN. *J. pr. Chem.* 65, 257.

Obtained by the action of sulphocyanide of potassium on chloride of ethylene (Buff, Sonnenschein):



Soluble to a certain extent in boiling water, and separates from the solution on cooling in small needles arranged in stellate groups. Dissolves readily in warm alcohol, and the solution, when cooled or evaporated, deposits the compound in large, beautiful, white, highly lustrous rhombic prisms. (Buff.) Has a peculiar odour intermediate between that of horse-radish and of asafœtida, and a pungent taste, producing a burning sensation in the throat. At 90°, it melts into a colourless oil, which is heavier than water, and on cooling solidifies in a beautiful radiate mass, which has a shining fatty appearance. By careful heating in the oil-bath, a small portion may be sublimed; but the greater part is carbonised, with evolution of hydrocyanic acid, and ammoniacal and other products (Sonnenschein); it gives off at the same time an odour like that of burnt onions. With vapour of water, it appears to volatilise without

(Dun.) The alcoholic solution does not give the characteristic reactions of the sulphocyanides with ferric salts. It is decomposed by potash, the liquid immediately acquiring a different odour and the reactions of a sulphocyanide, and depositing carbonate of potash. Ammonia does not immediately destroy the odour, but soon causes a white turbidity, and in the course of a few days, produces a flocculent precipitate; the solution then contains sulphocyanide of ammonium. Boiled for a while with baryta-water, it deposits carbonate of baryta and forms sulphocyanide of barium. — Recently precipitated lead-oxide is blackened by boiling with this compound, and the liquid is afterwards reddened by sesquichloride of iron; potash accelerates the blackening. Acids added to the liquid do not separate pseudosulphocyanogen. The alcoholic solution forms a white precipitate in a solution of mercuric chloride. (Sonnenschein.) — Sulphocyanide of ethylene boiled with baryta-water and lead-oxide or mercuric oxide, gives up sulphur; when mercuric oxide is present, there is formed, besides sulphide of mercury and carbonate of baryta, a sparingly soluble substance containing mercury. — With ammonia, sulphocyanide of ethylene forms a substance which dissolves easily in water, and yields sulphur to oxide of mercury. In this case also the desulphuretted product combines with the mercury. (Buff.)

Sulphocyanide of ethylene dissolves in chloride of ethylene. (Sonnenschein.)

The alcoholic solution of chloride of acetyl, C^4H^2Cl , forms with sulphocyanide of potassium a body which has a mustard-like odour. (Sonnenschein.)

ADDITIONS TO VOL. IX.

Page 16.

Acetone with Bisulphite of Soda. — Pure acetone shaken up with a concentrated solution of bisulphite of soda, dissolves with considerable evolution of heat, and the solution on cooling yields laminae of sulphite of acetone and sodium. This compound dissolves readily in water, less readily in alcohol. When heated alone, it gives off empyreumatic products. Distilled with a solution of carbonate of potash, it yields pure acetone. (H. Limpricht, *Ann. Pharm.* 93, 238.)

		Limpricht.	
6 C	36	22·2	21·3
7 H	7	4·3	4·1
3 O	24	14·8	15·7
NaO	31	19·1	19·2
2 SO ²	64	39·6	39·7
NaO, C ⁴ H ⁶ O ² , 2SO ² + Aq.		162	100·0

If acetone be regarded as aldehyde in which 1 At. H in the radical ethyl, is replaced by methyl, so that its formula is $\left. \begin{array}{c} \text{C}^4\text{H}^2(\text{C}^2\text{H}^2)\text{O}^2 \\ \text{H} \end{array} \right\}$, then the sulphite of acetone and sodium may be represented by the formula $\left. \begin{array}{c} \text{C}^4\text{H}^2(\text{C}^2\text{H}^2)\text{O}^2 \\ \text{Na} \end{array} \right\} \text{S}^2\text{O}^4 + 2\text{Aq.}$

Acetone with Bisulphite of Potash. — Prepared like the sodium-compound, which it resembles in all its properties. (Limpricht.)

		Limpricht.	
KO	47·2	27·90	27·21
C ⁶ H ⁶ O ²	58·0	34·28	
2 SO ²	64·0	37·82	
C ⁴ H ² (C ² H ²)O ² } S ² O ⁴ + 2Aq.		169·2	100·00

When acetone is mixed with a very strong aqueous solution of *bisulphite of ammonia*, it dissolves, with sufficient evolution of heat to make the mixture boil. — The solution does not, however, deposit any crystals, but, when evaporated, leaves the compound in the solid form, but still mixed with bisulphite of ammonia. The compound distilled with excess of lime yields ammonia, together with a volatile inflammable base. [Compare ix. 56.] (Limpricht.)

Stibethyl.

W. MERCK. *J. pr. Chem.* 66, 56.

Löwig and Schweizer, who discovered stibethyl (ix. 79) conclude from their analyses, that it combines with 2 atoms of O, Cl, I, &c., so that the formulæ of the oxide, chloride, &c. are SbAe^3O^2 ; SbAe^3Cl^2 , &c. Similar formulæ have also been assigned to the compounds of stibemethyl (vii. 322), and arsentriethyl (ix. 74). It is possible, however, that the true formulæ of the stibethyl-compounds may be $(\text{SbAe}^3\text{H})\text{I}^2$ or $(\text{SbAe}^3)\text{I,HI}$; $(\text{SbAe}^3\text{H})\text{Cl}^2$ or $(\text{SbAe}^3)\text{Cl.HCl}$, &c. the introduction of a single atom of hydrogen making but little difference in the percentage composition, e. g. in the chloride, 24.65 p. c. chlorine instead of 24.74.

To decide upon the true formula of stibethyl, Merck first tried the action of ammonia upon the iodide, but the results were not sufficiently definite to lead to any exact conclusion. — The action of stibethyl on an iodide of stibethyl was next tried. This action may be represented by one or other of the following equations, according to the formula adopted for the iodide :

- (1). $(\text{SbAe}^3)\text{I}^2 + \text{SbAe}^3 = 2(\text{SbAe}^3)\text{I}$
- (2). $(\text{SbAe}^3)\text{I}^2 + \text{SbAe}^3 = (\text{SbAe}^3)\text{I} + \text{SbAe}^3\text{I}$
- (3). $(\text{SbAe}^3)\text{I,HI} + \text{SbAe}^3 = (\text{SbAe}^3\text{H})\text{I} + (\text{SbAe}^3)\text{I}$
- (4). $(\text{SbAe}^3\text{H})\text{I}^2 + \text{SbAe}^3 = (\text{SbAe}^3\text{H})\text{I} + (\text{SbAe}^3)\text{I}$.

Stibethyl was dissolved in ether in a vessel filled with carbonic acid; one-half of the solution exactly saturated with iodine and added to the other; and the solution left to evaporate in a beaker, through which a stream of carbonic acid was continuously passed, by means of a caoutchic tube passing down the neck of a funnel inverted over the vessel, and reaching nearly to the surface of the liquid. After about half the quantity of ether present had been thus evaporated, large, hard, lustrous, regular octohedrons separated out. By further evaporation, more crystals of the same form were obtained, but at length a salt was obtained, differing from the first both by its form and by its greater solubility in water.

The octohedral crystals agreed in composition with the formula of iodide of stibtriethyl, SbAe^3I (p. 525), and the more soluble crystals gave, as a mean of three experiments, 36.72 p. c. iodine, agreeing with the formula $(\text{SbAe}^3\text{H})\text{I}$, which requires 36.73 per cent. The amount of iodine required by the formula SbAe^3I is much greater, viz. 40.26 p. c. As these results agree with the equations (3) and (4), and are inconsistent with (1) and (2), it follows that the formula of iodide of stibethyl cannot be $(\text{SbAe}^3)\text{I}^2$, but must be either $(\text{SbAe}^3\text{H})\text{I}^2$ or $(\text{SbAe}^3)\text{I,HI}$. This is further proved by the following experiments: 1. When an alcoholic solution of iodine is added to a solution of the octohedral salt $(\text{SbAe}^3)\text{I}$ in absolute alcohol, the iodine is but slowly taken up; but on gently heating the liquid [whereby hydriodic acid is formed,] the colour of the iodine disappears very quickly; the same

takes place when a little water is added. If iodine be added as long as its colour disappears, a white powder separates, and the filtered solution yields, by spontaneous evaporation, crystals of the so-called iodide of stibethyl. If, on the other hand, the aqueous solution of the octohedral crystals be mixed with hydriodic acid, the so-called iodide of stibethyl is immediately thrown down; this salt dissolves completely in alcohol, and may be obtained in beautiful crystals from the solution. But if iodine be added to the crystals last obtained, it cannot be made to disappear; and hydriodic acid added to this solution, produces no separation of iodide of stibethyl. — 2. When hydrochloric acid is added to the aqueous solution of the oxide ($\text{SbAe}^{\circ}\text{O}$), prepared from the octohedral iodide by means of oxide of silver (*vid. inf.*), each drop of the acid produces a white turbidity, which disappears on stirring; a certain quantity of acid, however, renders the turbidity permanent; and on adding a still larger quantity of acid, a colourless liquid separates, insoluble in water, containing 25.16 p. c. chlorine, and exhibiting all the properties of the so-called chloride of stibethyl. [$\text{SbAe}^{\circ}\text{Cl}^{\circ}$ or rather $\text{SbAe}^{\circ}\text{Cl.HCl}$, (ix. 83)]. If this liquid be added to an aqueous solution of the oxide, $\text{SbAe}^{\circ}\text{O}$, it dissolves immediately, and the solution yields by evaporation a chloride, readily soluble in water, and having the composition $\text{SbAe}^{\circ}\text{Cl}$; and if this solution be again mixed with hydrochloric acid, the insoluble chloride of stibethyl once more separates. — 3. If the so-called iodide of stibethyl be prepared directly, viz. by saturating an alcoholic solution of stibethyl with iodine (ix. 82), and its ethereal solution mixed with an alcoholic solution of the oxide ($\text{SbAe}^{\circ}\text{O}$), the mixture yields, by spontaneous evaporation, the same octohedral crystals that are obtained by the action of stibethyl upon the so-called iodide of stibethyl :



Whether the rational formula of the iodide, &c., of stibethyl be $(\text{SbAe}^{\circ})\text{I.HI}$ or $(\text{SbAe}^{\circ}\text{H})\text{I}^{\circ}$, &c., cannot be positively decided; but the former is the more probable.

From the preceding experiments, it appears that stibethyl, — or *stibtriethyl* as it is more exactly designated — is, like stibethylium, capable of uniting with 1 At. O, Cl, I, &c.; and the same is doubtless true with regard to the corresponding compounds, stibtrimethyl, arsentrimethyl, and arsentriethyl; we know also that the biethyl and bimethyl radicals, cacodyl, for example, form compounds of similar constitution; hence we may draw the general conclusion that: *All organo-metallic radicals are capable of uniting with 1 At. of oxygen, chlorine, &c.*

Compounds of Stibtriethyl, $(\text{C}^{\circ}\text{H}^{\circ})^{\circ}\text{Sb}$.

Oxide. $\text{SbAe}^{\circ}\text{O}$. — Obtained by decomposing the aqueous solution of the iodide with pure and recently precipitated oxide of silver. The filtrate contains a not inconsiderable quantity of silver-oxide in solution, which can only be partially separated by concentration, and must therefore be removed by careful precipitation with dilute hydriodic acid; hydrochloric acid cannot be used, because it dissolves the oxide in somewhat considerable quantity. The filtrate solution is then evaporated, first over the water-bath, and afterwards in vacuo over oil of vitriol.

an intensely bitter and biting taste, and a strong alkaline reaction. It is somewhat volatile, slight fumes being produced when a rod moistened with hydrochloric acid is held over its aqueous solution: it does not, however, diminish perceptibly in weight when kept, even for a long time, in vacuo over sulphuric acid.

<i>Calculation.</i>			
Sb	129	57.59
12 C	72	32.14
15 H	15	6.70
O	8	3.57
<hr/>			
(C ² H ⁵) ₃ SbO.....	224	100.00

The oxide dissolves readily in water, the solution being attended with considerable rise of temperature. The solution precipitates manganous, ferrous, ferric, cupric, mercuric and lead salts, without dissolving the precipitates in excess. In alumina and zinc salts, it forms white precipitates, soluble in excess.

Oxide of stibtriethyl is a strong base; its salts all dissolve readily in water, but sparingly in alcohol: they have a bitter taste, but no emetic action.

The oxide dissolves readily in alcohol, but sparingly in ether.

The *Sulphide* of stibtriethyl has not yet been obtained in the separate state. On saturating an alcoholic solution of the oxide with sulphuretted hydrogen and leaving it to evaporate, fine crystals are obtained, which appear to be identical with the so-called sulphide of stibethyl (ix. 81.)

Carbonate of Stibtriethyl. SbAe³O,CO².— Obtained by decomposing the iodide with carbonate of silver. On evaporating the filtrate over the water-bath, the salt remains in the form of a syrupy mass, without any trace of crystallisation.

Sulphate of Stibtriethyl. SbAe³O,SO³.— Obtained by decomposing the iodide with sulphate of silver. Does not crystallise; but by evaporation, first in the water-bath and then in vacuo over oil of vitriol, it is obtained in the form of a transparent gummy mass, which may be rubbed to a white powder. Deliquesces readily in the air, and dissolves in all proportions in water.

SbAe ³ O	224	84.93	Merck.
SO ³	40	15.07 14.91
<hr/>				
SbAe ³ O,SO ³	264	100.00	

Iodide of Stibtriethyl. SbAe³I.— Obtained either by exactly saturating the oxide with hydriodic acid, the latter being added in the state of dilute solution till it produces a permanent cloud, which may then be made to disappear by adding a drop of the oxide; or by the action of ammonia or stibtriethyl on iodide of stibtriethyl and hydrogen, SbAe³I,HI.

Crystallises very readily. By leaving the ethereal solution to evaporate large, hard, transparent, colourless, octohedrons or tetrahedrons are

obtained, which are inodorous, and have a glassy lustre. They exhibit no trace of decomposition when exposed to the air, even for weeks; they are anhydrous, and suffer no loss of weight in vacuo oil of vitriol. Crystals of the same form are obtained from the aqueous or alcoholic solution.

		Merck.			
		a.	b.	c.	d.
Sb.....	129	37.72	37.84		
12 C.....	72	21.05	20.69	20.65	20.70
15 H.....	15	4.39	4.53	4.63	4.52
I.....	126	36.84	36.68	37.70	37.10
<hr/>					
(C ⁴ H ⁶) ² SbI.....	342	100.00	99.74		36.93

a and *b* were obtained by the action of ammonia; *c* and *d* by that of stibethyl on the compound SbAe³I, HI.

An aqueous solution of mercuric bromide added to aqueous iodide of stibtriethyl, forms at first a yellow precipitate which, however, very soon changes to red, the decomposition being then complete. No doubt the yellow modification of mercuric iodide is formed at first, and afterwards passes into the red. This reaction distinguishes iodide of stibtriethyl from iodide of stibethylum (p. 528.)—When the bromide of mercury and iodide of stibtriethyl are mixed in exactly equal numbers of atoms and in the state of alcoholic solution, no precipitate is formed; but on evaporating the liquid, there remains a slightly yellowish oil, which, indeed, separates as the alcohol evaporates; when this oil is shaken up with water, red iodide of mercury immediately separates out, and bromide of stibtriethyl remains in solution.

Iodide of stibtriethyl is soluble in water, alcohol, and ether.

Bromide of Stibtriethyl. SbAe³Br. — Obtained by the action of bromide of mercury on iodide of stibtriethyl in alcoholic solution, in the manner just mentioned — or better, by adding bromide of barium to the aqueous sulphate of stibtriethyl, as long as a precipitate is formed. The filtrate evaporated over the water-bath, and then in vacuo over oil of vitriol, exhibited after a week, traces of crystallisation.

Chloride of Stibtriethyl. SbAe³Cl. — Obtained by decomposing the iodide with corrosive sublimate, the aqueous solutions of the two salts being mixed in exactly equal numbers of atoms; also by adding chloride of stibtriethyl and hydrogen to an aqueous solution of the oxide (p. 524.) Very soluble in water, and crystallises only from highly concentrated solutions; no definite crystals were obtained. Forms a white, radiated mass, which rapidly absorbs water from the air.

<i>Dried in vacuo over oil of vitriol.</i>		Merck.
Sb.....	129.0	51.35
12 C.....	72.0	28.63
15 H.....	15.0	5.96
Cl.....	35.4	14.06
<hr/>		
(C ⁴ H ⁶) ² SbCl.....	251.4	109.00

On adding hydrochloric acid to the aqueous solution of this salt, the acid chloride SbAe³Cl, HCl, separates in the form of a perfectly colourless liquid, containing 25.16 p. c. chlorine; the formula requiring 24.78 p. c.

substance is at length obtained, which, however, has not been further examined.

Nitrate of Stibtriethyl. — *a. Neutral.* — Prepared by decomposing the iodide with nitrate of silver. On evaporating the filtrate, first in the water-bath and then over oil of vitriol in vacuo, the whole solidifies in a solid radiated mass, which dissolves very easily in water, but does not deliquesce in the air.

<i>Dried in vacuo over oil of vitriol.</i>		Merck.
SbAc ² O	224	80.57
NO ⁵	54	19.43
SbAc ² O, NO ⁵		100.00

b. Acid. SbAc²O, HO, 2NO⁵. — When the neutral nitrate is dissolved in dilute nitric acid, and the solution evaporated over the water-bath, the acid salt separates in oily drops, which solidify in a crystalline mass on cooling; and on dissolving this mass in water and evaporating, the acid salt is obtained in beautiful rhomboidal crystals, which dissolve readily in hot water. The salt thus obtained exhibits all the properties of the nitrate of stibethyl obtained by Löwig & Schweizer (ix. 84), in which they found 32.01 p. c. nitric acid; the above formula requires 31.67.

Acetate of Stibtriethyl. — When the solution of the oxide is saturated with acetic acid and the solution evaporated over the water-bath, there remains a thick syrupy residue, which does not crystallise, even after long standing in a warm place. (Merck.)

Compounds of Stibethylium, (C⁴H⁵)⁴Sb.

R. LÖWIG. *J. pr. Chem* 64, 415; *Chem. Soc. Qu. J.* 8, 261.

Stibethylium is obtained in the form of an iodide by the action of iodide of ethyl on stibtriethyl. (Landol., ix. 85.)

The *Hydrated oxide* (C⁴H⁵)⁴SbO, HO, is obtained by decomposing the iodide with oxide of silver. Traces of dissolved oxide of silver are removed by the careful addition of hydrochloric acid. On evaporating the liquid in vacuo, the hydrate is obtained in the form of a thick, colourless, oily fluid, of a strongly alkaline and intensely bitter taste, which quickly renders litmus-paper blue. It dissolves in water and alcohol in all proportions, but is insoluble in ether. It sets ammonia free from its compounds, and precipitates the oxides of the heavy metals. Oxide of tin and alumina are again dissolved by the excess of the alkali. The salts of the alkaline earths are not decomposed by the base.

The salts are produced by bringing the base in contact with the

The carbonate is a tough deliquescent mass. The sulphate and nitrate crystallise. The formiate yields needle-shaped crystals, difficult of solution. The acetate forms similar crystals, but more soluble. The oxalate crystallises; the succinate does not. The neutral tartrate and racemate form large deliquescent crystals; the acid tartrate, fine needles.

Sulphide of Stibethylium. $(SbAe^4)S$, is obtained by treating oxide of stibethylium with sulphuretted hydrogen. When evaporated without access of air, it forms a yellowish oily liquid, which does not crystallise; it dissolves readily in water and alcohol, and behaves towards the salts of the metals like sulphide of potassium.

Iodide of Stibethylium. Prepared by introducing a mixture of equal parts of stibethyl and iodide of ethyl into a retort filled with carbonic acid, nearly filling the retort with water, sealing the neck, and then heating it in boiling water. Combination takes place in two or three hours, and the iodide may be obtained in crystals by evaporating the solution on the water-bath, and cooling. During this evaporation, the liquid generally acquires a yellow colour, which may, however, be removed by the addition of a few drops of ammonia.

Crystallises in beautiful hexagonal prisms, often an inch long, or in small pointed crystals, which become yellowish when exposed to the air. It has a very bitter taste. 1 pt. of it dissolves in 5.26 pts. of water at 20° . It dissolves more easily in absolute alcohol, but less easily in ether.

<i>Anhydrous.</i>				<i>Löwig.</i>
16 C	96	25.88 25.79
20 H	20	5.39 5.61
Sb	129	34.77	
I	126	33.96 34.28
$(C^4H^6)^4SbI$				371 100.00
<i>Hydrated.</i>				<i>Löwig.</i>
16 C	96	24.12 24.14
23 H	23	5.78 6.12
Sb	129	32.41	
I	126	31.66 32.06
3 O	24	6.03	
$(C^4H^6)^4SbI + 3Aq$				398 100.00

During the crystallisation of this compound, especially from warm solutions, another salt is often formed, with a different amount of water, viz. $2(C^4H^6)^4SbI + 3Aq$.

Bromide of Stibethylium. — $(C^4H^6)^4SbBr$ was obtained by saturating the oxide with hydrobromic acid. Crystallises in dazzling white, needle-shaped crystals, which dissolve very readily in water and alcohol, and do not deliquesce in the air. Gives by analysis 24.38 of bromine. Calculation gives 24.62.

Bromate of Stibethylium appears to be formed, together with the bromide, by the action of bromine on the oxide.

Chloride of Stibethylium is obtained by saturating the hydrated oxide with hydrochloric acid, or by decomposing 4 At. of the iodide with 3 At. corrosive sublimate, the decomposition yielding 3 At. chloride of stibe-

water-bath. Has a strong bitter taste.

<i>Anhydrous.</i>		<i>Löwig.</i>	
16 C	96·0	34·29	33·29
20 H	20·0	7·01	7·76
Sb	129·0	46·04	7·63
Cl	35·4	12·66	11·13
(C ⁴ H ⁵) ⁴ SbCl		280·4	100·00

Iodide of Stibethylium and Mercury.—*a.* 3HgI,(SbAe⁴)I. — When a solution of mercuric chloride is added to a solution of iodide of stibethylium, a white precipitate is produced, which melts into an oily liquid even at a gentle heat. — Insoluble in water and ether, and dissolves with difficulty in boiling alcohol. Crystallises from this solution in columnar crystals. If the precipitate be allowed to melt under water of 70° C, it solidifies to a white mass, and only exhibits single red spots, but becomes entirely red after some time. If the mass which has become red be dissolved in boiling alcohol, the white salt separates again in hexagonal prisms. Both forms of the salt have the same composition, but the red crystals appear to belong to the regular system.

		<i>Löwig.</i>	
SbAe ⁴	245	23·35	
3 Hg	300	28·60	29·30
4 I	504	48·05	49·00
3HgI,(C ⁴ H ⁵) ⁴ SbI		1049	100·00

b. 3HgI,2(SbAe⁴I), is obtained by adding iodide of mercury to a hot solution of iodide of stibethylium, until it no longer loses its red colour. The conversion of the excess of iodide of mercury is then effected by a fresh addition of iodide of stibethylium; none of the latter remains in the liquid. The precipitate melts when heated, forming a yellow oil.

		<i>Löwig.</i>	
2 SbAe ⁴	490	34·51	
3 Hg	300	21·13	20·86
5 I	630	44·36	44·56
3HgI,2(SbAe ⁴ I).....		1420	100·00

Chloride of Stibethylium and Mercury.— Compounds exactly similar to those of iodide of mercury with iodide of stibethylium are obtained by bringing in contact chloride of mercury and iodide or chloride of stibethylium. 1 At. iodide of stibethylium with 3 At. chloride of mercury furnishes the iodine-compound which melts under water, whilst the water takes up the corresponding chloride, 3HgCl,(SbAe⁴)Cl. If concentrated solutions of chloride of stibethylium and mercuric chloride be mixed, a compound of the formula 3HgCl,2(SbAe⁴)Cl is obtained. The former salt is soluble in alcohol and water; the latter forms a white powder, which is difficult of solution in water.

Chloride of Stibethylium and Platinum, 3PtCl²,2(SbAe⁴)Cl. — Produced by mixing a somewhat dilute alcoholic solution of chloride of stibethylium with a similar solution of chloride of platinum, and evaporating

the mixture. It is a fine yellow compound, tolerably soluble in water and alcohol, which yields 27.78 p. c. platinum; calculation requiring 27.75 p. c. (Löwig.)

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Zinc-ethyl. C^4H^5Zn .

FRANKLAND. *Phil. Trans.* 1855; *Ann. Pharm.* 95, 28; abstr. *Proc. Roy. Soc.* 7, 303.

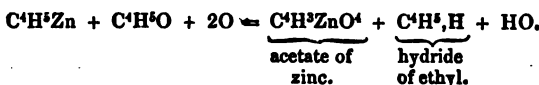
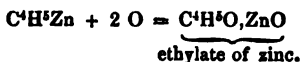
To obtain this compound in considerable quantity, Frankland uses a copper digester capable of resisting great pressure. Into this apparatus 4 oz. of finely granulated zinc, previously dried at 150° , are introduced, together with 2 oz. iodide of ethyl, and an equal volume of anhydrous ether, and the whole heated in an oil-bath to about 130° . The utmost care must be taken to ensure the perfect dryness of all the materials, as the smallest quantity of moisture gives rise to the formation of oxide of zinc and hydride of ethyl, and greatly diminishes the product; the addition of ether prevents, to a very great extent, the formation of these secondary products. When the action is complete, the digester is connected with a distilling apparatus of peculiar construction, and the product distilled in an atmosphere of carbonic acid. [For details of the digester and of the distilling apparatus, see the references above cited].

Colourless, transparent, mobile liquid, which refracts light strongly, and has a peculiar odour, rather pleasant than otherwise, thereby differing remarkably from zinc-methyl. Sp. gr. = 1.182 at 18° . Shows no tendency to solidify at -22° . Boils at 118° , and distils unchanged. Vapour-density 4.259.

						Frankland.
4 C	24.0	...	39.22	38.83
5 H	5.0	...	8.17	8.20
Zn	32.2	...	52.61	52.27
<hr/>						
C^4H^5Zn	61.2	...	100.00	99.30
Or:						Frankland.
C^4H^5	29.0	...	47.39	47.32
Zn	32.2	...	52.61	52.67
<hr/>						
C^4H^5Zn	61.2	...	100.00	99.99
		Vol.	Density.	Or:	Vol.	Density.
C-vapour	4	1.6640			
H-gas	5	0.3465	C^4H^5	1	2.0105
Zn-vapour	1	2.2471	Zn	1	2.2471
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Vap. of C^4H^5Zn	1	4.2576		1	4.2576

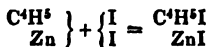
From this it would appear that the vapour-volume of zinc is equal only to that of oxygen, instead of that of hydrogen as is commonly supposed,—in other words that zinc-vapour is not monatomic but diatomic (i. 53). Zinc-ethyl appears therefore to belong to the so-called water-type (vii. 46), and to consist of 2 volumes of ethyl and 1 vol. of zinc-vapour, the three volumes being condensed into two; for, on the assumption that an atom of zinc occupies the same vapour-volume as an atom of hydrogen, we should have the anomaly of the combination of two gases in equal volumes attended with condensation.

upon zinc violence by oxygen, chlorine, bromine, &c.; nevertheless, it does not appear to be capable of forming any true compounds with electro-negative elements, its reactions being all double decompositions in which the constituents of the zinc-ethyl separate. On coming in contact with oxygen gas or atmospheric air, it takes fire spontaneously, and burns with a bright blue flame bordered with green, and gives off dense vapours of zinc-oxide. A cold body held in the flame soon becomes covered with a black film of metallic zinc, surrounded with a white border of oxide. The products of this rapid combustion are carbonic acid, water, and oxide of zinc. If, on the contrary, zinc-ethyl, diluted with three times its volume of ether, be introduced into a vessel filled with dry carbonic acid gas and immersed in a freezing mixture, and a stream of oxygen slowly directed upon it, a rapid action takes place, at first attended with formation of white fumes; but this soon ceases, and a white precipitate begins to separate; if the vessel be frequently shaken, to break a crust which forms on the surface, the action goes on slowly and steadily, and is complete in about four days. During the latter stage, after the white fumes have ceased to form, a considerable quantity of gaseous hydride of ethyl is evolved. The product of the oxidation is a white amorphous mass, consisting of ethylate of zinc $C^4H^5ZnO^3$, mixed with smaller quantities of acetate and oxide of zinc. One experiment yielded in 100 pts. : 68.28 p. c. ethylate of zinc, 16.70 acetate, and 15.02 oxide. The formation of these products is represented by the following equations:



The first action of the oxygen appears to be that represented by the first equation, and to continue as long as the vapours of zinc-ethyl are diffused through the vessel and absorb the oxygen as fast as it enters; after this, the second action takes place, hydride of ethyl and free oxygen being then present in the vessel together. Lastly, as hydrated oxide of zinc and zinc-ethyl could scarcely exist together, the action represented by the third equation probably takes place only after all the zinc-ethyl has been oxidised. The action of oxygen on pure zinc-ethyl was also tried in a similar manner, but did not yield any definite results, the oxidation being greatly disturbed and retarded by the formation of a solid crust on the surface of the liquid. As however the production of acetate of zinc and hydride of ethyl in the experiment above described is clearly due to the ether present, we may conclude that the essential product of the slow oxidation of zinc-ethyl is ethylate of zinc.

Zinc-ethyl is acted upon with great energy by *iodine*; when the violence of the action is moderated by the application of intense cold and the intervention of ether, the sole products are iodide of zinc and iodide of ethyl:



Bromine acts with explosive violence on zinc-ethyl, but the action may be moderated by adding the bromine in the form of diffused vapour, and cooling to 0°. The sole products are then bromide of ethyl and bromide of zinc.

Zinc-ethyl burns spontaneously, and with a lurid flame, in *chlorine* gas, forming chloride of zinc and hydrochloric acid, and depositing carbon. The products of a more moderate action are probably similar to the preceding.

When zinc-ethyl is gently heated with flowers of *sulphur*, a white precipitate is formed, and a strong odour of sulphide of ethyl developed. The principal product is mercaptide of zinc, C^2H^4S, ZnS .

Zinc-ethyl is decomposed by water into zinc-oxide and hydride of ethyl:



Hydrated acids act upon it in a similar manner.

The action of the electro-negative elements upon zinc-ethyl, combining as they do, partly with the zinc and partly with the ethyl, affords a striking example of the peculiar condition,—polarity as it may be called,—of elements at the moment of chemical change, originally pointed out by Brodie. (*Phil. Trans.* 1850, 789.) Ethyl in the free state shows no inclination to unite with oxygen, chlorine, &c., but in presence of zinc, it enters readily into combination with those elements. (Frankland.)

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Phosphate of Hydrargethyl.—Prepared by digesting tribasic phosphate of silver and chloride of hydrargethyl with weak alcohol, concentrating the filtrate at the gentlest possible heat, extracting the phosphate of hydrargethyl from the syrupy solution with water, and leaving the solution to evaporate in vacuo; it forms a viscid, translucent, nearly colourless mass.

Sulphate of Hydrargethyl was prepared by agitating 1 At. of finely pulverised sulphate of silver with the alcoholic solution of 1 At. chloride of hydrargethyl and evaporating the filtered liquid. Crystallises in silvery laminae.

				Dünhaupt.
2 Hg	200	...	72·20 71·43
4 C	24	...	8·66 8·88
5 H	5	...	1·81 1·90
O	8	...	2·89 3·39
SO ³	40	...	14·44 14·40
<hr/>				
C ² H ⁴ Hg ² O, SO ³	277	...	100·00 100·00

Nitrate of Hydrargethyl.—Obtained by saturating the base with nitric acid. Remains when the aqueous solution is evaporated over the water-bath, in the form of an oily liquid, which solidifies in a tallowy mass on cooling. It dissolves readily in water and alcohol, and burns away with slight detonation when heated.

2 Hg	200	...	08 75	
4 C	24	...	8 23	8 44
5 H	5	...	1 74	1 84
O	8	...	2 75	
NO ²	54	...	18 55	10 80
<hr/>				
C ⁴ H ⁵ Hg ² O, NO ²	291	...	100 00	

The Oxalate and Acetate of hydrargethyl are crystallisable. (Dünha. J. pr. Chem. 61, 399; Ann. Pharm. 92, 382.)

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Sodio-antimonic Oxalate. — When bioxalate of soda is boiled with large quantity of water and an excess of antimonic oxide, the solution yields on cooling an abundant crop of transparent shining crystals belonging to the oblique prismatic system. They are rhombic prisms with the acute lateral edges slightly truncated; and an oblique terminal face resting thereon. — (For the figures and crystallographical details of these the following salts, see Rammelsberg's Memoir, Pogg. 95, 177.) They are decomposed by water, like the potash-salt *a* (ix. 149,) with separation of antimonic oxide. (Rammelsberg.)

	Crystals.		Rammelsberg	
11 C ² O ³	396	...	39 54	39 11
5 NaO	156	...	15 62	16 41
2 SbO ³	306	...	31 36	30 39
15 HO	135	...	13 48	13 17
<hr/>				
5(NaO, C ² O ³) + 2(SbO ³ , 3C ² O ³) + 15 Aq.	993	...	100 00	99 08

This salt corresponds in composition, excepting that the amount of water is so great, with the potash salt above referred to, and like that salt may be regarded as consisting of [3(NaO, C²O³) + (SbO³, 3C²O³)] + [2(NaO, C²O³) + (SbO³, 3C²O³)]. It has not however been found possible to obtain one of these component salts separately, as was the case with the potash-salt. The mother-liquor contained one or two salts of different composition, but they could not be separated or obtained in distinct crystals. (Rammelsberg.)

Page 152.

Ammonio-cadmio Oxalate. — Recently precipitated cadmic oxide dissolves when boiled with a solution of neutral oxalate of ammonia, the liquid on cooling deposits the double salt in indistinct crystalline masses. This salt decomposes when heated in a covered crucible, ammonia being evolved and cadmium reduced, part of which volatilises; opening the crucible, the mass burns with a glimmering light, and forms brown cadmic oxide. (Rammelsberg, Pogg. 95, 196.)

			Rammelsberg	
5 C ² O ³	180	...	42 90	42 76
CdO	64	...	15 19	15 89
4 NH ⁴ O	104	...	24 78	25 01
8 HO	72	...	17 13	
<hr/>				
4(NH ⁴ O, C ² O ³) + (CdO, C ² O ³) + 8Aq.	420	...	100 00	

Page 152.

Stannous oxalate. — According to an analysis by Lürmann, this salt is anhydrous.

		Lürmann.	
2 SnO	136	65·37	64·45
C ⁴ O ⁶	72	34·63	35·00
<hr/>			
C ⁴ Sn ² O ⁸	208	100·00	99·45

Ammonio-stannous Oxalate. — Colourless transparent crystals, the form of which could not be determined, but appears to be identical with that of the potash-salt. (*inf.*) Analysis gave 40·23 p. c. oxalic acid, and 28·63 stannous oxide, agreeing with that of Hausmann & Löwenthal. (Rammelsberg, *Pogg.* 95, 195.)

Potassio-stannous Oxalate. — Obtained by precipitating protochloride of tin with oxalic acid, and boiling the precipitate with a solution of neutral oxalate of potash. Separates from the solution in transparent crystals, mostly very small: they belong to the doubly oblique prismatic system. (Rammelsberg.)

		Lürmann.	
SnO	68	34·66	34·79
KO	47	24·05	24·17
C ⁴ O ⁶	72	36·70	36·93
HO	9	4·59	
<hr/>			
C ⁴ SnKO ⁶	196	100·00	

The analysis agrees with that of Hausmann & Löwenthal.

Potassio-cobaltous Oxalate. — Oxalate of cobalt dissolves in a solution of neutral oxalate of potash, forming a red liquid, which deposits a double salt in small deep red crystals. Rhombic prisms, with truncated acute lateral edges and four-sided summits, the acute lateral edges of these summits being also truncated by faces resting on the lateral edges of the prism. Being very small, and having but little lustre, it was found impossible to measure them exactly, or to determine whether they belong to the right or the oblique prismatic system. They dissolve in water, forming a clear solution. (Rammelsberg, *Pogg.* 95, 197.)

Crystals.		Rammelsberg.	
CoO	37·5	17·79	18·37
KO	47·0	22·38	21·13
C ⁴ O ⁶	72·0	34·18	33·40
6 HO	54·0	25·65	
<hr/>			
C ⁴ CoKO ⁵ + 6Aq	210·0	100·00	

Potassium-nickel Oxalate. — Obtained like the cobalt-salt in green indistinct crystals of analogous composition. (Rammelsberg.)

Crystals.		Rammelsberg.	
NiO	37·5	17·82	17·98
KO	47·0	22·38	22·23
C ⁴ O ⁶	72·0	34·18	34·04
6 HO	54·0	25·62	
<hr/>			
C ⁴ NiKO ⁵ + 6Aq	210·5	100·00	

Ammonio-cupric Oxalate. — By heating cupric oxalate with neutral oxalate of ammonia, this salt is obtained in small but well defined rhomboidal prisms, belonging to the doubly oblique prismatic system, and isomorphous with those of the potash-salt with 2 At. water. Sometimes macled-crystals are obtained. (Rammelsberg.)

<i>Crystals.</i>		Lürmann.	
CuO	40	25·64	25·31
NH ⁴ O	26	16·67	16·72
C ⁴ H ⁶	72	46·15	45·60
2 HO	18	11·54	
<hr/>			
C ⁴ (Cu,NH ⁴)O ⁸ + 2Aq.	156	100·00	

The analysis agrees nearly with that of Vogel (ix. 165.)

Potassio-cupric Oxalate. — *a. With 2 At. water.* — Cupric oxalate obtained by precipitating the acetate with oxalic acid, is boiled with a solution of neutral oxalate of potash, so as to saturate the latter as completely as possible. On cooling, the double salt separates in crystals, belonging to the double oblique prismatic system, and having the colour of blue vitriol. The salt is decomposed by water, with separation of cupric oxalate. (Rammelsberg, *Pogg.* 95, 184.)

		Lürmann.	
CuO	40·0	22·57	22·42
KO	47·2	26·64	26·09
C ⁴ O ⁶	72·0	40·63	39·54
2 HO	18·0	10·16	
<hr/>			
C ⁴ CuKO ⁸ + 2Aq.	177·2	100·00	

The water is wholly expelled at 100°. At 200° the salt begins to decompose, and if the air be excluded, leaves a mixture of carbonate of potash and cuprous oxide. — In an experiment in which the salt was ignited in a small retort, the residue amounted to 57·8 p. c. Supposing this to contain 39·41 pts. of carbonate of potash, there remains 18·7 for the copper and oxygen. Now 22·57 CuO = 20·31 Cu²O. The experiment gave somewhat less, and yet no *metallic* copper could be detected in the residue. (Rammelsberg.)

b. With 4 At. Water. C⁴CuKO⁸ + 4Aq. The needle-shaped salt described by Vogel. It is often deposited after the preceding, but sometimes alone, especially when the solution contains an excess of oxalate of potash, a circumstance likewise observed by Vogel. The crystals do not admit of exact measurement, partly from their smallness, partly from the rapidity with which they effloresce. They are extremely thin six-sided prisms, in which angles of 108° 52' and 72° 30' have been observed. Lürmann's analysis gives 20·63 p. c. CuO and 23·42 KO. (Rammelsberg.)

Isomorphous mixture of Ammonio-cupric and Potassio-cupric Oxalates. — When cupric oxalate is heated in a mixed solution of the oxalates of ammonia and potash, crystals are obtained, having the form of either salt, and containing 2 At. of the ammonia-salt with 3 At. of the potash-salt. (Rammelsberg.)

			Lürmann.
CuO	40.0	23.70	23.96
$\frac{1}{2}$ KO	28.3	16.78	17.56
$\frac{1}{2}$ NH ⁴ O	10.4	6.17	6.90
C ⁴ O ⁵	72.0	42.68	41.27
2 HO	18.0	10.67	
C ⁴ Cu $\frac{1}{2}$ K $\frac{1}{2}$ (NH ⁴)O ⁵ + 2Aq.			168.7 100.00

Page 195.

Chloride of Othyl. (Acetyl) — C⁴H³O³,Cl. — According to H. Ritter, (*Ann. Pharm.* 95, 208,) Gerhardt's method of preparing this compound by the action of oxychloride of phosphorus on acetate of soda, never yields the calculated quantity, because a considerable quantity of anhydrous acetic acid is formed at the same time; the formation of the latter product may be diminished by gradually adding the acetate of soda to the oxychloride, but cannot be prevented altogether. But with glacial acetic acid and pentachloride of phosphorus, the chloride of othyl may be readily obtained in a state of purity, and in large quantity. 1 At. glacial acetic acid is added by separate portions to 1 At. pentachloride of phosphorus contained in a tubulated retort. Each portion added produces effervescence from escape of hydrochloric acid gas, and a large portion of the chloride of othyl distils over. The remainder and the resulting oxychloride of phosphorus are driven into the receiver by gentle heat, and the two liquids separated by distillation, the separation being easily effected, as their boiling points differ considerably. The mixture which ultimately remains in the retort, may be utilised for the preparation of anhydrous acetic acid, by distillation with acetate of soda.



Anhydrous acetic acid, distilled with pentachloride of phosphorus, likewise yields chloride of othyl, but without formation of hydrochloric acid.

Oxychloride and terchloride of phosphorus do not act upon glacial acetic acid. (Ritter.) According to Bechamp, on the other hand, terchloride of phosphorus acts both on monohydrated and upon anhydrous acetic acid, forming chloride of othyl (p. 487).

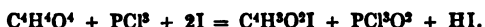
Bromide of Othyl. — C⁴H³O³,Br. — 1 At. glacial acetic acid and 1 At. pentabromide of phosphorus form bromide of othyl, oxybromide of phosphorus, and hydrobromic acid.



Colourless strong-smelling liquid, which instantly turns yellow on exposure to the air. A drop of it placed on the skin colours it yellow, and imparts to it a persistent odour, like that of phosphuretted hydrogen. Water quickly decomposes it, forming hydrobromic and acetic acid. Boils at about 81°.

			Ritter.
C ⁴ H ³ O ³	43	34.96	
Br	80	65.04	65.00
C ⁴ H ³ O ³ Br			123 100.00

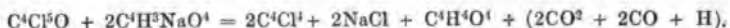
successful. Iodide of mercury or silver, heated with chloride of ethyl in a sealed tube, at the temperature of the water-bath, for several days produced no perceptible action. — When iodine and phosphorus were added alternately to glacial acetic acid, and the liquid distilled, a large quantity of hydriodic acid was evolved, and a liquid strongly coloured by iodine distilled over below 100°; but it continually gave off hydriodic acid, and did not exhibit a constant boiling point, even after several rectifications. The phosphorus was completely converted by this reaction into the red modification. — It might be expected that iodide of ethyl would be produced by the simultaneous action of the iodine and terchloride of phosphorus on glacial acetic acid, according to the equation :



but the process yields nothing but biniodide of phosphorus. (Ritter.)

Page 216.

Comburent properties of Perchlorinated Ether, C^4Cl^6O. — When perchlorinated ether acts upon an organic salt containing a volatile acid, the two bodies decompose each other, the perchlorinated ether being reduced to protochloride of carbon, C^4Cl^4, the metal being converted into chloride, and the other elements arranging themselves in such a manner as to produce the normal [monohydrated acid], together with carbonic acid and combustible gases. Thus with acetate of soda :

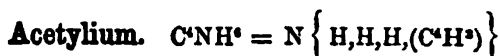


Similarly with the butyrates, valerates, benzoates, succinates, pyrocitrates, phthalates, camphorates, and salicylates. The alkaline salicylates, however, exhibit an exception in this respect, that, instead of salicylic acid, there is formed a mixture of various substances soluble in alkalis, which have not been further examined. — With the formiates, the result is more simple, inasmuch as the oxygen and chlorine present are sufficient for the complete combustion of the elements of the salt; thus,

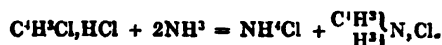


With the salts of bibasic acids, *e. g.* camphoric acid, a similar reaction occurs, excepting that, instead of the hydrated acid, there is obtained a mixture of the anhydrous acid [anhydride] with water. (Malaguti, *Compt. rend.* 41, 625.)

Page 247.

J. NATANSON. *Ann. Pharm.* 92, 48; *Chem. Soc. Qu. J.* 8, 150.*Acetylammonium.*

Obtained in the form of chloride by the action of chloride of ethylene (chloride of acetyl and hydrogen) on ammonia at high temperatures :



When 1 pt. of chloride of ethylene and 5 pts. of strong ammonia are enclosed in a sealed tube, and heated in an oil-bath to 150° (no action takes place at 100°), the chloride of ethylene is completely absorbed in a few hours, and the whole converted into a yellow, watery, homogeneous liquid. On opening the tube, the odour of chloride of ethylene is no longer perceptible; and if the liquid be left to evaporate over oil of vitriol, or in a warm place, sal-ammoniac separates, and a mother-liquor is obtained, which yields nothing but water and ammonia by distillation with hydrate of lime, and therefore does not contain any volatile organic base; but on treating it with recently precipitated oxide of silver, evaporating the filtrate to dryness at a gentle heat to expel the ammonia, and exhausting the residue with water, a solution is obtained, having a strong alkaline reaction, and therefore indicating the presence of a non-volatile base. This solution blackens on exposure to the air, and deposits reduced silver; and on removing the silver by sulphuretted hydrogen, expelling the excess of that gas from the filtrate by heat, neutralising the liquid with sulphuric acid, decomposing the sulphate with caustic baryta (taking care to avoid an excess), and extracting with alcohol, the base is obtained in the free state.

Hydrated oxide of Acetylium thus obtained is a yellowish, inodorous, viscid mass, which dissolves readily in water and alcohol. It is charred by heat, giving off a faint but characteristic odour. The aqueous solution has a strong alkaline reaction, a slightly caustic taste, and when boiled, gives off the peculiar faint odour of alkaline solutions. It absorbs carbonic acid from the air, and afterwards effervesces with acids. It expels ammonia from ammoniacal salts. Does not dissolve alumina. Dissolves oxide of silver with great facility, but the silver is quickly reduced when the liquid is heated.

<i>Calculation.</i>			
4 C	24	39.34
N	14	22.96
7 H ¹	7	11.48
2 O	16	26.22
<hr/>			
$\text{C}^4\text{H}^3 \left. \begin{matrix} \text{H}^3 \\ \text{H}^3 \end{matrix} \right\} \text{NO}, \text{HO}$	61	100.00

Metameric with aldehyde-ammonia, $\text{NH}^3, \text{C}^4\text{H}^4\text{O}^2$, with which it agrees in certain respects, *e. g.*, in its reactions with silver-salts (*inf.*); it is however sufficiently distin-

only one of the hydrogen-atoms of the ammonium is replaced by an organic radical. The salts of acetylium are very hygroscopic, becoming moist in a few seconds after drying; hence their analysis presents great difficulties. Alcohol precipitates them from their aqueous solutions. They are all insoluble in ether. They are decomposed by aqueous ethylamine at ordinary temperatures; but on boiling the liquid, the ethylamine is expelled, in consequence of its volatility.

When ammonia and nitrate of silver are added to a solution of the base or of either of its salts, and the liquid is boiled for some time, an extremely beautiful specular deposit of silver is formed. This reaction is slower with the chloride than with the other salts, because the separated chloride of silver is difficult to reduce. — When nitrite of silver is added to a solution of the chloride of acetylium, and the liquid heated, aldehyde is copiously evolved, especially on addition of a few drops of sulphuric acid :



Sulphate of Acetylium. — Precipitated by alcohol from a moderately concentrated aqueous solution in white flakes; from a stronger solution as a non-miscible yellow liquid. Has a slight acid reaction, even if the aqueous solution, before precipitation, has been made alkaline by excess of base. When dried, it forms a yellow viscid mass.

	Dried at 100°.		Natanson.	
$\text{C}^{\text{A}}\text{NH}^{\text{O}}$	52	56.53		
SO^{S}	40	43.47	40.77	41.13
$\text{C}^{\text{A}}\text{NH}^{\text{O}},\text{SO}^{\text{S}}$	92	100.00		

The deficiency of sulphuric acid arises from the great difficulty of drying the salt. Such an analysis not being sufficient to establish the constitution of the salt, confirmation was sought in the relative quantities of carbonic acid and nitrogen obtained by combustion. The ratio found by experiment was $\text{N} : \text{CO}^{\text{S}} = 1.391$; calculation giving 1 : 4.

Nitrate. — Resembles the sulphate.

Chloride. — The formation of this salt has been already described. It may also be obtained by neutralising the solution of the oxide with hydrochloric acid. Its aqueous solution does not mix in the concentrated state with alcohol, but remains as a heavy stratum at the bottom; but in the dilute state, the chloride, unlike the other salts, is not precipitated by alcohol.

Mercury-salt. — Corrosive sublimate added to the chloride forms a white precipitate, very sparingly soluble in cold, but dissolving pretty readily in hot water, and separating out again on cooling; it is insoluble in alcohol.

Gold-salt. — Chloride of gold forms with chloride of acetylium an orange-yellow amorphous precipitate, which dissolves readily when the liquid is heated, but is decomposed almost immediately, the gold being reduced to the metallic state.

Platinum-salt. — Bichloride of platinum forms with chloride of acetylium a deep orange-yellow, filmy precipitate, which afterwards cakes together.

				Natanson.
C ⁴ NH ⁶	44.0	17.66	
Pt.....	99.0	39.73 38.22
3 Cl.....	106.2	42.61	
C ⁴ NH ⁶ Cl ₃ PtCl ³				249.2 100.00

Oxalate. — Precipitated by alcohol from the aqueous solution, in the form of a white gelatinous precipitate, which, if the solution is concentrated, converts the liquid into a pasty mass. (Natanson.)

Page 300.

Fulminating Mercury. — Liebig (*Ann. Pharm.* 95, 284) gives the following process for preparing this compound: 3 pts. of mercury are dissolved in 36 pts. of nitric acid of sp. gr. 1.34 to 1.345, in a wide glass flask capable of holding at least 18 times the quantity of liquid actually used, so that the greater part of the cooled nitrous acid gas may remain within it. As soon as the metal has completely disappeared, the solution is decanted into a second vessel containing 17 pts. of alcohol of 90° to 92° (Tralles), then immediately poured back again into the first vessel, and briskly agitated to promote the absorption of the nitrous acid. In 5 to 10 minutes, gas-bubbles begin to rise, and there is formed at the bottom of the vessel a strongly refracting, specifically heavier liquid, which must be mixed with the rest by gentle agitation. A moment then arrives when the liquid becomes black from separation of metallic mercury, and an extremely violent action is set up, with evolution of a thick white vapour, and traces of nitrous acid; this action must be moderated by gradually pouring in 17 pts. more of the same alcohol. The blackening then immediately disappears, and crystalline fulminating mercury begins to separate; towards the end of the operation, the little crystals are kept floating on the surface in curdy masses by the rising gas-bubbles, which however escape as the alcohol is poured in, so that ultimately, when the liquid has cooled, all the fulminating mercury is found at the bottom. By this method, not a trace of mercury is left in solution, and the quantity of fulminating mercury obtained is exactly that which calculation assigns, viz. 4.6 pts. (Liebig.)

Schischkoff (*Bull. de St. Petersb. Cl. Phys. Math.* 14, 98; *Ann. Pharm.* 97, 53; *Chem. Gaz.* 1855, 420.) has analysed fulminating mercury prepared from a solution of mercury in excess of nitric acid, and obtained results agreeing with the formula C⁴N²Hg²O⁴ (or C⁴NXHg², ix. 301). By recrystallisation from water, the salt is obtained in white or slightly yellowish silky needles, which, when dried at 100°, contain 1 At. water of crystallisation. The drying, even at this temperature, is attended with the greatest danger.

<i>Anhydrous.</i>				Schischkoff.
4 C.....	24	8.45 8.48
2 N	28	9.86 9.92
2 Hg	200	70.42 70.33
4 O	32	11.27 11.27
C ⁴ N ² Hg ² O ⁴				284 100.00 100.00

2 N	28	9.56	
2 Hg	200	68.26 68.25
4 O	32	10.92	
HO	9	3.07	

$C^4N^2Hg^2O^4 + Aq$ 293 100.00

[The mercury-determinations formerly given by Liebig and by Howard (ix. 301) were probably made upon the hydrated salt; but they are too small even for that.]

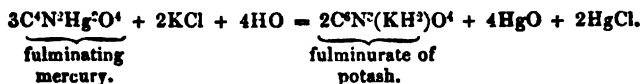
A slightly heated solution of mercuric nitrate, acidulated with nitric acid, dissolves a large quantity of fulminating mercury; at a higher temperature, violent evolution of carbonic acid and nitrogen takes place, and a yellow precipitate is formed, which is blackened by ammonia, and when the mercury is separated from it by sulphuretted hydrogen, yields a mixture of two acids. When the operation is complete, the filtrate contains a large quantity of mercurous nitrate.

The two acids thus obtained may be separated by adding ammonia, evaporating to dryness, and treating the residue with absolute alcohol. The undissolved portion, recrystallised from water, forms, with lime and baryta salts, a precipitate containing nitrogen, and an extremely explosive salt with silver. The portion which dissolves in the alcohol does not precipitate lime-salts; with nitrate of silver, it forms a detonating salt also containing nitrogen. These two acids appear to be identical with those which are obtained by the action of nitrous acid and of hydrochloric acid and the alkalis on fulminuric acid (p. 557); the mercuric nitrate, in passing to the state of mercurous salt, acts upon the fulminating mercury in the same manner as nitrous acid, more readily however, because the fulminating mercury is in solution. (Schischkoff.)

A solution of caustic potash, even when very concentrated, has no action upon fulminating mercury at ordinary temperatures; but if the potash be heated, and the fulminating mercury added by small portions, a violent action takes place at each addition, the liquid boiling strongly, and an olive-green precipitate being formed: cyanate of potash remains in solution. No ammonia is evolved during this reaction; but when the operation is ended and the excess of potash neutralised by an acid, the liquid is found to contain a large quantity of ammoniacal salt. A portion of the nitrogen is contained in the olive-green precipitate; for when this precipitate is dissolved in hydrochloric acid, the salt $NH^2Cl, 2HgCl + HO$ is formed, besides mercuric chloride, and crystallises on evaporation. — The olive-green precipitate was formerly supposed to be mercurous oxide, and on this account some chemists regarded fulminating mercury as a mercurous salt. This supposition, however, is negatived, both by the composition of fulminating mercury, and by its solubility in hydrochloric acid. (Schischkoff.)

Fulminating mercury forms crystalline compounds with the chlorides and iodides of the alkali-metals. When gently heated with a dilute solution of iodide of potassium, it dissolves, forming a yellow solution, which at a stronger heat becomes darker, and afterwards cherry-red. In both cases, small, white shining laminae separate on cooling. These crystals are highly explosive; become red when exposed to light in a dry state, from formation of small crystals of mercuric iodide; and are insoluble in water and alcohol. They contain 52.4 per cent. of mercury, approximating to the formula $KI, 2C^4N^2Hg^2O^4$, which requires 54.4. — The chlorides of potassium, sodium, and ammonium, form similar compounds, under the same circumstances. (Schischkoff.)

When fulminating mercury is boiled with a solution of chloride or iodide of potassium, the fulminic acid is converted into a new acid, *fulminaric acid*, $C^6N^3H^3O^6$, isomeric with cyanuric acid. (Liebig, Schischkoff.) — According to Liebig (*Ann. Pharm.* 95, 283), when fulminating mercury recently precipitated, well washed, and still moist, is boiled with a very dilute solution of the chloride of an alkali-metal, it dissolves completely after a quarter of an hour's boiling; but soon afterwards decomposition takes place, attended with separation of light yellow mercuric oxide, and the liquid filtered after the precipitate has settled down, contains a fulminatrate of the alkali, together with chloride of mercury:



The mercury may be precipitated from the filtrate by ammonia, and the liquid, after sufficient concentration and cooling, yields crystals of the alkaline fulminatrate. — Schischkoff, who added the fulminating mercury to a boiling and nearly saturated solution of chloride of potassium, gives a different view of the process. According to his observations, the yellow precipitate formed during the reaction is not mercuric oxide, but is a somewhat indefinite product, containing about 2 p. c. carbon, 3.1 nitrogen. 9 to 9.2 chlorine, and 81.5 to 83.6 mercury, besides hydrogen and oxygen. Now, as the fulminatrate of potash is the only organic substance contained in the solution, it follows that all the carbon and nitrogen of the fulminic acid not employed in the formation of the fulminaric acid, must be contained in the yellow precipitate, and in the ratio of 2 At. C to 1 At. N, which is not very far from that of the numbers above given. It may be supposed then that 2 At. fulminic acid are resolved into 1 At. fulminaric and 1 At. cyanic acid:



and that the yellow precipitate is formed by the mutual action of the chloride and oxide of mercury and the elements of cyanic acid in presence of water.

The yellow precipitate is amorphous, insoluble in water, and decomposes without detonation when heated, water being first given off, then carbonate of ammonia, and lastly, at a stronger heat, a sublimate of mercurous chloride, and a small quantity of metallic mercury. It does not give off ammonia when heated with potash-ley, or even change colour when boiled with that liquid; but when heated with sulphide of potassium, it readily gives off ammonia. — Oil of vitriol diluted with an equal amount of water, does not act upon the yellow precipitate at ordinary temperatures; but on the application of heat, a small quantity of carbonic acid is driven off, and at the end of the operation, ammonia remains in the liquid, together with a small quantity of mercurous salt, — strong hydrochloric acid dissolves the yellow precipitate, leaving only a small residue of calomel; the filtrate, which does not give off ammonia when mixed with caustic potash, solidifies on cooling to a pulpy mass of long silky needles of the salt $NH^4Cl, 2HgCl + 4HO$ (analysis gave 3.81 p. c. N and 59.11 Hg, the formula requiring 4.17 N and 59.70 Hg); corrosive sublimate crystallises out at the same time. — The yellow precipitate is decomposed by sulphuretted hydrogen, sulphide of mercury being sepa-

sal-ammoniac, contaminated, however, with an organic acid. — The yellow precipitate heated with iodide of potassium, turns brown, and gives off ammonia, part of the mercury passing into the solution, and the liquid containing carbonate of potash. An excess of chloride of potassium acts like the iodide, though less strongly; hence, as an excess of the chloride is required for the preparation of fulminate of potash (see page 559), this excess must affect the constitution of the yellow precipitate. That this precipitate is not a body of perfectly definite constitution, is likewise shown by its always leaving a certain quantity of chloride of potassium when sublimed, even after long-continued washing with boiling water; also by its behaviour with hydrochloric acid and sulphuretted hydrogen (Schischkoff.)

Iodide of potassium acts like the chloride. When a solution of fulminating mercury in iodide of potassium is heated to the boiling point, it gradually acquires a darker colour, and deposits an abundant brown precipitate containing mercuric iodide. The filtrate evaporated over the water-bath, gives off ammonia at a certain degree of concentration; and as the liquid cools, crystals of mercuric iodide are deposited, together with crystals of fulminate of potash. The evolution of ammonia appears to arise from the decomposition of the brown precipitate. (Schischkoff.)

Fulminating silver treated with excess of chloride or iodide of potassium, does not yield fulminuric acid; half of the metal separates out immediately, whilst the other half remains in solution, and the liquid, even after long boiling, yields nothing but a double fulminate of silver and potassium. (Schischkoff.)

Page 377.

Acetate of Acryl. $C^{10}H^8O^4 = C^4H^3(C^6H^5)O^4$. — *Acetate of Propylenyl, Acetopropylenyl* (Zinin): *Acetate of Allyl.* — Formed by the action of iodopropylene C^6H^5I (iodide of acryl) on acetate of silver.



When pure and well-dried acetate of silver is mixed in a retort with rather less than an equivalent quantity of iodopropylene and the mixture shaken up, the action begins in a few minutes, attended with sufficient evolution of heat to distil off nearly all the resulting acetate of acryl. Any undecomposed iodopropylene that may pass over may be decomposed by returning the distillate to the residue in the retort, and the acetate of acryl obtained in the pure state by subsequent distillation between 100° and 115° , and rectification, first over acetate of silver, then over oxide of lead, and lastly by itself.

Colourless liquid, lighter than water, neutral, having an odour like that of acetate of ethyl, but rather pungent, and a sharp ethereal taste. Boiling point 105° , being about as much above that of acetic ether (viii. 497), as the boiling point of iodide of acryl (ix. 427), is above that of iodide of ethyl (viii. 360.) Dissolves sparingly in water, but in all proportions in alcohol and ether. (N. Zinin, *Petersb. Acad. Bull.* 13, 360; *Ann. Pharm.* 96, 361.)

8 H	8	8	8	8	8	8
4 O	32	32	32	32	32	32
C¹⁰H⁸O⁴	100	100	100	100	100	100

Benzoate of Acryl, C¹⁴H⁸(C⁶H⁵)O⁴, is obtained in a similar manner by the action of benzoate of silver on iodopropylene. (Zinin.)

Hydrargacryl. C⁶H⁶Hg². — *Hydrargopropyleneyl* (Zinin); *Hydrargallyl*. — Iodopropylene combines with mercury much more readily than iodide of methyl or ethyl, the mixture quickly solidifying to a yellow crystalline mass, from which the iodide of hydragacryl is easily extracted by hot alcohol or ether, and separates from the alcoholic solution on cooling, in silver-shining scales which turn yellowish in drying, especially if exposed to light.

Iodide of hydrargacryl volatilises at 100°, in white shining rhombic tables, melts at 135°, and solidifies in a yellow crystalline mass on cooling; when more quickly and strongly heated, it is for the most part decomposed, leaving a carbonaceous residue and yielding a yellow sublimate. It is nearly insoluble in water, and dissolves but very sparingly in cold alcohol. (Zinin.)

				Zinin.
6 C	36	9.78	9.59	
5 H	5	1.35	1.38	
2 Hg	200	54.36		
I	126	34.51	34.49	
C⁶H⁶Hg²I	367	100.00		

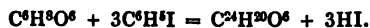
When the alcoholic solution of this compound is mixed with nitrate of silver, the whole of the iodine is precipitated in the form of iodide of silver. Oxide of silver introduced into the alcoholic solution likewise forms iodide of silver, the liquid at the same time becoming strongly alkaline, and yielding by evaporation a thick, syrupy, strongly alkaline mass, which is soluble in water, and volatilises when more strongly heated, emitting an odour like that of angelica and of garlic. This substance forms salts with acids, and is doubtless the *hydrated oxide of hydrargacryl*. (Zinin.)

Cahours & Hofmann, by treating iodide of acryl with various silver-salts, have obtained a number of acryl-salts or compound ethers, and in particular the oxalate of acryl, a liquid which is decomposed by ammonia in a similar manner to oxalate of ethyl (ix. 180), yielding oxamide and *Acrylic alcohol* C⁶H⁶O², or $\left. \begin{matrix} \text{C}^6\text{H}^6 \\ \text{H} \end{matrix} \right\} \text{O}^2$; and from this a large number of derivatives have been formed, viz., acrylic ether, sulphacrylic acid, xanthacrylate of potassium, &c., &c. (*Compt. rend.* 42, 217.)

Berthelot & De Luca have also obtained several compound acrylic ethers, e. g. the butyrate, benzoate, &c., by the action of silver-salts on the iodide of acryl. They find also that the iodide, when decomposed by mercuric oxide, yields acrylic ether C⁴H⁶O; treated with potash dissolved in vinic or amylic alcohol, it yields vinaerylic ether $\left. \begin{matrix} \text{C}^4\text{H}^6 \\ \text{C}^6\text{H}^5 \end{matrix} \right\} \text{O}^2$, or amylic acrylic ether, $\left. \begin{matrix} \text{C}^6\text{H}^6 \\ \text{C}^{10}\text{H}^{11} \end{matrix} \right\} \text{O}^2$; and with potash and glycerine, it forms *triaerylin*.

equation :

(C¹⁸H¹³)



Iodide of acryl decomposed by sodium, yields the radical *acryl* C⁶H⁸, which is a very volatile liquid, having a pungent odour like that of horse-radish. It boils at 59°. Its density is 0.684 at 14. Vapour-density = 2.92 (monatomic). Burns with a very bright flame. (*Compt. rend.* 42, 233.)

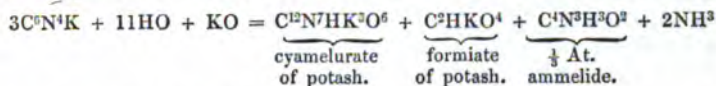
[All these compounds will be more fully described in the next volume.]

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Mellonides.

LIEBIG. *Ann. Pharm.* 95, 257.

The formula C⁶N⁴M, originally assigned by Liebig to the mellonides, does not render a satisfactory account of the decomposition of those compounds by acids or caustic alkalis. According to this formula, mellonide of potassium, decomposed by potash-ley, should yield cyamelurate of potash, formiate of potash, ammelide, and ammonia. (ix. 392.)



Now, when mellonide of potassium is boiled with potash-ley, ammonia is evolved; crystals of cyamelurate of potash are obtained at a certain degree of concentration; and if the alkaline liquid be then mixed with sal-ammoniac, a copious precipitate of ammelide (ix. 476) is obtained. But if the mixture be kept boiling for some time, sal-ammoniac no longer produces any precipitate in it; if, however, the liquid, after addition of sal-ammoniac, be neutralized with acetic acid, a white precipitate of melanurenic acid (ix. 470,) is obtained. On continuing the boiling, ammonia is continually evolved, the melanurenic acid disappears, and after saturating the alkaline liquid with acetic acid, crystals of cyanurate of potash are obtained, which by solution in dilute hydrochloric acid yield crystals of pure hydrate of cyanuric acid. No formiate of potash is obtained. Neither does the alkaline liquid yield any formic acid, when neutralised with sulphuric instead of acetic acid, and subjected to distillation. This discrepancy between the results of theory and experiment, and a similar difficulty in explaining the decomposition of mellonides by acids, induced Liebig to subject these compounds to a careful re-examination, the result of which has been to show that the original formula assigned to them was erroneous, and that they really contain 6 At. carbon and 4½ At. nitrogen to 1 At. metal, or 18C and 13N to 3 At. metal, that is to say, that their general formula is C¹⁸N¹³M³.

Hydromellonic acid. C¹⁸N¹³H³.—By mixing a warm solution of corrosive sublimate with mellonide of potassium, a fine-grained, dazzling

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2 N

chlorides of other metals by rectification in the same apparatus. Before being used, it is again melted, pulverised while still hot after solidification, and the powder added to the fused sulphocyanide. The proportions used are 1 pt. of bismuth-chloride to 2 pts. sulphocyanide of potassium; with a larger proportion of the former, the mass will not melt. — 2. From *Melam*. — 8 pts. of sulphocyanide of potassium are fused with 4 pts. of melam, previously slightly ignited, and added in successive small portions. The temperature must not be allowed to rise too high; if the gas-bubbles which rise from the melted mass, do not burn with a blue flame (sulphide of carbon), but with a red colour, indicating the formation of cyanogen, the heat must be moderated. The melam is prepared by heating in a porcelain basiu, a mixture of equal parts of sal-ammoniac and sulphocyanide of potassium, stirring constantly till no more vapours of sulphocarbonate of ammonia are evolved, and sal-ammoniac begins to sublime. The mass is then exhausted with cold water, the residue dried, and gently ignited before being used. — 4. In preparing mellonide of potassium by fusing sulphur with yellow prussiate of potash, the addition of carbonate of potash towards the end of the fusion is positively injurious; for the slightest excess of that salt induces the decomposition of the mellonide of potassium previously formed.

Pure mellonide of potassium forms soft, white, very slender interlaced needles, having a silky lustre, and scarcely distinguishable in appearance from sulphate of quinine. — 1 pt. of the salt dissolves in 37.4 pts. of water at ordinary temperatures, and in a much smaller quantity of hot water; it is insoluble in alcohol. Crystallises with difficulty, even from a solution saturated while warm, but very easily on addition of alcohol. Its solubility in cold water is greatly diminished by the presence of other salts. A warm saturated solution, which would stand for days after cooling without crystallising, instantly deposits crystals on addition of a few drops of solution of sulphocyanide of potassium. — The aqueous solution tastes as bitter as sulphate of quinine. In doses of a dram, the salt exhibits no decided action on man or other animals, none at least which would distinguish it from other bitter substances. — The crystals heated to 200°, give off 18.06 p. c. (10 At.) water. — This result differs considerably from the former determination (viii. 392). Liebig expresses himself unable to account for the difference.

<i>Anhydrous.</i>				Liebig.
18 C.....	108.0	26.50 26.12
13 N.....	182.0	44.65 44.38
3 K.....	117.6	28.85 28.72
<hr/>				
C ¹⁸ N ¹³ K ³	407.6	100.00 99.22
<hr/>				
<i>Crystallised.</i>				Liebig.
C ¹⁸ N ¹³ K ³	407.6	81.91	
10 HO	90.0	18.09 18.06
<hr/>				
C ¹⁸ N ¹³ K ³ + 10 Aq.....	497.6	100.00	

The salt burnt in a stream of oxygen yielded only 0.06 p. c. water; now if it contained 1 At. hydrogen to 3 At. potassium, it should have yielded 2.19 p. c. water; it may therefore be safely concluded that the salt does not contain hydrogen.

b. Insoluble acid Salt. — Separates in the form of a white, chalky precipitate, on pouring a moderately dilute solution of neutral mellonide

of potassium into warm dilute hydrochloric acid. Insoluble in cold and sparingly soluble in boiling water; the solution has a strong acid reaction; easily soluble in a solution of acetate of potash.

				Liebig.
18 C.....	108.0	32.61 31.97
13 N	182.0	54.95	
2 H	2.0	0.60 0.76
K.....	39.2	11.84 11.93
<hr/>				
$C^{12}N^{13}H^2K$	331.2	100.00	

When hydrochloric acid is poured into a solution of mellonide of potassium, a translucent gelatinous precipitate is obtained, of very doubtful composition.

c. Soluble acid Salt. — Obtained by mixing a warm saturated solution of the neutral salt with an equal value of strong acetic acid. Crystallises from this mixture in oblique rhombic laminae, which effloresce in a warm atmosphere. When boiled with water, it is resolved into the neutral salt *a*, and the insoluble acid salt *b*. The crystals, after drying in the air, give off 13.03 p. c. water.

				Liebig.
<i>Dried at 150°.</i>				
18 C.....	108.0	29.23 28.75
13 N	182.0	49.28	
H	1.0	0.27 0.43
2 K	78.4	21.22 21.13
<hr/>				
$C^{12}N^{13}HK^2$	369.4	100.00	
<i>Air-dried.</i>				Liebig.
$C^{12}N^{13}HK^2$	369.4	87.27	
6 HO	54.0	12.73 13.03
<hr/>				
$C^{12}N^{13}HK^2 + 6Aq$	423.4	100.00	

Mellonide of Silver. — Obtained as a white precipitate by mixing a boiling solution of neutral mellonide of potassium with nitrate of silver.

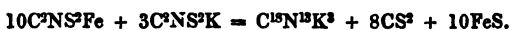
				Liebig (mean).
18 C.....	108	17.59 17.48
13 N	182	29.64 29.54
3 Ag	324	52.77 52.48
<hr/>				
$C^{12}N^{13}Ag^3$	614	100.00 99.50

The salt burnt in a stream of oxygen yielded in two experiments 0.4 and 0.3 p. c. water, whereas if, as supposed by Gerhardt, it contained 1 At. H to 12 At. C, the quantity of water should be 2.17 p. c., or about six times as great as that actually found. Hence we may safely conclude that mellonide of silver does not contain hydrogen.

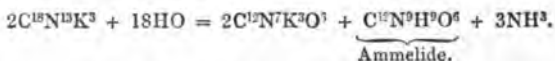
a. Comparing the composition of hydromellonic acid with that of the bodies from which, by fusion with sulphocyanide of potassium, mellonide of potassium may be produced, we obtain the following relations:

Melam, $C^{12}N^{11}H^9$	contains the elements of ...	$3NH^3 + C^{12}N^3$
Melamine, $C^{12}N^{12}H^{12}$	" "	$4NH^3 + C^{12}N^3$
Ammelide, $C^{12}N^9H^9O^6$	" "	$6HO + NH^3 + C^{12}N^3$
Ammeline, $C^6N^6H^6O^3$	" "	$2HO + NH^3 + C^6N^3$
Chlorocyanamide, $C^6N^6H^4Cl$	" "	$ClH + NH^3 + C^6N^3$
Melanurenic acid, $C^6N^6H^4O^4$	" "	$4HO + C^6N^3$
Hydrosulphomellonic acid, $C^6N^6H^4S^4$	" "	$4SH + C^6N^3$

acid, $C^{16}N^{15}H^3$, which contains the elements of ammonia and tricyanamide, $NH^3 + C^{16}N^{12}$ or $NH^3 + 3Cy^2N$, the formation of these compounds by the usual processes is satisfactorily explained. The formation of mellonide of potassium by fusing the yellow ferrocyanide with sulphur is less obvious. It must, however, be assumed as certain that the radical mellone is formed by the decomposition of sulphocyanide of iron, a process which may perhaps be represented by the following equation :



β . The new formula of mellonide of potassium affords a satisfactory explanation of the decomposition of that salt by potash into cyamelurate of potash, ammeline and ammonia. Henneberg gave for cyameluric acid the two formulæ $C^{12}N^7H^3O^6$ and $C^{12}N^7H^4O^6$, leaving it undecided which should be preferred. According to the latter, the acid should contain 1 At. H not replaceable by a metal, and the formula of the potash-salt should be $C^{12}N^7HK^3O^6$; whereas, according to the former, this salt should not contain hydrogen. Liebig found in cyamelurate of potash prepared by Henneberg's process (ix. 382), 21.01 p. c. C and 0.09 H, whereas the formula $C^{12}N^7HK^3O^6$ requires 0.29, or about three times as much as that which is obtained by experiment. Consequently, cyamelurate of potash contains no hydrogen, and its formula is $C^{12}N^7K^3O^6$. The decomposition of mellonide of potassium by potash is represented by the equation :

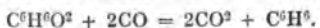


γ . By abstraction of ammonia and addition of water, ammeline is converted into melanurenic acid. (Laurent & Gerhardt regard the two as identical, but without having analysed the latter.)



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Propylene. — When a mixture of an alkaline acetate and oxalate is distilled in such a manner as to place the resulting acetone, when in the nascent state, in contact with carbonic oxide, the acetone is deoxidised, with formation of a carbonate and evolution of propylene :



The quantity of propylene obtained is, however, by no means equal to that which is indicated by calculation: for the decomposition of the two salts is not simultaneous, and the oily matter observed in the preparation of acetone is always produced. — The mode of conducting the process is as follows: 1 At. acetate of lime is added to 1 At. oxalate of potash dissolved in water, so as to form oxalate of lime and acetate of potash; the liquid evaporated and constantly stirred, so as to obtain an intimate mixture; and the mass, when dried as completely as possible, put into a retort which is heated over a moderate fire. The gas passes

first into a flask filled with carded cotton, then into another containing oil of vitriol to absorb the oily matter, and is finally condensed in bromine, after being washed with water. A kilogramme of acetate of lime thus treated yields about 60 grms. of crude propylene. — The liquid thus obtained is washed with potash and distilled; then shaken up again with an alkaline solution, to saturate the hydrobromic acid formed during the distillation; after which it is dried over chloride of calcium and rectified. Bromide of propylene, $C^3H^5Br^2$, forms about two-thirds of the product; it has the odour and the boiling point (145°) of the bromide of propylene obtained from amylic alcohol (ix. 397).

The compound C^3H^5Br , obtained by the action of alcoholic potash on the preceding product, heated in a tube with sulphocyanide of potassium, yields oil of mustard (*comp.* page 42). (L. Dusart, *Compt. rend.* 41, 495.)

Propylene is also found among the products of the dry distillation of butyrate of baryta (p. 555). When the gas evolved in that process was passed into a mixture of hydrochloric acid and peroxide of manganese, and that mixture afterwards distilled, a distillate was obtained consisting of chlorinated substitution-products of propylal and propione, mixed with chloride of propylene. The excess of chlorine was removed by washing with water, the liquid then dried over chloride of calcium and rectified. The whole of the chloride of propylene passed over below 120° , and was obtained sufficiently pure for analysis when the boiling point was between 104° and 110° , and the vapour no longer excited tears, a property possessed in a high degree by chlorinated propylal or propione. The chloride of propylene thus purified gave by analysis 61.86 p. c. chlorine, the formula $C^3H^5Cl^2$ requiring 62.51 p. c. — 500 grms. of butyrate of baryta yielded 1 gm. of chloride of propylene. (Limpricht & v. Uslar, *Ann. Pharm.* 94, 329.)

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Formation of Propylic Alcohol from Propylene. — Oil of vitriol rapidly absorbs propylene-gas; and on subsequently diluting the acid with water, filtering, and distilling, propylic alcohol is obtained in the form of a spirituous liquid, having a peculiar pungent odour, soluble in water, but precipitated from the solution by carbonate of potash. In a state of concentration, but still mixed with a certain quantity of water, it has a density of 0.817, and begins to boil at 81° or 82° , [the pure alcohol boils at 96° ; see ix. 399]. It mixes in all proportions with water, and forms with crystallised chloride of calcium, either a homogeneous solution or two distinct strata, according to the proportion of the salt. Burns with a brighter flame than common alcohol. Heated with oil of vitriol and sand, it blackens, decomposes rapidly, and yields propylene-gas, mixed with about $\frac{1}{4}$ of another combustible gas, probably hydride of propyl, C^3H^6 . — Distilled with oil of vitriol and butyric acid, it yields *butyrate of propyl*, $C^3H^7(C^3H^7)O^2$, which is a neutral liquid, lighter than water, volatile below 130° , and having an odour like that of butyric ether, but not so agreeable; it is decomposed at 100° by potash, yielding

and acetic acid, it yields acetate of propyl, $C^6H^3(C^6H)O^2$, which volatilises below 90° .

A mixture of propylic alcohol and oil of vitriol, gently heated, and then saturated with carbonate of baryta, yields sulphopropylate of baryta, $C^6H^7BaO^3, 2SO^3 + 6 Aq.$ This salt parts with its water of crystallisation in vacuo. With benzoate of potash it yields benzoate of propyl. By immediately saturating with carbonate of baryta the solution of propylene in sulphuric acid, two salts were obtained, viz., $C^6H^7BaO^3, 2SO^3 + 6 Aq.$ identical with that just mentioned, and $C^6H^7BaO^3, 2SO^3 + 2 Aq.,$ corresponding with the sulphovinate. These two hydrates exhibit the same degree of stability and behave in the same manner with various salts, both producing the acetate, butyrate, and benzoate of propyl. The compound formed with propylene and fuming oil of vitriol, does not reproduce these ethers.

Propylene is likewise absorbed by hydrochloric acid. When left to stand at ordinary temperatures over the fuming acid, it is slowly taken up, and disappears after some weeks, the absorption taking place even in a sealed tube. At 100° it is complete in 30 hours. The product is a neutral liquid, lighter than water, and insoluble in that liquid. After being purified with potash and distilled, it consists for the most part of chloride of propyl, C^6H^7Cl , which volatilises at about 40° , and has the odour, taste, and flame of chloride of ethyl. (Berthelot, *N. Ann. Chim. Phys.* 43, 385; *Compt. rend.* 40, 102.)

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Propylal, $C^6H^6O^2$. — Obtained by the dry distillation of butyrate of baryta. Boils at about 66° . Has a peculiar ethereal odour. Mixes with water, alcohol, and ether. The ethereal solution saturated with ammonia, does not yield any crystals of propylal-ammonia. Neither is that compound produced by passing ammoniacal gas over propylal surrounded with snow, or by leaving the propylal in contact with aqueous ammonia. Propylal dissolves with evolution of heat in concentrated aqueous solutions of the alkaline bisulphites, but the solution, even after long standing, deposits only a few crystalline geodes exhibiting the character of wavellite.

Limpricht & v. Usler.							
6 C.....	36	62.0	63.29	63.00
6 H.....	6	10.3	11.11	10.98
2 O.....	16	27.7	25.60	26.02
$C^6H^6O^2$	58	100.0	100.00	100.00

The excess of carbon found in the analysis was probably due to the presence of propione. — Propylal is isomeric with propylic aldehyde (ix. 400), and is related to that body in the same manner as butyral to butylic aldehyde, and valeral to valeric aldehyde. (Limpricht & v. Usler, *Ann. Pharm.* 94, 326.) — The shorter names propylal, butyral, &c., are applied by the authors to those modifications of the compounds which do not combine with ammonia.

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Propione. $C^{10}H^{10}O^2$. — The distillate of butyrate of baryta (p. 555), boiling at 95° to 120° , was shaken up with a concentrated solution of bisulphite of potash or soda; the resulting crystals separated from the mother-liquor; and dried between paper frequently renewed. On distilling these crystals with a solution of carbonate of potash, the propione passed over, together with water, from which it was mechanically separated and then dehydrated. The product thus obtained smelt like acetone, and boiled at 110° . The boiling point found by Morley (ix. 410°), was 10° lower, viz., 100° , which agrees better with the position of propione in the series of ketones, being exactly intermediate between that of acetone (56°) and that of butyrene (144°).

		Limpricht & v. Uslar.			
10 C	60	69.77	69.31	68.94	
10 H	10	11.63	11.72	11.65	
2 O	16	18.60	18.97	19.41	
<hr/>					
$C^{10}H^{10}O^2$	86	100.00	100.00	100.00	

Sulphite of Propione and Potassium. — This salt, obtained as above, formed, after drying over oil of vitriol, small scales having a pearly lustre.

		Limpricht & v. Uslar.	
10 C	60	27.90	26.37
12 H	12	5.60	5.40
K	39	18.14	18.43
5 O	40	18.66	
2 SO^2	64	29.70	30.50
<hr/>			
$C^{10}H^{10}KO^2, 2SO^2 + 3Aq.$	215	100.00	

Sulphite of Propione and Sodium. $C^{10}H^9NaO^2, 2SO^2 + 3Aq.$ — Corresponds exactly with the potassium-compound. Gave by analysis, 12.01 Na and 32.97 SO^2 , the formula requiring 11.5 Na and 32.1 SO^2 . (Limpricht & v. Uslar.)

Sulphite of Propione and Ammonium is so very soluble that it could not be obtained in crystals. (Limpricht & v. Uslar, *Ann. Pharm.* 94, 327.)

Pages 402 and 414.

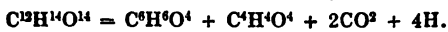
Propionic and Butyric Acids.

A. STRECKER. *Ann. Pharm.* 92, 80.

LIMPRICHT & VON USLAR. *Ann. Pharm.* 94, 321; *J. pr. Chem.* 66, 234.

Strecker suggests that the propionic acid obtained in the fermentation of sugar in contact with chalk and old cheese (ix. 403) may be produced by the oxidising action of the air on the butyric acid previously formed from the lactic acid, which is the first product of the fermentation, — inasmuch as Kolbe's experiments have shown that the fatty acids (*e. g.*, valerianic acid) are, under certain circumstances, converted by oxidation

the mannite, another product of the fermentation, may be resolved into propionic acid, acetic acid, carbonic acid, and hydrogen; :



Mannite.

Limpricht & v. Uslar found that propionic acid prepared by boiling cyanide of ethyl with alcoholic potash, boiled constantly at 142°, dissolved in water in all proportions, and was separated from the solution by chloride of calcium.

To obtain butyracetic acid, Limpricht & v. Uslar dissolved butyrate of lime (prepared by Nollner) in hot water; decomposed the filtered solution with carbonate of soda; and distilled the dried soda-salt with oil of vitriol diluted with one-fourth of its bulk of water. The acid which distilled over had a faint odour very much like that of propionic acid, and possessing but little of the butyric acid odour. Like propionic acid, it mixed with water in all proportions, but not with a concentrated solution of chloride of calcium, by which indeed it was separated out unaltered, and not resolved into acetic and butyric acid.

Butyracetic acid dehydrated as completely as possible begins to boil at about 120°, and the boiling point gradually rises to above 160°, without becoming stationary near 140°, as is the case with propionic acid. By repeated fractional distillation, and separation of the portions which boiled between 120° and 124°, and between 158° and 161°, the acid was completely separated (with the exception of a trifling residue) into acetic acid boiling between 120° and 124°, and butyric acid boiling between 158° and 161°; no propionic acid was found. The acetic acid thus obtained yielded a silver-salt containing 64.1 p. c. Ag (calculation 64.6), and the butyric acid a silver-salt containing 55.6 p. c. Ag (calculation 55.4. (Limpricht & v. Uslar.)

Anhydrous Propionic acid. $\text{C}^{12}\text{H}^{10}\text{O}^6 = \left. \begin{array}{l} \text{C}^6\text{H}^6\text{O}^3 \\ \text{C}^6\text{H}^6\text{O}^3 \end{array} \right\} \text{O}^2$, was obtained by the action of 1 At. oxychloride of phosphorus on 6 At. dry propionate of soda. It is a colourless liquid, having a disagreeable odour, slightly recalling that of valerian-root. Boils at 165°. Does not mix with water.

				Limpricht & v. Uslar.
12 C	72	...	55.38 55.01
10 H	10	...	7.69 8.00
6 O	48	...	36.93 36.99
$\text{C}^{12}\text{H}^{10}\text{O}^6$				130 100.00 100.00

Neither anhydrous butyracetic acid nor the corresponding chloride appears to exist. 6 At. butyrate of soda distilled with 1 At. oxychloride of phosphorus yielded a mixture of anhydrous acetic and butyric acids; and 3 At. of the same soda-salt with 1 At. PCl^3O^2 yielded a mixture of chloride of ethyl and chloride of butyryl. (Limpricht & v. Uslar.)

The following salts of propionic acid were prepared by Strecker with the acid obtained as above by the fermentation of sugar; they agree in all respects with those prepared with the acid obtained from cyanide of ethyl.

Propionate of Potash. — The acid obtained by fermentation of sugar in contact with chalk and cheese, was exactly neutralised with carbonate

of potash, and the solution evaporated. The residue, when absolute alcohol was poured upon it, crystallised in colourless laminæ; the alcoholic solution yielded, on addition of ether, nacreous scales, unctuous to the touch. The salt, when heated, melts without decomposing, and on cooling solidifies in a laminar crystalline mass, like acetate of soda. Deliquesces in the air, and crystallises again according to the degree of humidity present. (Strecker.)

		Strecker.	
KO	47.2	42.1	41.9
C ⁶ H ⁶ O ³	65.0	57.9	
<hr/>			
C ⁶ H ⁶ KO ⁴	112.2	100.0	

The potash-salt of *butyric acid* does not crystallise; it dissolves readily in absolute alcohol, and is not separated from the solution by ether. (Limpricht & v. Uslar.)

Propionate of Soda. — Crystallises with difficulty, so that it may be separated from acetate of soda, by the property which the latter possesses of separating in crystals from a concentrated solution, while the propionate remains in the mother-liquor. By neutralising propionic acid with carbonate of soda and evaporating, the salt is obtained on cooling, in a mass having the consistence of tallow. The air-dried salt gives off 16.6 p. c. (2 At.) water at 120°. (Strecker.)

		Strecker.	
<i>Dried at 120°.</i>			
NaO	31	32.3	32.7
C ⁶ H ⁶ O ³	65	67.7	
<hr/>			
C ⁶ H ⁶ NaO ⁴	96	100.0	
<i>Air-dried.</i>			
C ⁶ H ⁶ NaO ⁴	96	84.2	
2 HO	18	15.8	16.6
<hr/>			
C ⁶ H ⁶ NaO ⁴ + 2Aq	114	100.0	

Butyrate of Soda does not crystallise from water or alcohol, but separates in needles from the alcoholic solution on addition of ether. (Limpricht & v. Uslar.)

Propionate of Baryta. — When propionic acid is neutralised with carbonate of baryta and the solution evaporated to the crystallising point, the baryta-salt separates in colourless prisms belonging to the right prismatic system, probably isomorphous with acetate of baryta. The crystals give off their water, amounting to 6.1 p. c. (1 At.), at 100°. The salt dissolves in 1.3 pts. of water at 16°, and the solution, when evaporated over the water-bath, solidifies in the crystalline form. The salt is nearly insoluble in absolute alcohol, but dissolves pretty easily in boiling spirit of 85 p. c., whence it separates out unaltered on cooling.

		Strecker.	
<i>Dried at 100°.</i>			
BaO	76.5	54.1	54.2
C ⁶ H ⁶ O ³	65.0	45.9	
<hr/>			
C ⁶ H ⁶ BaO ⁴	141.5	100.0	
<i>Air-dried.</i>			
C ⁶ H ⁶ BaO ⁴	141.5	94	
HO	9.0	6	6.1
<hr/>			
C ⁶ H ⁶ BaO ⁴ + Aq	150.5	100	

When subjected to dry distillation it melts, swells up slightly, gives off gaseous products, among which is propylene C^3H^6 , and yields a brownish distillate, having an ethereal odour, and consisting chiefly of *propylal* boiling at 66° , and *propione* at 110° . The lead-salt yields the same products. (Limpricht & v. UsLAR.)

Propionate of Lime. — Separates by evaporation in crystalline laminæ having a fatty lustre. Appears to effloresce on exposure to the air. Sparingly soluble in alcohol.

<i>Dried at 100°.</i>		Strecker.
CaO	28	30.1
$C^6H^8O^3$	65	69.9
$C^6H^8CaO^4$ 93 100.0		
<i>Air-dried.</i>		Strecker.
$C^6H^8CaO^4$	93	91.2
HO	9	8.8
$C^6H^8CaO^4 + Aq$ 102 100.0		

Propionate of Magnesia was not obtained in crystals, but remained, when the solution was left to evaporate in an open vessel, in the form of a transparent, fissured mass. (Strecker.)

Propionate of Zinc crystallises readily when a solution of zinc-oxide in the aqueous acid is evaporated, in colourless laminæ, which give off part of their acid at 100° . (Strecker.)

Propionate of Lead. — a. Basic. — A concentrated solution of the neutral salt, mixed with ammonia, yields an amorphous precipitate which dissolves on boiling, and crystallises in slender needles on cooling. A crystalline basic lead salt is likewise obtained by boiling propionic acid with excess of lead-oxide; on evaporating the solution by heat, the salt crystallises out readily, but if the solution be evaporated in vacuo, the salt crystallises less quickly in slender needles. After drying over oil of vitriol, it does not diminish in weight at 120° . (Strecker.)

<i>Dried over oil of vitriol.</i>		Strecker.
2 PbO	224	77.5
$C^6H^8O^3$	65	22.5
$PbO, C^6H^8PbO^4$ 289 100.0		

b. Neutral. — Does not crystallise under any circumstances, but dries up in the air to a transparent, strongly refracting mass. (Strecker, compare ix. 406.)

Propionate of Copper crystallises in small dark green prisms containing 1 At. water.

Propionate of Silver. — Obtained by adding nitrate of silver to the aqueous acid neutralised with ammonia. The precipitate is white at first, but blackens considerably when boiled with water, and as the liquid cools the salt crystallises in small colourless needles. Does not alter much in colour by exposure to light, but blackens when heated to 50° or 60° , and still more at 100° . At a higher temperature, it fuses readily, and leaves coherent metallic silver. (Strecker.)

$C^2H^2O^2$	65	...	59·7	59·7
$C^2H^2AgO^4$	181	...	100·0	

Propionic Ether. — Obtained by distilling propionate of soda with alcohol and sulphuric acid. Lighter than water. Has a decided odour of rum, and not so strong as that of acetic or butyric ether. Boils at 101°. (Limpricht & v. Uslar.)

					Limpricht and v. Uslar.
10 C	60	...	58·82	59·20
10 H	10	...	9·80	10·41
4 O	32	...	31·38	30·39

$C^2H^5(C^4H^5)O^4$	102	...	100·00	100·00
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Butyric ether was not obtained by distilling the soda-salt, either with alcohol and sulphuric acid, or with sulphovinate of potash. Both methods yielded an ethereal liquid of very pleasant odour which, however, after washing with water and drying over chloride of calcium, was completely separated by distillation into butyric and acetic ether. In like manner, butyrate of soda distilled with sulphuric acid and wood-spirit, yielded nothing but a mixture of butyrate and acetate of methyl. (Limpricht & v. Uslar.)

The observations above cited are sufficient to show that butyric and propionic acids are distinct bodies, but it is not yet clearly made out whether the former is a definite compound or merely a mixture of acetic and butyric acid. The former view is supported by the formation of salts of butyric acid and by the production of propylal and propione by the distillation of the baryta-salt; the latter by the facility with which the acid, both hydrated and anhydrous, and the ether, are resolved into the corresponding acetic and butyric compounds. (Limpricht & v. Uslar.)

Fulminuric Acid. $C^2N^2H^2O^4$.

LIEBIG. *Ann. Pharm.* 95, 282.
 SCHISCHKOFF. *Petersb. Acad. Bull. Classe Phys. Math.* 14, 98; *Ann. Pharm.* 97, 53; *Chem. Gaz.* 1855, 241.

Isocyanuric acid. (Schischkoff.) — Appears to have been discovered independently, and about the same time, by Liebig and by Schischkoff.

Formation. By the action of alkaline chlorides or iodides at a boiling heat on fulminating mercury (p. 542). According to Liebig's view of the reaction, 3 At. fulminuric acid, (regarded as containing 4C,) are converted into 2 At. fulminuric acid :



According to Schischkoff, on the other hand, 2 At. fulminuric acid are resolved into 1 At. fulminuric and 1 At. cyanic acid :



is obtained by decomposing the lead or silver salt, (prepared from the potash-salt by double decomposition,) with sulphuretted hydrogen, or the silver-salt with hydrochloric acid.

Properties. The aqueous solution of the acid left to evaporate in a warm place, solidifies in a compact, yellowish, indistinctly crystalline mass. (Liebig. Schischkoff.) From a saturated alcoholic solution, the acid separates in small colourless prisms. (Schischkoff.)—Liebig did not obtain crystals from the alcoholic solution.—The crystals are anhydrous, and permanent in the air. (Schischkoff.) The solution has an acid reaction and an agreeable taste (Schischkoff); a very sour taste. (Liebig.)

	Dried at 100°.		Liebig.	Schischkoff.
6 C	36	27·90	27·82	28·16
3 N	42	32·55		32·66
3 H	3	2·32	2·68	2·44
6 O	48	37·23		36·74
<hr/>				
C ⁶ N ³ H ³ O ⁶	129	100·00		100·00

Isomeric with cyanuric acid (ix. 449).

Decompositions. 1. The acid and its salts explode when heated, the decomposition of the acid taking place at 150° (Schischkoff); the acid detonates slightly when heated (Liebig).—2. The aqueous solution of the acid is decomposed by boiling with mineral acids, a salt of ammonia being formed, carbonic acid evolved, and a brown substance produced, which has not been further examined. (Liebig.) Oil of vitriol decomposes the salts of fulminuric acid, without blackening, forming sulphate of ammonia, and eliminating a mixture of carbonic acid and carbonic oxide. Weak hydrochloric acid has scarcely any action on the fulminurates; but the strong acid decomposes them, with formation of ammonia and evolution of carbonic acid. On saturating the excess of hydrochloric acid with an alkali, and adding a lime or baryta salt, a white precipitate is formed; but if the action of the hydrochloric acid has been long continued, and the liquid has been afterwards evaporated to dryness, no such precipitation takes place.—3. Nitrous acid passed through a solution of fulminuric acid, decomposes it, with evolution of gas (carbonic acid), and forms an acid which does not precipitate lime-salts, but yields with nitrate of silver an insoluble salt containing nitrogen.—4. Caustic potash heated with fulminuric acid or its salts, gives off a large quantity of ammonia and forms carbonate of potash; and the solution, when neutralised by an acid, forms no precipitate with chloride of calcium or nitrate of silver.—5. Caustic baryta heated with fulminuric acid or its salts, decomposes them, with evolution of ammonia and formation of a white precipitate containing carbonate of baryta. This precipitate dissolves in hydrochloric or nitric acid; and after the excess of acid has been neutralised by ammonia, a precipitate is formed, probably identical with that which is produced on adding a baryta-salt to fulminuric acid which has been decomposed by hydrochloric acid. (Schischkoff.)—Hydrosulphate of ammonium and hydrosulphate of potassium have no action on fulminuric acid, even at a boiling heat. (Schischkoff.)

Combinations. Fulminuric acid dissolves very readily in water. The solution in a small quantity of water forms a syrup, and may be heated and evaporated without decomposition. (Liebig.)

The acid is monobasic, the formula of its salts being $C^N^2H^3MO^6$. It decomposes carbonates with effervescence.

Fulminurate of Ammonia. — Well washed fulminating mercury (60—75 grammes), is mixed in a glass flask with 700 to 800 cubic centimetres of water; 60 cub. cent. of a cold-saturated solution of sal-ammoniac then added; and the whole heated to the boiling point. In a few minutes, a yellow crystalline powder begins to separate, the same in fact that is produced from white precipitate, by boiling with water or with alkalis. As soon as the deposition of this precipitate has ceased, the vessel is removed from the sand bath, and caustic ammonia added as long as a white precipitate is formed, after which the liquid is immediately filtered and evaporated to the crystallising point. The yellow crystals thus obtained are washed with water and afterwards with alcohol, then dissolved in hot water, and the solution decolorised by well-washed blood-charcoal or bone-charcoal. The filtrate on cooling yields dazzling white crystals of great beauty. (Liebig.)

The crystals belong to the clinorhombic or monoclinohedral system [oblique prismatic] (O. R. Rood. *Ann. Pharm.* 95, 291; A. Gadolin. *Chem. Gaz.* 1855, 457.) They possess great refractive and dispersive power, and exhibit double refraction. (Liebig, Rood.) The mean refraction of one of the rays is, as nearly as could be estimated, = 1.755. Dispersive power = 0.1006 nearly. For a perpendicularly incident ray, the angle of refraction of the extraordinary ray = $4^\circ 22'$, while in calcspar it is $6^\circ 12'$. The acute angles of the crystals exhibit prismatic colours, in consequence of their high dispersive power. They also exhibit a splendid scarlet colour, arising from the superposition of the coloured images of the ordinary and extraordinary rays, the violet of the first falling on the red of the second: the beauty of the red is moreover heightened by the neutralisation of the yellow. (Rood.) — The crystals are anhydrous: when heated they fuse, blacken, and give off hydrocyanic acid ammonia, and afterwards hydrated cyanic acid, which, combining with the ammonia, forms in the upper part of the tube, a solid crystalline mass of urea. (Liebig.) The salt sustains a heat of 150° without alteration, but above that temperature it explodes like the other fulminurates. (Schischkoff.) Dissolves sparingly in cold, readily in hot water; is insoluble in alcohol and ether. (Liebig.)

			Liebig.	Schischkoff.
6 C	36	24.66	24.69	24.57
4 N	56	38.35	37.58	37.80
6 H	6	4.10	4.29	4.05
6 O	48	32.89	33.44	23.58
<hr/>				
$C^N^2H^3(NH^3)O^6$	146	100.00	100.00	100.00
<hr/>				
Or:			Liebig.	
NH ³	17	11.64	11.94	
$C^N^2H^3O^6$	149	88.36		
<hr/>				
NH ³ , $C^N^2H^3O^6$	166	100.00		

Fulminurate of Potash. — Prepared like the ammonia-salt. (Liebig.) — 2 pts. of moist fulminating mercury are added, by small portions and with constant stirring, to a nearly saturated and gently boiling solution of 1 pt. chloride of potassium, the ebullition being continued till no more fulminating mercury remains at the bottom. The liquid, which has a

fulminate of potash with mercuric oxide, which is a curdy substance, sparingly soluble in cold water, may not be deposited during the filtration; and the yellow precipitate on the filter washed with hot water. The filtrate, on cooling, deposits the curdy compound of mercuric oxide and fulminate of potash, a further quantity of which may be obtained by concentrating and cooling the mother-liquor and the wash-water. The portions which separate out in the second and third coolings, are contaminated with the yellow precipitate, but may be purified by solution in boiling water. Ultimately a mother-liquor is obtained, containing an excess of chloride of potassium and a considerable quantity of mercuric chloride. To obtain the fulminate of potash from the curdy compound, water is poured upon the latter, and sulphuretted hydrogen passed through the liquid, whereupon sulphide of mercury separates, together with crystals of the potash-salt; and to obtain the latter, the entire liquid is heated, filtered hot, and left to crystallise. On cooling, it deposits shining colourless crystals of the potash-salt, a further quantity of which may be obtained by repeatedly evaporating and cooling the mother-liquor. In this manner 150 pts. of fulminating mercury yield 20 pts. of fulminate of potash. (Schischkoff.) [Liebig makes no mention of the curdy compound of mercuric oxide and fulminate of potash. The reason of Schischkoff's having obtained it, is probably that he used a saturated solution of chloride of potassium, whereas Liebig used a dilute solution. Liebig's method is evidently the easier of the two.]

Fulminate of potash forms long prisms, having a strong lustre and great refracting power. (Liebig.) A hot saturated solution rapidly cooled, solidifies from formation of a mass of very small silky needles; but by gentle evaporation, the salt is obtained in large and very regular crystals isomorphous with the ammonia-salt. (Schischkoff.) The crystals are doubly refracting, and for perpendicular incidence, the angle of refraction of the extraordinary ray is between 5° and 6° . (Rood.) They are anhydrous. (Liebig.) The salt when heated exhibits a faint glow, and gives off a small quantity of gas, like a mixture of an organic substance with nitre. It undergoes no change at 225° , but at a higher temperature melts, gives off a large quantity of hydrocyanic acid, and afterwards becomes black, and explodes with a red flame. When slowly decomposed in a covered crucible by a heat gradually raised to redness, it yields pure white cyanate of potash mixed with cyanide of potassium. (Schischkoff.) Heated with chloride of potassium in a combustion tube, it gives off hydrocyanic acid, then carbonate of ammonia, and a gaseous mixture containing 2 vol. carbonic acid to 1 vol. nitrogen, like the gas evolved by the decomposition of dry fulminate and cyanate of silver mixed with sulphate of potash. The residue consists of cyanide of potassium mixed with chloride. (Liebig.) The salt is less soluble in cold water than the ammonia-salt (Liebig, Schischkoff), but dissolves in hot water as easily as the latter. (Liebig.) Dissolves in 10 pts. of cold and a much smaller quantity of boiling water; insoluble in alcohol and ether. (Schischkoff.)

	<i>Crystals.</i>		Liebig.	
KO	47.2	28.23
C ⁶ N ³ H ³ O ⁶	120.0	71.77
<hr/>				
C ⁶ N ³ H ³ KO ⁶	167.2	100.00	

Fulminurate of Potash with Mercuric oxide. — The curdy compound above-mentioned. May be obtained directly by heating a solution of fulminurate of potash with mercuric oxide (especially the yellow oxide) and filtering the hot solution. — The mercury in this compound is not separated by boiling with copper; neither does caustic potash or iodide of potassium act upon it as upon other mercuric compounds. (Schischkoff.)

Fulminurate of Soda. — More soluble in water than the potash-salt. Crystallises from the aqueous solution by slow evaporation in long prisms. (Schischkoff.)

Fulminurate of Lithia. — Soluble in water and alcohol. (Liebig.)

Fulminurate of Baryta. — When a warm-saturated solution of fulminurate of ammonia or potash is mixed with chloride of barium, fulminurate of baryta separates after a few minutes in the form of a crystalline pulp, consisting of short, thin, white needles, which dissolve completely in a very large quantity of hot water, and separate on cooling in hard isolated crystals. These crystals are colourless and transparent, and often take the form of rhombic prisms terminated by a macrodiagonal doma. (Liebig.) Refracts doubly, but in a much less degree than the potash and ammonia-salts, the angle of refraction of the extraordinary ray for perpendicular incidence being only $1^{\circ} 9'$. (Rood.) Between 150° and 180° the crystals give off 8.52 p. c. (2 At.) water, and become opaque; at a higher temperature the salt decomposes like the potash-salt. (Liebig.)

	Crystals.		Liebig.	
6 C.....	36.0	16.79	16.36	
3 N	42.0	19.58	19.42	
2 H	2.0	1.86	2.17	
BaO.....	76.6	31.93	32.08	
5 O.....	40.0	21.45	21.45	
2 H O	18.0	8.39	8.52	
<hr/>				
$C^6N^3H^2BaO^6 + 2Aq.$	214.6	100.00	100.00	

The salt burnt with oxide of copper, yields a gaseous mixture containing 3 vol. N, 5 vol. CO_2 ; if to this we add the carbonic acid retained by the baryta, we obtain the ratio 6 : 3, as in cyanogen. (Liebig.)

The *Fulminurates of Lime and Magnesia* are soluble in water and alcohol. (Liebig.)

Fulminurate of Lead. — Neutral lead-salts are not precipitated by the alkaline fulminurates. (Liebig, Schischkoff.) — *Basic salt.* — Basic acetate of lead forms with the alkaline fulminurates a white crystalline precipitate, which dissolves in boiling water, and separates in hard yellowish crystals on cooling. When decomposed by sulphuretted hydrogen, it yields the acid. (Liebig.)

			Liebig.	
2 PbO	224	65.11	64.0	
$C^6N^3H^2O^5$	120	34.89		
<hr/>				
$PbO, C^6N^3H^2PbO^6$	344	100.00		

Ferrous Fulminurate. — Separates in beautiful pale green crystals on heating a fulminurate with ferrous acetate. (Schischkoff.)

fulminic acid, and with a solution of copper in excess of ammonia, and the liquid heated to boiling, it deposits this double salt on cooling, in beautiful, shining, dark blue prisms, which undergo no change in the air at ordinary temperatures, or even at 150°, but are decomposed with explosion at higher temperatures. Nearly insoluble in water, and very sparingly in ammonia, so that very small quantities of fulminuric acid may be separated in this form. The salt gave by analysis 16·23 p. c. copper (calculation gives 16·32.) (Schischkoff.)

Fulminurate of Mercury. — The acid is not precipitated by mercurous or mercuric salts. Mercuric oxide heated in a solution of the acid dissolves in it, and the liquid on cooling deposits a mass resembling the curdy compound of mercuric oxide with fulminurate of potash. (Schischkoff.)

Fulminurate of Silver. — A hot solution of fulminurate of ammonia or potash mixes with nitrate of silver without turbidity; but as the liquid cools, fulminurate of silver separates from it in long, very thin needles having a silky lustre. (Liebig, Schischkoff.) The crystals retain their lustre at 100°, and do not diminish in weight. (Liebig.) The salt is not blackened by light, and does not undergo any change at 150°, but at a higher temperature, it explodes without noise, and gives off hydrocyanic acid. (Schischkoff.) Decomposed by heat in the same manner as cyanate of silver. (Liebig.) Dissolves very sparingly in cold, but pretty easily in boiling water, and may be recrystallised without alteration. (Liebig, Schischkoff.)

			Liebig.	Schischkoff.
6 C	36	15·25	15·17	15·09
3 N	42	17·79	17·68	17·93
2 H	2	0·84	0·89	0·98
Ag	108	45·76	45·15	45·43
6 O	48	20·36	21·11	20·57
<hr/>				
C ⁶ N ³ H ² AgO ⁶	236	100·00	100·00	100·00

Fulminuric acid dissolves in boiling alcohol (Liebig); in alcohol and in ether. (Schischkoff.)

It combines with urea and with aniline, forming crystalline compounds. (Schischkoff.)

Fulminuric Ether. — When fulminurate of potash is immersed in alcohol, and hydrochloric acid gas passed through the liquid, chloride of potassium is formed, together with fulminuric ether; as soon as the reaction is complete, the stream of gas must be discontinued, because an excess of hydrochloric acid decomposes the ether, with formation of a crystalline body. After the excess of alcohol and the chloride of ethyl formed at the same time have been distilled off, and a sufficient quantity of water has been added to the solution of chloride of potassium, the fulminuric ether separates in the form of an aromatic liquid; the portion which remains dissolved may be separated by agitating the watery liquid with common ether. — Fulminuric ether is decomposed by alcoholic potash, even at ordinary temperatures, with formation of fulminurate of potash; it cannot be distilled without decomposition. Its alcoholic solution mixed with aniline, deposits, after a few days, colourless silky prismatic crystals, which melt and turn brown at 100°, and perhaps consist of the anilide of fulminuric acid. (Schischkoff.)

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Nitroglycerine or *Glonolna*. — The following is given by De Vrij as the most advantageous process for preparing this compound: 100 grms. of glycerine, of sp. gr. 1.262, dried at 150°, are poured gradually into 200 cub. cent. of monohydrated nitric acid, cooled to — 10°, care being taken that the mixture never becomes heated above 0°. As soon as the two bodies have united into a homogeneous liquid, 200 cub. cent. of strong sulphuric acid are added in small quantities. If the temperature be kept constantly below 0°, there is no danger of the mass going off in vapour; but this effect readily takes place above 0°. The nitroglycerine separates in the form of an oily stratum on the surface of the acids, from which it may be separated by a tap-funnel. — The quantity thus obtained weighed 200 grms., and the separated acids yielded 20 grms. more on being mixed with water. The whole, amounting to 220 grms., was dissolved in the smallest possible quantity of ether, and the solution repeatedly agitated with fresh water till it no longer reddened litmus paper; it was then evaporated over the water-bath, and the product dried till its weight became constant. It then weighed 184 grms.

From this result, the formula of nitroglycerine appears to be $C^3H^5(NO^2)_3O^2$: for $C^3H^5O^2$ (glycerine) = 92, and $C^3H^5(NO^2)_3O^2 = 182$. [This result differs materially from Railton's (ix. 501)].

Nitroglycerine is a pale yellow oily liquid, of sp. gr. 1.595 to 1.600 at 15°. Decomposes at 160°, and detonates with violence at higher temperatures; also when struck with a hammer on an anvil. Sulphuretted hydrogen decomposes it, with copious deposition of sulphur. (J. E. de Vrij, *N. J. Pharm.* 28, 38; *Chem. Gas.* 1855, 383.)

ADDITIONS TO VOL. X

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Butyl. — According to recent experiments by Wurtz, (*N. Ann. Chim. Phys.* 44, 275; *Ann. Pharm.* 96, 364,) it appears that sodium may be used in the preparation of butyl with greater advantage than potassium, because it acts less violently on iodide of butyl, and does not form so large a quantity of gaseous secondary products. 100 pts. of iodide of butyl and 13 or 14 pts. of sodium are introduced into a flask provided with an upright condensing tube kept cool by ice-water. The action begins at ordinary temperatures, and with evolution of heat, the sodium swelling up and gradually becoming covered with a blue crust. As the action slackens, it must be accelerated by external heat, and the liquid kept boiling till the blue colour of the sodium has disappeared, and the flask contains a white mass of iodide of sodium saturated with butyl. The butyl is then distilled from the flask, and the distillate rectified over sodium till the metal completely retains its lustre in the boiling liquid, and is no longer attacked. The portion which in the last rectification distils over between 105° and 108°, is pure butyl.

Butyl has a density of 0.7057 at 0°. It boils at 106°. Vapour-density = 4.070 (*comp. p.* 68.) — None of the butyl-compounds can be directly prepared from it. Chlorine and bromine act upon it, but form substitution-products. With perchloride of antimony, it yields hydrochloric acid and chlorinated products not yet examined. Pentachloride of phosphorus is decomposed by it only after long boiling, with formation of terechloride of phosphorus, chlorinated butyl, and hydrochloric acid. — When the vapours of iodine and butyl are passed together over spongy platinum, heated in a tube to 300°, a large quantity of hydriodic acid is formed, together with a small quantity of an iodised organic substance, probably a substitution-product. — Hydrochloric acid has no action upon butyl, either at ordinary temperatures or at a temperature near that of boiling oil. (Wurtz.)

Ethylbutyl. $C^{12}H^{14} = \left. \begin{matrix} C^4H^6 \\ C^8H^8 \end{matrix} \right\}$ Obtained by decomposing 40 pts. of iodide of butyl and 34 pts. of iodide of ethyl with 11 pts. of sodium, as in the preparation of butyl. The action begins spontaneously, but requires external heat to keep it up; and the boiling must be continued till the sodium is converted into a white mass. On subsequently distilling the contents of the flask in the oil-bath, the thermometer remains stationary for some time between 60° and 70°. The portion which passes over at below 100°, must be collected apart, (between 100° and 110° a considerable quantity of butyl distils over,) heated with sodium in a sealed glass tube, and redistilled as soon as the fused sodium immersed in it retains its metallic lustre. The thermometer then remains nearly constant between 60° and 65°; and by a second rectification of the portion which distils over between these temperatures, the ethylbutyl is obtained in the pure state.

Transparent, very mobile liquid, of sp. gr. 0.7011 at 0°. Boils at 62. Vapour-density = 3.053.

12 C	72	83.72	Wurtz.
14 H	14	16.28	83.48
$C^{12}H^{14}$	86	100.00	16.50
			99.98
		Vol.	Density.
C-vapour	12	4.9920	
H-gas	14	0.9702	
Vap. of $C^{12}H^{14}$	2	5.9622	
	1	2.9811	

Ethyl-amyI, C^4H^6 , $C^{10}H^{11}$, and *Butyl-amyI*, C^8H^9 , $C^{10}H^{11}$, are prepared by exactly similar processes; *Butyl-caproyl*, C^8H^9 , $C^{12}H^{13}$, by the electrolysis of a mixture of valerate and œnanthylate of potash; and *Methyl-caproyl*, C^3H^3 , $C^{12}H^{13}$, by the electrolysis of a mixture of acetate and œnanthylate of potash.

The mode of formation of these compound radicals, and a comparison of their properties with those of the simple radicals, affords an additional argument in favour of the theory which supposes the simple radicals, in the free state, to form diatomic vapours, regarding methyl in the free state as C^3H^3 , ethyl as C^4H^6 , &c. (vii. 173). In fact, on comparing the physical properties of the simple and compound radicals, as exhibited in the following table, it is plainly seen that they are members of the same series, and that, to establish a regular connection between the properties of these bodies and their formulæ, it is absolutely necessary to double the formulæ of the simple radicals. (Wurtz.)

Radical.	Formula.	Sp. gr. at 0°.	Vapour-density.		Boiling Point.
			Observed.	Calculated.	
Ethyl-butyl	$C^{12}H^{14} = C^4H^6$ C^8H^9	0.7011	3.053	2.972	62°
Ethyl-amyI	$C^{14}H^{16} = C^4H^6$ $C^{10}H^{11}$	0.7069	3.522	3.455	88
Methyl-caproyl?	$C^{14}H^{16} = C^3H^3$ $C^{12}H^{13}$?	3.426	3.455	82?
Butyl.....	$C^{10}H^{12} = C^8H^9$ C^8H^9	0.7057	4.070	3.939	106
Butyl-amyI	$C^{18}H^{20} = C^8H^9$ $C^{10}H^{11}$	0.7247	4.465	4.423	132
AmyI.....	$C^{20}H^{22} = C^{10}H^{11}$ $C^{10}H^{11}$	0.7413	4.956	4.907	158
Butyl-caproyl	$C^{20}H^{22} = C^{10}H^{11}$ $C^{12}H^{13}$?	4.917	4.907	155
Caproyl.....	$C^{24}H^{26} = C^{12}H^{13}$ $C^{12}H^{13}$	0.7574	5.983	5.874	202?

Schweinfurt Green with Butyric acid. — When butyric acid is saturated with recently precipitated carbonate of copper, and the solution mixed with a solution of arsenious acid saturated at a boiling heat, a yellowish green amorphous precipitate is formed, which after a while becomes crystalline, and exhibits the fine green colour belonging to ordinary Schweinfurt green (viii. 330), which it also resembles in its other properties. (Wöhler, *Ann. Pharm.* 94, 44.)

		Springmann.	
3 CuO	120	30.2	30.5
2 AsO ³	198	49.9	50.1
C ⁸ H ⁷ O ³	79	19.9	19.4
2 (CuO,AsO ³) + C ⁸ H ⁷ CuO	397	100.0	100.0

This salt differs therefore in stoichiometrical composition from the true Schweinfurt green, the latter containing 3 At. arsenite of copper to 1 At. acetate.

Page 160.

Alloxanic acid. — To obtain alloxantin from the mother-liquor which remains in the preparation of alloxan by the action of nitric acid upon uric acid; Schlieper recommends (p. 173) that the excess of acid be neutralised with chalk before passing sulphuretted hydrogen through the liquid, in order to prevent oxidising action. With due care not to add too much chalk, this process succeeds well enough; but if the nitric acid be completely neutralised with chalk, bicarbonate of lime is formed at the same time, and rapidly converts the alloxan into alloxanic acid.

This process may be advantageously applied to the preparation of alloxanic acid. If the dilute acid mother-liquor be mixed with excess of chalk, acid alloxanate of lime immediately separates, partly on the surface of the liquid, partly as a precipitate, in well defined crystals or crystalline crusts, which may be easily freed from admixed chalk by elutriation. It is best to add a considerable excess of chalk and to stir frequently; the salt then forms and separates out very quickly. The heavy crystals remaining after the elutriation may be purified by dissolving them in water, not quite at a boiling heat, and filtering while still hot; the alloxanate of lime is then deposited in white crusts as the liquid cools. — Extremely beautiful crystals are often found in the scum which forms when the mother-liquor of alloxan is saturated with chalk. These crystals are perfectly transparent, glassy, oblique six-sided prisms, but generally having two of their faces so little developed, that they appear like acute rhombohedrons. In dry air, they very soon give off a portion of their water of crystallisation, and become milk white.

<i>Milk-white crystals dried over oil of vitriol.</i>		Städeler.	
CaO	28	12.50	12.59
8 C	48	21.43	21.12
2 N	28	12.50	12.72
8 H	8	3.57	3.63
14 O	112	50.00	49.94
C ⁸ N ² H ⁸ CaO ¹⁰ + 5Aq.	224	100.00	100.00

			Städeler.
CaO	28	12.50	12.59
C ² N ² H ² O ⁹	151	67.41	
5 HO	45	20.09	19.70
<hr/>			
C ² N ² H ² CaO ¹⁰ + 5Aq.....	224	100.00	

This is the composition which Schlieper assigns to the transparent, air-dried salt; but according to Städeler, the transparent crystals contain 1 At. water more, their composition being C²N²H²CaO¹⁰ + 6Aq. When dried over oil of vitriol, they give off 3.86 p. c. water; calculation for 1 At. requiring 4.25 p. c.—When acid alloxanate of lime crystallises from a solution saturated while warm, the crystals are not perfectly transparent, and contain between 5 and 6 At. water; when dried over oil of vitriol, they give off 2 to 3 p. c. water.

From the lime-salt, the *free acid* may be readily obtained as follows: The concentrated solution supersaturated with ammonia is precipitated by carbonate of ammonia; the liquid heated and filtered (in the cold the precipitation is imperfect); the filtered solution of the ammonia-salt left for a while over oil of vitriol to remove the free ammonia, and then precipitated with acetate of lead; the lead-salt, which is free from ammonia, suspended while yet moist, in alcohol, and decomposed by sulphuretted hydrogen; and the alcoholic solution of alloxanic acid evaporated at a gentle heat. The acid then remains in the form of a colourless viscid mass, which has a very sour taste, and gradually solidifies in the crystalline form. Schlieper (*Ann. Pharm.* 55, 259) is of opinion that the amorphous state is brought about by the application of too much heat during the evaporation; but the observation just quoted shows that the acid at first assumes the amorphous state when the alcoholic solution is evaporated over oil of vitriol at ordinary temperatures. (G. Städeler, *Ann. Pharm.* 97, 120.)

R E P O R T
OF
THE NINTH ANNIVERSARY MEETING
OF THE
CAVENDISH SOCIETY.

THE Anniversary Meeting of the Cavendish Society for the year 1856, was held at the rooms of the Chemical Society, No. 5, Cavendish Square, on Saturday, the 1st of March, at three o'clock in the afternoon.

The Chair was taken by THOMAS GRAHAM, Esq., F.R.S., PRESIDENT, who called upon the Secretary to read

THE REPORT OF THE COUNCIL.

“ In this Report the Council have but a brief statement to make with reference to their proceedings for the last twelve months. The first of the books for 1855 was ready for distribution when the Council came into office last March; a third book for 1854, which was then in progress, has since been completed; and both of these works have been supplied to Members.

“ As a second book for 1855, it is proposed to give a volume of BISCHOF'S ‘ Elements of Chemical and Physical Geology,’ which is being prepared for that purpose, and is expected to be ready for distribution in about a month. The translation of this, the second volume of the work, is made by DR. PAUL.

“ The first of the books for the present year, 1856, will be the tenth volume of GMELIN'S ‘ Hand-book of Chemistry,’ the preparation of which is in a forward state, so that it will probably be in the hands of Members about Midsummer.

“ The Council are gratified in being enabled to refer to the continued prosperity of the Society as indicated by the financial statement which accompanies this report. It will be seen that there

has been no falling off in the income of the Society; on the contrary, the amount received since the last Anniversary Meeting exceeds the income of any previous year. The support of the Society has, indeed, for several years past, been characterized by great uniformity, accompanied by a gradual, although slight, improvement. These circumstances cannot be considered as otherwise than highly satisfactory, especially as the political events of the last year or two have been calculated rather to depress than to encourage or promote the desire of the public for scientific literature. That there has been no sensible defalcation in the income of the Society, is, no doubt, mainly to be ascribed to the high appreciation which has been formed of the works which have, from year to year, been produced. Of this the continued demand for the first six volumes of GMELIN'S 'Hand-book of Chemistry,' and the frequent applications which are made for LEHMANN'S 'Physiological Chemistry,' afford abundant evidence. Sixty-three sets of the Inorganic part of the 'Hand-book of Chemistry' have been supplied to Subscribers during the last twelve months.

"The selection of suitable works to be undertaken when those now in hand have been completed, is a part of the duty of the Council, which frequently occupies their deliberate attention. Several new works have been suggested, and some of these are still under consideration, but the arrangements for future publication are yet incomplete. The Council trust they may be enabled to keep up such a succession of valuable works as will maintain the character which the Society has hitherto acquired in this respect.

TREASURER'S STATEMENT OF THE RECEIPTS AND EXPENDITURE OF THE CAVENTISH SOCIETY,
from the 1st of March, 1855, to the 26th of February, 1856.

RECEIPTS.		EXPENDITURE.	
	£	s.	d.
Balance from previous year	337	18 3
5 Subscriptions for 1848	2	12 6
1 Ditto 1849	1	1 0
3 Ditto 1850	3	3 0
6 Ditto 1851	6	6 0
30 Ditto 1852	31	10 0
119 Ditto 1853	121	9 0
171 Ditto 1854	177	19 0
469 Ditto 1855	488	11 0
153 Ditto 1856	160	13 0
63½ Sets GMELIN'S 'Inorganic Chemistry'	133	7	0
		<u>£1464</u>	<u>9 9</u>
		Stationery, Postage, Delivery of Books, } &c.	17 18 11½
		Insurance	2 5 0
		Collector's Commission	8 2 0
		Secretary	100 0 0
		Editorial expenses	231 15 0
		Paper	74 4 0
		Printing and Engraving	264 1 0
		Binding and wrapping	126 0 11
		Balance in hand	824 6 10½
			<u>640 2 10½</u>
		<u>£1464</u>	<u>9 9</u>

We have examined the above statement, and find it correct.

February 27th, 1856.

THOS. PELHAM DALE, M.A.
DAN. HANBURY.

It was resolved,

“That the Report just read be received, approved, and adopted.”

The Meeting then proceeded to the election of Officers for the ensuing year, and the following Gentlemen were declared to have been duly elected:—

President.

THOMAS GRAHAM, F.R.S.

Vice-Presidents.

PROFESSOR BRANDE, F.R.S.
EARL OF BURLINGTON, F.R.S.
SIR JAMES CLARK, M.D., F.R.S.
WALTER CRUM, F.R.S.
JOHN DAVY, M.D., F.R.S.
CHARLES G. B. DAUBENY, M.D., F.R.S.
MICHAEL FARADAY, D.C.L., F.R.S.

JOHN GRAHAM, Esq.
HENRY BEAUMONT LEESON, M.D.
F.R.S.
W. A. MILLER, M.D., F.R.S.
PROFESSOR WHEATSTONE, F.R.S.
COLONEL PHILIP YORKE, F.R.S.

Council.

ALEXANDER BAIN, Esq.
G. B. BUCKTON, F.C.S.
DUGALD CAMPBELL, F.C.S.
PHILIP JAMES CHABOT, M.A., F.C.S.
HENRY DEANE, Esq.
WARREN DE LA RUE, Ph.D., F.R.S.
W. FERGUSON, F.C.S.
A. B. GARROD, M.D.

JOHN HALL GLADSTONE, Ph.D., F.R.S.
A. W. HOFMANN, Ph.D., F.R.S.
HENRY LETHEBY, M.B.
R. PORRETT, F.R.S.
ALFRED SMEE, F.R.S.
JOHN STENHOUSE, LL.D., F.R.S.
R. D. THOMSON, M.D., F.R.S.
A. W. WILLIAMSON, Ph.D., F.R.S.

Treasurer.

GEORGE DIXON LONGSTAFF, M.D., 9, Upper Thames Street.

Secretary.

THEOPHILUS REDWOOD, Ph.D., 19, Montague Street, Russell Square,
and 17, Bloomsbury Square.

Collector.

MR. THOMAS WEST, 32, Soho Square.

It was resolved,

“ That DR. LIONEL BEALE, DR. ODLING, and MR. TRENHAM REEKES, be appointed Auditors for the ensuing year.”

The following Resolutions were unanimously adopted:—

“ That the thanks of the Meeting be given to the PRESIDENT, TREASURER, and COUNCIL, for their services to the Society.”

“ That the thanks of the Meeting be given to the HONORARY LOCAL SECRETARIES for their services to the Society.”

“ That the thanks of the Meeting be given to the CHEMICAL SOCIETY for the use of their rooms on the present occasion.”

The Meeting was then adjourned.

THEOPHILUS REDWOOD, SECRETARY,
19, Montague Street, Russell Square,
and 17, Bloomsbury Square.

MARCH 1st, 1856.

OBJECTS, &c., OF THE CAVENDISH SOCIETY.

The Cavendish Society was instituted for the promotion of Chemistry and its allied sciences, by the diffusion of the literature of these subjects.

The subscription, constituting membership, is one guinea a-year, to be paid in advance; and the subscription becomes due on the 1st of January of each year. A member is entitled to a copy of every book published by the Society for the year for which he has subscribed, but no member can receive the Society's publications until his subscription has been duly paid.

WORKS OF THE CAVENDISH SOCIETY.

1848.

- 1.—CHEMICAL REPORTS AND MEMOIRS. Edited by THOMAS GRAHAM, F.R.S. (Out of Print.)
- 2.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Translated by HENRY WATTS, B.A., F.C.S. Vol. I.

1849.

- 3.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. II.
- 4.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. III.
- 5.—THE LIFE AND WORKS OF CAVENDISH. By Dr. GEORGE WILSON.

1850.

- 6.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. IV.
- 7.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. V.

1851.

- 8.—PHYSIOLOGICAL CHEMISTRY. By PROFESSOR LEHMANN. Translated by GEORGE E. DAY, M.D., F.R.S. Vol. I. (Out of Print.)
- 9.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. VI.

1852.

- 10.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. VII. (Organic Chemistry, Vol. I.)
- 11.—PHYSIOLOGICAL CHEMISTRY. By PROFESSOR LEHMANN. Vol. II.
- 12.—ATLAS OF PLATES RELATING TO PHYSIOLOGICAL CHEMISTRY. By Dr. OTTO FUNKE. (Supplement to LEHMANN'S PHYSIOLOGICAL CHEMISTRY.)

1853.

- 13.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. VIII. (Organic Chemistry, Vol. II.)
- 14.—ELEMENTS OF CHEMICAL AND PHYSICAL GEOLOGY. By PROFESSOR BISCHOF. Vol. I.

By Dr. W. C. HENRY, F.R.S.

- 16.—**PHYSIOLOGICAL CHEMISTRY.** By PROFESSOR LEHMANN. Vol. III.
- 17.—**LAURENT'S CHEMICAL METHOD.** Translated by WM. ODLING, M.B.
1855.
- 18.—**HAND-BOOK OF CHEMISTRY.** By LEOPOLD GMELIN. Vol. IX. (Organic Chemistry, Vol. III.)
- 19.—**ELEMENTS OF CHEMICAL AND PHYSICAL GEOLOGY.** By PROFESSOR BISCHOF. Vol. II.
1856.
- 20.—**HAND-BOOK OF CHEMISTRY.** By LEOPOLD GMELIN. Vol. X. (Organic Chemistry, Vol. IV.)
- 21.—A second book for this year will be issued.

CHEMICAL REPORTS AND MEMOIRS. Edited by PROFESSOR GRAHAM. This work is out of print.

GMELIN'S HAND-BOOK OF CHEMISTRY. Translated and Edited by HENRY WATTS, B.A., F.C.S.

Members of the Cavendish Society, or others through a Member of the Society, may obtain one or more copies of THE FIRST SIX VOLUMES of this work, comprising the whole of the INORGANIC CHEMISTRY, for a Subscription of TWO GUINEAS.

Members may also have for one year's subscription the SEVENTH AND EIGHTH VOLUMES OF GMELIN'S HAND-BOOK, which are the first two volumes of the part treating of ORGANIC CHEMISTRY.

The Ninth volume of the Hand-book is the first of the books for 1855.

LEHMANN'S PHYSIOLOGICAL CHEMISTRY. Translated and Edited by Dr. G. E. DAY, F.R.S.

The First Volume of this work is out of print. There still remain a sufficient number of copies of the Second and Third Volumes, and of Dr. Otto Funke's Atlas of Physiological Plates, for supplying those members who have not completed their sets.

BISCHOF'S ELEMENTS OF CHEMICAL AND PHYSICAL GEOLOGY.

The First Volume of this work having been issued for the year 1853, in conjunction with the Eighth Volume of Gmelin's Chemistry, members who do not possess, and do not desire to subscribe for, the previous volumes of Gmelin, may have the Life and Works of Cavendish instead of the Hand-Book of Chemistry, as the second book for that year. Or the First and Second Volumes of Bischof's Geology may be had for one year's subscription.

* * * Applications for the books of the Society, or for information relating to them, are to be made, if by letter, to the Secretary, or personally to Mr. Charles Wood, No. 17, Bloomsbury Square.

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Bathgate—James Young, Esq.
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York—W. G. Procter, Esq.

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Philadelphia—William Procter, jun., Esq.
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MAR 24 1936

