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Issued May 8, 1913.

U. S. DEPARTMENT OF AGRICULTURE,  
BUREAU OF SOILS—BULLETIN No. 94.  
MILTON WHITNEY, CHIEF.

THE OCCURRENCE OF POTASSIUM SALTS IN  
THE SALINES OF THE UNITED STATES.

BY

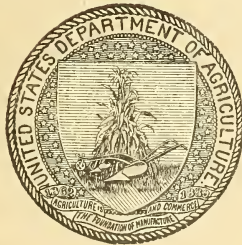
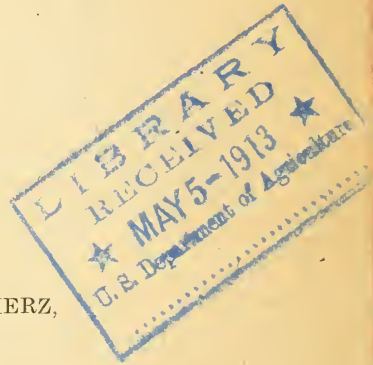
J. W. TURRENTINE,

WITH

ANALYSES

BY

W. H. ROSS, R. F. GARDNER, A. R. MERZ,  
AND J. A. CULLEN.



WASHINGTON:  
GOVERNMENT PRINTING OFFICE.

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## BUREAU OF SOILS.

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## LETTER OF TRANSMITTAL.

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U. S. DEPARTMENT OF AGRICULTURE,  
BUREAU OF SOILS,  
*Washington, D. C., September 12, 1912.*

SIR: I have the honor to transmit herewith the manuscript of an article on the Occurrence of Potassium Salts in the Salines of the United States, by J. W. Turrentine, scientist in physical and chemical investigations in this bureau. This bulletin details the results of investigations into the possible commercial value of natural and artificial brines of the United States as a source of potash. I recommend that this material be published as Bulletin No. 94 of the Bureau of Soils.

Very respectfully,

MILTON WHITNEY,  
*Chief of Bureau.*

HON. JAMES WILSON,  
*Secretary of Agriculture.*



## PREFACE.

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The Sixty-second Congress, first session, authorized and directed that investigations should be carried on, in part by the Bureau of Soils, United States Department of Agriculture, and in part by the United States Geological Survey, looking to the fertilizer resources of the United States, with special reference to possible sources of potash salts. A preliminary report was prepared by the Bureau of Soils, from which it appears that the United States contains within its borders ample supplies of raw materials, suitable for commercial exploitation, for the manufacture of standard types of fertilizers. This report was submitted to the President and by him transmitted to Congress and printed as Senate Document No. 190, Sixty-second Congress, second session. The discussion of certain features of the investigations which have been inaugurated were quite full in the preliminary report cited. Subsequent work, however, requires more detailed reports of other features, and these will be given from time to time, as the progress of the work justifies, in appropriate form.<sup>1</sup>

The present bulletin covers another phase of this investigation of the Nation's fertilizer assets, namely, the probable value of natural brines and salt wells as a source of potash salts. Potassium is practically always present, and sometimes in appreciable quantities. A careful consideration of all the factors involved makes it appear quite improbable, however, that any known American occurrences of neutral salt mixtures can be worked economically for potash under such commercial conditions as now exist or are likely to exist, so far as the future can be foreseen. Certain alkaline deposits containing carbonates or borates or both may have an importance in this connection and will be discussed in later publications when fuller investigation shall have justified the formation of a sound judgment concerning them. At present while other American sources of potash hold promise of commercial importance, the giant kelps of the Pacific littoral seem to be the largest and most practicable source for this material yet determined.

FRANK K. CAMERON,  
*In charge Chemical and Physical Laboratories.*

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<sup>1</sup> See in this connection the following publications of this bureau:

Bul. No. 69. A Review of the Phosphate Fields of Idaho, Utah, and Wyoming, by W. H. Waggaman.

Bul. No. 76. A Review of the Phosphate Fields of Florida, by W. H. Waggaman.

Bul. No. 81. A Report on the Natural Phosphates of Tennessee, Kentucky, and Arkansas, by W. H. Waggaman.

Circ. No. 61. An Investigation of the Otero Basin, N. Mex., for Potash Salts, by E. E. Free.

Circ. No. 62. Report of a Reconnoissance of the Lyon Nitrate Prospect, Near Queen, N. Mex., by E. E. Free.

Circ. No. 70. Alunite as a Source of Potash, by W. H. Waggaman.

Circ. No. 71. The Extraction of Potash from Silicate Rocks, by William H. Ross.

Several publications along similar lines have appeared from the U. S. Geological Survey.



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# THE OCCURRENCE OF POTASSIUM SALTS IN THE SALINES OF THE UNITED STATES.

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## GENERAL CONSIDERATIONS CONCERNING THE ORIGIN OF SALINE SEGREGATES.

The ocean may be regarded as the recipient of the soluble matter dissolved by rain water as it flows over and percolates through the upper strata of the earth's crust. The view is, in the main, correct. Thus the ocean has become the storehouse of the great bulk of the soluble saline constituents of the earth's crust. But there are certain drainage waters which never reach the ocean. These flow into certain depressions, found on several continents, which have no outlet to the sea and where the conditions are favorable to rapid evaporation. The dissolved matter carried therein accumulates and results in the formation of saline lakes or the deposition of saline crusts.

The source of the bases entering into the composition of much of the saline material found in the ocean and in the waters flowing into the ocean is the decomposing minerals of the earth's crust, igneous and sedimentary. The ultimate source of all the saline material of the ocean is a matter of speculation. Thus the sodium feldspars, on decay under atmospheric influences, yield the sodium as oxide to the percolating waters. This uniting with the carbon dioxide from the atmosphere becomes sodium carbonate. The potassium feldspars (microcline and orthoclase) in like manner lead to the formation of soluble potassium compounds. The nature of the bases dissolved then is determined by the nature of the rocks leached, and the nature of the salts conveyed into a basin is determined by that of the rocks surrounding that basin. The ocean may be regarded as such a basin whose inclosing rocks are those of all the land areas. In the ocean water are to be found accordingly all the commoner inorganic salts which occur in nature and are capable of existing, under the circumstances, as soluble salts. In this discussion, however, the continental basin will be treated as different from the ocean. In small continental basins the rocks comprising the watershed or drainage areas are more easily defined and likewise the formation of the salt mixture which accumulates therein. Just as the rocks surrounding one basin may vary from those surrounding another, so the salts occurring in or deposited from lakes may vary widely in composition from those of sea-water and, as well, from those of other continental basins.

While the igneous rocks are the ultimate source of the bases composing such salts, it must be borne in mind that some if not a major part of the sodium chloride found in some streams may be the cyclic salt which has been carried from the ocean and arid regions bordering the ocean by eolian agencies. In certain saline basins near the ocean the sodium chloride may be entirely derived from this source. With sodium chloride must be transferred the other saline constituents of the ocean, as the particles of saline dust borne by the winds originate from the desiccation of minute drops of ocean water. Or it may be in part the salts found in sedimentary rocks, originating from occlusions of ocean brine or from adsorption of saline materials from ocean water.

It is to be expected that the salts laid down in continental basins would be made up of mixtures in which the ratio between the bases is the same as that in which they exist in the rim rocks of the basin. That such is not the case is explicable in part by the selective adsorption created by the earth filters through and over which the seeping waters pass. Thus potassium is very largely eliminated, while sodium is allowed to pass. This fact, at least in part, accounts for the preponderance of sodium over potassium in the accumulated water from drainage areas.

Analyses of ocean water and the water from certain typical saline lakes are given in the following tables.

From an examination of these tables it will be seen that the difference between the salts contained in the various basins (regarding the ocean as a basin) is in general one of relative amounts of the constituents rather than of kind.

Data gathered from a study of one, then, may be applied, within limits, to the study of the others.

TABLE I.—*Analysis of ocean salts.*<sup>1</sup>

[Parts per 100,000.]

| Constituents determined.                              | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 10    |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Cl.....   | 55.29 | 55.18 | 55.04 | 55.21 | 55.01 | 55.62 | 55.24 | 55.25 | 55.46 | 55.22 |
| Br.....   | .19   | .18   | .19   | .19   | .13   |       | .17   |       |       | .14   |
| SO <sub>4</sub> .....                                 | 7.69  | 7.91  | 7.86  | 7.69  | 8.00  | 8.01  | 7.54  | 7.56  | 7.59  | 7.88  |
| CO <sub>3</sub> .....                                 | .21   | .21   | .18   | .09   | .14   | .27   | .34   | .37   | .30   | .10   |
| Na.....   | 30.59 | 30.26 | 30.71 | 30.82 | 30.47 | 30.20 | 30.80 | 30.76 | 30.53 | 30.65 |
| K.....  | 1.11  | 1.11  | 1.06  | 1.16  | .96   | 2.10  | 1.10  | 1.14  | 1.12  | .93   |
| Rb.....   |       |       |       |       | .04   |       |       |       |       | .04   |
| Ca.....   | 1.20  | 1.24  | 1.27  | 1.21  | 1.67  | 1.36  | 1.22  | 1.22  | 1.21  | 1.21  |
| Mg.....   | 3.72  | 3.90  | 3.69  | 3.61  | 3.53  | 3.36  | 3.59  | 3.70  | 3.79  | 3.75  |
| Fe <sub>2</sub> Si <sub>2</sub> PO <sub>4</sub> ..... |       |       |       |       | .05   |       |       |       |       | .08   |

<sup>1</sup> From Clarke, Bul. 491, U. S. Geol. Survey, with modifications.

1. Mean of 77 analyses of ocean water from many localities; salinity, 3.301 to 3.737 per cent. W. Dittmar, analyst.

2. Mean of 22 samples Atlantic water, Cape of Good Hope to England. Average salinity, 3.631 per cent. C. J. S. Maxim, analyst.

3. From the Atlantic near Dieppe. Salinity, 32.420 grains per liter. T. Schloesing, analyst.

4. From Irish Sea; trace of Li reported. T. E. Thorpe and E. H. Morton, analysts.

5. From the Baltic Sea. Salinity, 0.7215 per cent. C. Schmidt, analyst.

6. Mean of two samples from the Atlantic, coast of Argentina. Salinity, 3.365 per cent. F. Lahille, analyst.

7. From Gulf of Mexico, near Florida. Salinity, 3.549 per cent. G. Steiger, analyst.

8. Mean of 5 analyses of samples from near Beaufort, coast of North Carolina. Salinity, 3.179 to 3.607 per cent. A. S. Wheeler, analyst.

9. Mean of 51 incomplete analyses of samples from the north Atlantic. Salinity, 3.37 to 3.56 per cent. L. Schmelck, analyst.

10. Average of 3 samples of water from the White Sea. Salinity, 2.598 to 2.968. C. Schmidt, analyst.



TABLE II.—*Analysis of water from Great Salt Lake.*<sup>1</sup>

[Parts per 100,000.]

| Constituents determined.                                 | 1      | 2     | 3     | 4      | 5     | 6      | 7     | 8     |
|--|--------|-------|-------|--------|-------|--------|-------|-------|
| Cl.....  | 55.99  | 56.21 | 55.57 | 55.69  | 55.54 | 55.25  | 55.11 | 53.72 |
| Br.....  | Trace. |       |       | Trace. |       | Trace. |       |       |
| SO <sub>4</sub> .....                                    | 6.57   | 6.89  | 6.86  | 6.52   | 5.97  | 6.73   | 6.66  | 5.95  |
| CO <sub>2</sub> .....                                    |        | .07   |       |        |       |        |       |       |
| Li.....  | Trace. |       |       | .01    |       | Trace. |       |       |
| Na.....  | 33.15  | 33.45 | 33.17 | 32.92  | 33.39 | 34.65  | 32.97 | 32.81 |
| K.....   | 1.60   | (?)   | 1.59  | 1.70   | 1.08  | 2.64   | 3.13  | 4.99  |
| Ca.....  | .17    | .20   | .21   | 1.05   | .42   | .16    | .17   | .31   |
| Mg.....  | 2.52   | 3.18  | 2.60  | 2.10   | 2.60  | .57    | 1.96  | 2.22  |
| (FeAl) <sub>2</sub> O <sub>3</sub> Si <sub>2</sub> ..... |        |       |       | .01    |       |        |       |       |
| Salinity, per cent.....                                  | 14.9   | 13.79 | 15.67 | 23.04  | 19.56 | 27.72  | 22.99 | 17.69 |

<sup>1</sup> From Clarke, Bul. 491, U. S. Geol. Survey.

- |  |   |
|--|---|
| 1. Analyst, O. D. Allen, 1839.         | 5. Analyst, J. E. Talmage, 1839.                |
| 2. Analyst, Charles Smart, 1877.       | 6. Analyst, W. Blum, 1904.                      |
| 3. Analyst, E. von Cochenhausen, 1879. | 7. Analyst, W. C. Ebaugh and K. Williams, 1907. |
| 4. Analyst, E. Waller, 1891 (?).       | 8. Analyst, W. Macfarlane, 1910.                |

TABLE III.—*Analysis of water from Lahontan Basin.*<sup>1</sup>

[Parts per 100,000.]

| Constituents determined.                 | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9       |
|--|-------|-------|-------|-------|-------|-------|-------|-------|---------|
| Cl.....                                  | 1.18  | 7.59  | 41.04 | 47.88 | 7.50  | 23.77 | 2.19  | 31.82 | 36.51   |
| SO <sub>4</sub> .....                    | 7.47  | 12.87 | 5.25  | 3.67  | 16.14 | 21.29 | 13.92 | 3.27  | 10.36   |
| CO <sub>2</sub> .....                    | 38.73 | 33.30 | 14.28 | 7.93  | 30.34 | 17.34 | 39.55 | 21.57 | 13.78   |
| PO <sub>4</sub> .....                    |       |       |       |       |       |       |       | .07   |         |
| B <sub>4</sub> O <sub>7</sub> .....      |       |       |       |       |       |       |       |       | .25     |
| Na.....                                  | 10.10 | 17.26 | 33.84 | 36.68 | 18.08 | 34.83 | 13.63 | 29.97 | 36.63   |
| K.....                                   | 4.56  |       | 2.11  | 1.94  |       |       | 2.92  | 6.54  | 2.01    |
| Ca.....                                  | 12.86 | 11.02 | .25   | .55   | 12.96 | .90   | 14.28 | 1.35  |         |
| Mg.....                                  | 4.15  | 3.49  | 2.28  | .49   | 2.21  | 1.56  | 3.62  | 1.88  | .22     |
| SiO <sub>2</sub> .....                   | 18.95 | 14.47 | .95   | .77   | 12.78 | .31   | 9.51  | 3.53  | .24     |
| (FeAl) <sub>2</sub> O <sub>3</sub> ..... |       |       |       |       |       |       | .38   |       |         |
| Salinity, P. P. M.....                   | 73    | 153   | 4,386 | 3,602 | 180   | 2,500 | 361   | 929   | 113,700 |

<sup>1</sup> From Clarke, loc. cit.

1. From Lake Tahoe, Cal. F. W. Clarke, analyst.
2. From Truckee River, Nev., mean of 2 analyses from Southern Pacific R. R.
3. Pyramid Lake, Nev., mean of 4 analyses by F. W. Clarke.
4. Winnemucca Lake, Nev. F. W. Clarke, analyst.
5. Walker River. F. W. Clarke, analyst.
6. Ibid, mean of 2 analyses.
7. Humboldt River, Nev. T. M. Chatard, analyst.
8. Humboldt Lake, Nev. O. D. Allen, analyst.
9. Large Soda Lake, Ragtown, Nev. Sample from surface. T. M. Chatard, analyst.

The continued desiccation of any isolated body of salt-laden water results in the deposition of some of the salts. Since evaporation takes place from the surface more rapidly than diffusion, the solution there becomes more concentrated and of higher specific gravity. It is presumed that as a consequence it flows from the surface to the bottom of the basin and that the more concentrated solution accumulates near the bottom. Eventually the concentration there reaches successively the saturation point of the respective saline constituents and the latter are deposited in the order of their solubilities.

This theory of the concentration of saline waters really accounts only for the formation of concentrated brines and not for the actual

crystallization. Obviously, crystallization does not occur from saturated brine unless it is chilled or further evaporated. Chilling may take place in the bottom of a lake, but evaporation can not. The phenomena observed as accompanying crystallization induced by evaporation lead one to conclude that crystallization takes place on the surface of the evaporating solution and that the crystals formed on the surface drop to the bottom, either as a meal or as parts of a crust. This is known to be the case in the beaker, the salt pan evaporators, and likewise in Great Salt Lake, where, during the winter, thin crusts of sodium sulphate form and undoubtedly fall to the bottom of the lake.

As desiccation proceeds there should be built up in the bottom of the basin a stratified deposit of salts, the order of which from the bottom upward represents the order of their solubility under the conditions existing. As it is not a case of the solubility of the salts in pure water, values which are familiar, but rather their solubility in the solutions of each other or their reciprocal solubilities, it is not at first apparent what the order of deposition will be. Numerous variables exert mutual influences. Desiccation may proceed at once to complete dryness, when all the constituents will crystallize. Periods of humidity may succeed periods of aridity, when the strata of salt will be repeated. Seasonal periods of humidity may cause a deposition of sand or clay as an interstratification of the salt layers, or a long period of humidity following a long period of aridity may lead to the resolution of the deposit or, more probably, its complete covering by a deposition of clay. The latter would tend to preserve the salts from further disturbance. In subsequent geologic ages they may become buried hundreds of feet deeper. In such manner the known deposits of salts may be explained.

It has been seen that the difference between the compositions of the various bodies of salt-bearing water is one of the relative proportions of the saline constituents rather than of the nature of the constituents, though differences of the latter sort are also to be found. Sodium chloride, in general, is found to be present in preponderance. It is generally true that the first substances to crystallize are calcium carbonate, calcium sulphate, and sodium chloride, in the order named. As the period of crystallization of sodium chloride is a very long one, it may frequently be interrupted by periods of humidity. And, too, before the end of this period is reached, the conditions favoring crystallization may come to a permanent end, so that succeeding salts do not make their appearance in the solid form.

The most complete series of stratified salt deposits known in nature are those of the Magdeburg-Halberstadt region of Germany, commonly known as the Stassfurt deposits. The entire column of strata

has a total thickness of about 2,700 feet. The lower masses are pure rock salt with interstratifications of calcium sulphate, above which is more rock salt, which is contaminated by some of the more soluble substances with which the evaporating solution had become concentrated; these are found crystallized in the superimposed strata as sulphate of magnesium and the complex salts, chlorides, and sulphates, of magnesium, calcium, sodium, and potassium. The borates, likewise, have formed segregated layers of crystalline double salts; and interposed with all the salt bodies are strata of sodium chloride. An impervious layer of clay blankets the entire deposit.

The Stassfurt deposit, it is commonly accepted, was laid down by an evaporating arm of the sea into which renewed volumes of sea water continually flowed. That it was not the result of the complete desiccation of an inland lake is indicated by the enormous mass of salts segregated. It is taken as the criterion by which one is able to predict what will happen upon the evaporation of analogous bodies of water and to say what has happened in the case of other deposits of salts.

As the deposition of rock salt is dependent only on suitable conditions of topography and aridity, it is not confined to any geologic age. This fact is brought out by the following table of distribution:<sup>1</sup>

TABLE IV.—*Distribution of saline segregates.*

| Geologic formation.    | Locality.  |
|------------------------|--|
| Recent.....            | Kirghiz steppes; Arabia; South America; Dead Sea; Great Salt Lake, and numerous other ancient lakes in western United States.                    |
| Tertiary.....          | Cardona, Spain; Wieliczka and Bachnia, Galicia; Siebenburgen; Asia Minor; Armenia; Rimini, Italy; Petit Anse, La.; California, Utah, and Nevada. |
| Cretaceous.....        | Westphalia brines; Algiers.  |
| Jura.....              | Rodenburg on the Deister; Bex in Canton of Waadt, Switzerland.   |
| { Keuper.....          | Lorraine; Hall, Tyrol; Hallein and Berchtesgaden (near Salzburg).  |
| { Muschelkalk.....     | Wurttemberg; in Thuringia, Ernstthal, Stottenheim.   |
| { Buntersandstein..... | Hanover, Schoeningen near Brunswick, Salzderhelden; Cheshtre, England; Kansas and Texas.   |
| Permian.....           | Gera, Artern (Thuringia); Staasfurt, Halle, Spenberg; Segeberg (Holstein); Kirghiz steppes on the river Ileck (Kansas). <sup>1</sup>             |
| Carboniferous.....     | Kanawha and New River, W. Va.; Durham and Bristol, England.  |
| Devonian.....          | Winchell, Mich.  |
| Upper Silurian.....    | New York; West Virginia; Saginaw, Mich.; Goderich, Canada.   |

<sup>1</sup> Haworth, Geol. Survey, Kansas; Ann. Bul., 1897, p. 56. Harris, La. Geol. Survey, Bul. 7, p. 94.

The deposition of a stratum of sand or gravel upon the bottom of a basin occupied by a saline lake or sea, followed by that of an impervious stratum of clay, would result in the occlusion of a certain amount of the brine in the pervious layer; or the passage of percolating water through beds of deposited salts would result in a brine which would find lodgment in pervious strata, such as sandstones,

<sup>1</sup> From Credner (Elemente der Geologie, 6th Auflage S. 40) as arranged by Merrill, Bul. N. Y. State Museum, 3, No. 11; Salt and Gypsum Industries of New York, April, 1893. With modification by the Bureau of Soils.

or would be forced to the surface by pressure from below. One or the other of these ways accounts for the formation and occurrence of the so-called natural brines.

In the United States salts are obtained, or have been obtained, commercially from every form of salt segregate discussed in the foregoing paragraphs from the brine of the ocean on the Pacific coast; of certain salt lakes, such as the Great Salt Lake; of the brine-impregnated strata underlying certain portions of Ohio, Pennsylvania, West Virginia, and Michigan; of salt springs in the early days of the salt industry in the United States; and from the beds of rock salt encountered in New York, Ohio, Michigan, Kansas, and Louisiana.

In the main, sodium chloride, or common salt, has been the substance sought, and in most instances it has been the only one of the salts whose recovery has been commercially possible. Exceptions to this generalization are found in the recovery of borates from certain of the desert basins of the western deserts, of sulphates and carbonates from salt lakes and salt deposits, and of calcium and magnesium chlorides and of bromides from the natural brines of Ohio, Michigan, and West Virginia.

Since the crystallization of salt is the product of an evaporated body of brine and since most natural brines contain, in general, the same constituents, though in different amounts, the occurrence of one such saline constituent is taken as an indication of the possible presence of others. In a quest for potassium salts, search has been made in those masses of natural products which have been known to contain the other salts.

## GEOLOGY OF SALIFEROUS DEPOSITS.

### THE SALINA FORMATION.

The Salina formation derives its name from the strata of rock salt which it incloses. The salt beds of New York, Ohio, Michigan, and Ontario are referred to this formation.

### STRATIGRAPHY.

The Salina group of rocks, sometimes spoken of as the Onondaga salt group, is classified with the Upper Silurian. It lies between the Niagara formation below and the Helderberg above.<sup>1</sup>

The relative position of the rocks of the Salina age is seen from the following tabulation, as constructed from a study of the Silurian strata of New York.<sup>2</sup> The Helderberg series here is classified with

<sup>1</sup> Newberry. Geol. Surv. Ohio Geol. 1, Chart op. p. 56.

<sup>2</sup> From Chamberlin and Salisbury, Geology II, p. 370, as quoted from Clark and Schuchert, Science 10, 876 (1898), and Hartnagel, N. Y. State Museum, Bul. 69, p. 1160, 1903.

the Devonian system. This would place the Salina at the top of the Silurian, as in the following outline:

| Era or system.         | Period or group.          | Age or stage.   |
|------------------------|---------------------------|---|
| Siluric (Ontaric)..... | Cayugan (Neontaric).....  | { Manlius limestone.<br>Rondout waterlime.<br>Cobleskill limestone.<br>Salina beds. |
|                        | Niagaran (Mesontaric) ... | { Guelph dolomites.<br>Lockport limestones.<br>Rochester shale.<br>Clinton beds.    |
|                        | Oswegan (Paleontaric)...  | { Medina sandstone.<br>Oneida conglomerate.<br>Shawangunk grit.                     |

The Salina is composed of four general sorts of formations, shale, limestone, gypsum, and rock salt. Since the latter two are similar in that they are the products of evaporation, the formations may be regarded as of three sorts, shale, limestones, and beds of crystallized salts.

The beds of rock salt, interstratified with shale, lie near the middle of the series, and are overlain and underlain by strata of gypsum, limestone, and shale (or argillaceous limestone). In fact, the strata from the top of the series downward toward the middle or from the bottom upwards toward the middle are a repetition of each other, indicating a reversal of conditions after the deposition of the rock salt. This is illustrated by the following tabulation.<sup>1</sup>

| Formation.      | Material.   |
|-----------------|---|
| Cobleskill..... | A and B. Niagara-guelph fauna.<br>{ C. Waterlime <sup>2</sup> (with Eurypterus).<br>D. Gypseous shales. |
| Salina.....     | E. Rock salt.<br>{ D. Gypseous shales.<br>C. Pittsford shales (with Eurypterus).                        |
| Niagara.....    | { B. Guelph fauna.<br>A. Niagara fauna.   |

Merrill<sup>3</sup> describes the Salina formation, as it appears in New York, as follows:

The Onondaga (Salina) salt group may be divided into four deposits. There are no well-defined lines of division between the deposits, but for practical purposes the divisions are sufficiently obvious.

The first, or lowest, deposit is the red shale, showing green spots in the upper part of the mass. Second, the lower gypseous shales, the lower part alternating with red shale, which ceases with this mass. Third, the gypseous deposit, which embraces the great masses quarried for plaster, consisting of two ranges, between which are the hopper-shaped cavities, the vermicular lime rock of Eaton and other porous rocks.

<sup>1</sup> Hartnagel. loc. cit., cf. p. 1159; with modifications.

<sup>2</sup> The water lime is "composed of a great variety of calcareous, dolomitic, cherty, and calcareo-argillaceous rock fragments, mixed and thrown about through the recemented rock mass." From Graubau and Sherzer, "Monroe Formations," Mich. Geol. and Biol. Sur. 2 (series 1), p. 17 (1909).

<sup>3</sup> Bul. N. Y. State Museum 11, p. 22, from Vanuxem (Report on Geol. Third District, N. Y.).

Fourth and lastly, those rocks which show groups of needle-form cavities, placed side by side, caused by the crystallization of sulphate of magnesia,<sup>1</sup> and which may from that circumstance be called the magnesian deposit.

As a substitute for the name "Lower Helderberg," the term "Monroe" was proposed to apply to the group of rocks which in Michigan lies between the top of the Niagara and the base of the Onondaga.<sup>2</sup> This would include the Salina formation.

The Monroe formation was defined as lying between the limestones of the Dundee above and the lowest beds in which gypsum occurred, and was described as consisting "mainly of buff dolomites and of calcareous and argillaceous marls, associated with anhydrite and rock salt." This series, designated the Monroe, is stated to have a thickness of 600 feet in northern Ohio. It extends into southeastern Michigan, where it appears to be 1,300 to 1,400 feet in thickness. It here dips toward the northwest, varying between 26 and 56 feet per mile.

A later restriction of the Monroe formation excluded the Salina and included only those strata lying between the Salina below and the Dundee above. This group of rocks has a thickness in eastern Michigan and Ontario of 500 to 900 feet.

#### DISTRIBUTION.

The eastern terminus of the Salina has been located a few miles west of the Hudson River, in New York. Here it extends beyond the edge of both the Niagara and Clinton groups and finally rests upon the Frankfort slate. In Otsego County it appears as an outcrop and extends thence westward along the surface to the Niagara River. From the region of its outcrop it dips to the south, in the neighborhood of Livingston County its dip being at the rate of 60 feet per mile, and underlies the State to its southwestern borders. At Ithaca and Watkins, in Tompkins and Schuyler Counties, respectively, are the southernmost points where the rock salt beds have been explored. Its southern border, then, has not been determined, though the formation is known to underlie a part of western Pennsylvania, where it is said to have attained its maximum development. In Pennsylvania, however, the stratified salt beds are lacking from the Salina series.<sup>3</sup>

Other outcrops of the formation have been seen in Ohio, Michigan, and Canada.<sup>4</sup>

From New York the Salina formation extends westward through Ohio until it encounters the eastern slope of the ancient anticlinal fold in Ohio, known as the Cincinnati axis. This is an eroded elevation of the older strata, extending in a general direction parallel to

<sup>1</sup> Regarded by Merrill as more probably caused by the crystallization of sulphate of calcium.

<sup>2</sup> Graubau and Sherzer, loc. cit.

<sup>3</sup> Chamberlain and Salisbury, loc. cit., cf. p. 389.

<sup>4</sup> Newberry, loc. cit.

the Appalachian system, from the region of Nashville toward Lake Erie. As it was not overlain by rocks of the Silurian and, probably, Devonian age, it is evident that the uplift of the arch had taken place before the deposition of these formations, and that it projected above the Silurian and, probably, Devonian seas as dry land. East of the Cincinnati axis, at Moore's Mill, in Sandusky County, the Salina is represented by a thin stratum of soft, bluish, shaly limestone. This is the extreme southwestern edge of the great sheet of the Salina which in central and western New York has a thickness of nearly 1,000 feet.

The following record of a boring, made a few miles east of Sandusky shows that the Salina is entirely missing there:<sup>1</sup>

|  | Feet.  |
|--|--------|
| Drift.....                               | 10     |
| Corniferous limestone.....               | 100    |
| Monroe and Niagara limestone.....        | 970    |
| Niagara shale and Clinton formation..... | 105    |
| Medina shale.....                        | 175    |
| Cincinnati shale and limestone.....      | 500    |
| Utica shale.....                         | 310    |
| Trenton limestone at.....                | 2, 210 |

While the main divisions of the Monroe group, as restricted,<sup>2</sup> have been traced into Indiana, where they appear in limited exposures, no evidence is found of the occurrence here of the closely associated Salina rocks.

To the north the Salina is heavily represented in Ontario Province, Canada, where at Goderich its salt beds are being worked. In his summary of the Paleozoics of southern Ontario, in 1893, Brunell assigns the Lower Helderberg and Onondaga salt group a thickness of 300 to 1,000 feet, with an average of 650 feet.<sup>3</sup> A stratum of dolomite conglomerate out-cropping on the Island of St. Helens, near Montreal, has been referred to the Lower Helderberg. The Salina underlies the State of Michigan and extends to the northern and beyond the western borders of the Lower Peninsula, and reaches the eastern borders of the State of Wisconsin.<sup>4</sup>

#### FORMATION.

Two theories have been advanced to account for the formation of the rock salt of the Salina group of strata. These theories are at variance in that one supposes a marine origin and the other a continental origin. It has been pointed out that the rocks of the Salina describe conditions of increasing salinity up to a certain degree, marked by a heavy precipitation of sodium chloride, and a succeeding period of decreasing salinity.

<sup>1</sup> Bownocker, Geol. Surv. Ohio, Bul. 8, p. 39.

<sup>3</sup> Grabau and Sherzer, loc. cit., cf. p. 24.

<sup>2</sup> Grabau and Sherzer, loc. cit., cf. pp. 20 and 27.

<sup>4</sup> Chamberlain and Salisbury, loc. cit., cf. p. 387.

The former theory describes the Salina sea as an arm of the ocean. This covered the area, of course, now underlain by the Salina strata. This arm was separated from the ocean by a bar reef, or flat, whose traces, supposedly, are to be seen in the rocks of Ohio, where ripple-marks and mud cracks are observed. Great tidal waves flowed over this bar into the Salina Sea. The period was one of great aridity. Only slight accessions of fresh water entered the Salina Sea; and as its waters evaporated fresh volumes of ocean water were acquired in the manner mentioned. Eventually concentration continued to the saturation point of sodium chloride, whereupon that substance was deposited. Short seasons, or periods, of humidity recorded themselves in interlying strata of shale, being produced by accessions of water, presumably fresh, bearing erosion products. Later the periods of humidity lengthened—the strata of rock salt became thinner and those of shale thicker, indicating freshening conditions—until crystallization of rock salt ceased altogether, and the succeeding rocks were entirely nonsaline in character.

The study of the rocks of the Salina where they are pierced by the salt wells of southeastern Michigan has led to the belief that there were three main periods of desiccation. During the first period rock-salt strata aggregating 900 feet in thickness were deposited. This was the period of greatest evaporation. The second period was marked by the deposition of gypseous or salty dolomites or gypseous marls.<sup>1</sup>

The second theory to account for the formation of the Salina rocks presupposes that it was continental. The area now covered by the Salina formations was a continental basin. Into it flowed the water from the surrounding drainage area with its burden of detrital material. The latter was derived from the rocks of the preceding geological era, the Niagaran. These were largely calcareous. Therefore the rocks (the Salinan), built up of the sediment derived from them, were largely argillaceous calcilutites or lime-mud rocks. The saline matter originally included in the limestones of the Niagara rocks, presumably constituting about 1 per cent of the mass, was dissolved by the water producing the erosion of these rocks. This likewise was carried into the Salina Basin. During the period of great aridity, which existed in mid-Salinan times, the Salina Sea was evaporated to the point of saturation with respect to sodium chloride. At this point it should have been greatly restricted in area; it occupied only the deeper basin, where rock salt is now found.

It is supposed that the salt of the Niagara limestone appeared as an efflorescence on the surface of the so-called Salina Desert and was dissolved and carried thence by seasonal rains into shallow playa

<sup>1</sup> Grabau and Sherzer, loc. cit.



lakes. This latter supposition introduces a number of doubtful elements and, furthermore, is unnecessary. Efflorescence upon the surface could be brought about through the assisting agency of two forces—hydrostatic pressure and capillarity. The former could bring the solution of the occluded salts to the surface by downward flow of seepage water through the strata from more elevated levels. Since the theory of the continental origin of the Salina rocks involves the supposition of the entire disintegration of strata by rain water, and since the eroding water certainly would have dissolved any occluded, soluble, saline material more or less completely, therefore further suppositions to account for the actual solution of the rock-occluded salts are unnecessary.

To produce a salt bed in this manner, covering an area of 25,000 square miles and 100 feet thick, "which is probably in excess of the area covered by the thick salt beds, it would require the erosion of \* \* \* 400 feet of limestone, covering an area of 625,000 square miles, and the concentration of the derived salt in the basin, 25,000 square miles in area. Thus, \* \* \* the erosion of 400 feet of limestone from Wisconsin, Minnesota, the upper Great Lake region, and the Ontario region west of Toronto, would suffice. But since we know that the thickness of the Niagaran limestone over this region was at least 400 feet, not to mention the thickness of the lower marine strata, which have also been removed by erosion, it will be seen that the removal of the Niagaran limestones from this area would give a salt mass 200 feet thick and covering an area of 25,000 square miles, or approximately 1,000 cubic miles of rock salt. \* \* \* It is therefore probable that the Niagara formation alone was able to furnish all the salts found in the succeeding Salina formation of New York, Ontario, and Michigan."<sup>1</sup> The close of the Salina period was marked by a fresh invasion of the ocean, from the Atlantic, as is shown by the fossilized fauna of the Monroe formation.

This theory could be made to account also for the peculiar composition of the natural brines of the Marshall sandstones. In another paragraph the possible effect of adsorption on the composition of natural brines has been discussed. If the Salinan rock salt has been deposited, as supposed, from a continental basin, adsorptional forces have had a double opportunity to come into play. Therefore, the brine of the Salinan sea may have been, and most probably was, markedly different from the brine of the ocean; it may have represented the intermediate change in composition between the ocean, the original source of the rock salt of the Salina, and the natural brines now lying in the formation above the Salina.

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<sup>1</sup> Grabau and Sherzer, loc. cit., cf. p. 236.

## ORIGIN OF NATURAL BRINES.

There are certain features of the prevalently accepted theories concerning the origin of the natural brines which are open to criticism. Theoretically, natural brines are actual occlusions of sea water, bottled up, so to speak, within the porous strata which now contain them, by so-called impervious strata; they have remained unaltered since their occlusion and therefore are representative of the sea which was instrumental in the formation of their inclosing rocks (assuming that these are of marine origin), and the high bromine content of some of the brines is the result of the segregation of bromides through the instrumentality of marine algæ.

Certain physio-chemical and geo-chemical considerations make these suppositions appear extremely doubtful. Some of these will here be mentioned briefly.

The permeability of rock strata to water and other mobile substances under pressure is too well known a factor to need elaboration here. This would militate against the idea of the confinement of the brine in one stratum, or its freedom from contamination or dilution by other solutions. The gradual permeation of lower strata by fresh surface water from the upper would account for the greater concentration of the brines in the lower than those in the upper strata—a phenomenon which has been explained on the basis of specific gravities.

Assuming for the moment that the natural brines are occlusions of the water of the sea from which their inclosing strata were deposited, from the chemical composition of the brines it is evident that the sea of which they are a remnant was of a quite different composition from the ocean of the present age, or from the sea from which the Stassfurt deposits of salts were crystallized—the sea of an earlier geologic age. Natural brines differ most markedly from ocean water in the ratio between calcium and sulphate ions. In the ocean water that ratio is small, while in natural brines it is large; nor do we know of an inland sea whose composition is similar to that of natural brines.

To suppose the introduction into the body of brine lying in the porous strata of a solution bearing a precipitant for the sulphate ion is to abandon the supposition of the complete isolation of the brines by impermeable strata and to admit the probability of the migration of brines through the strata. The introduction of a solution bearing calcium, strontium, or barium salts would have caused an elimination of sulphates. All three of these bases are found in some of the natural brines, the latter two, however, only in small amounts. The hypothetical introduction of calcium salts could explain the presence of such large amounts of calcium, but this would lead to the necessity of explaining the source of soluble calcium

salts. Or, some physio-chemical process, eliminating the bases and leaving an acid solution, might have resulted in a resolution of calcium carbonate by the brine. This would have been attended by a precipitation of sulphate as calcium sulphate. However, these hypotheses are altogether extreme and can not be entertained.

The supposition that marine algæ add bromides to the sea, of which the natural brines are the supposed remains, is scarcely tenable. The marine algæ are chlorophyll-bearing plants and therefore are dependent on light for their metabolism. Consequently, they grow in water of a depth that enables them to reach the sunlight with their fronds. It is essential, then, where the plants are tall that they be provided with a means of holding themselves upright in the water. This is accomplished by means of gas-filled, bulbous enlargements of stem and frond, known as pneumatocysts. Thus the algæ growing in depths as great as 100 feet are able to reach the surface of the water.

It is known that certain marine algæ have the power of absorbing certain substances, presumably as salts, from the ocean water in which they grow. Perhaps portions of all the constituents of their growing medium are taken into the tissues of the plants, but there is a pronounced selective absorption whereby certain of them are absorbed to the practical exclusion of others. Thus potassium salts, in amazing amounts, are absorbed by the giant kelps of the Pacific coast—*Macrocystis pyrifera*, *Pelagophycus porra*, and *Nereocystis luetkeana*—while sodium, magnesium, and calcium are taken up in much smaller amounts. In these, also, are found bromine and iodine. In certain sea plants of the Atlantic, especially of the European coast, is found iodine in larger amounts than in those growing on the American Pacific littoral. However, comparatively little is known concerning the bromine content of algæ, as it has received but little attention on account of the comparatively low value of bromine. Still, it is definitely known that some species of seaweeds do absorb bromine from sea water.

Sea algæ grow only in circulating water. They are dependent on the water for supplies of carbon dioxide and other materials essential to their growth. These supplies are provided only by circulation. The larger the plants and the more extensive their groves the more pronounced must be the circulation of their medium. It is evident that this must always have been a condition of their growth.

Marine algæ have a physical construction which may be described as gelatinous rather than fibrous. Accordingly, the dead plants are very easily disintegrated. Furthermore, even preceding their disintegration, their saline constituents are quite readily leached out.

These considerations have a direct bearing on the question of the segregation of bromine in a sea or lake by algæ. Certainly it is true

that no plant growing in a sea could add more bromine thereto than the sea originally contained. At most, then, the algæ were instrumental only in causing a segregation of bromides in that portion of the sea which subsequently was to be occluded within the strata undergoing formation. It is hard to imagine any set of conditions favorable to this process. The accumulation of large masses of sea plants, freshly torn from their anchorage, on the bottom of the sea, there to disintegrate and leave their salts, the only way in which conceivably the segregation could have been brought about, is scarcely believable, as the loosened plants would not have fallen upon the bottom, but would have been lifted to the surface by their pneumatocysts, where they would have been carried to and fro by the winds and tides or whence they would have been cast ashore by the waves. If the latter, their salts might have been leached out by rain water and the resulting solution flowed into the porous sand of the shore. However, this would involve the filling of the strata with surface water and not with sea or lake brine.

In short, the theories accounting for the origin and composition of the natural brines, on examination, are scarcely tenable.

As a substitute theory for those briefly stated above, it is proposed that natural brines be regarded as the product of the leaching of beds of rock salt or, less probably, of great masses of rocks laid down in brines, and not the ocean or lake brine itself. In support of this theory it is pointed out that the so-called impervious strata are after all pervious—imperviousness, as commonly employed, being a relative term. The porous rocks, or sandstones, in which natural brines now occur should be regarded merely as natural reservoirs where the migrating seepage waters—and other mobile constituents of the earth's crust—are found in largest quantities. It is accepted that oil and gas have passed into these porous strata from others. In cases, two or all three—brine, petroleum, and gas—are found in one sandstone. It is quite as easy to assume that the brine likewise has had an extraneous origin, if there is any occasion for such an assumption.

It can not be said from existing data what the composition of seepage water would be on emerging from a bed of rock salt. It probably would be a saturated solution of sodium chloride and perhaps of calcium sulphate, since these are the two solids present in largest amounts. Its contents in these two constituents would be determined by their solubility in that solution, or mutual solubility. Beyond that concentration, of course, no more of them could be dissolved whatever their actual or relative amount present in the beds of salt. In addition, the other impurities present in the rock salt would be found in the seepage water. Their origin would be the mother liquor from the sodium chloride crystallization. Their

concentration would be determined by several factors, among which may be mentioned the amount in which they were present in the rock salt and the thickness of the strata penetrated by the seepage water. Their concentration in the seepage water would be limited ultimately by their solubility in that solution and not by the relative amounts in which they were present. In other words, the seepage water from a salt bed may not be at all representative in composition of the rock salt which it has penetrated. Qualitatively, the seepage water might be expected to contain the same salts that are found in the sea from which the rock salt was crystallized, since the impurities in the rock salt had their origin in this sea water. That the natural brines are so markedly different from any sea or lake water with which we are acquainted is at first sight a strong indication of the erroneousness of our theory.

At least two factors are operative in the occlusion of other saline substances which takes place in the crystallization of sodium chloride from an impure brine—namely, mechanical occlusion of droplets of mother liquor and adsorption. Impurities occluded in the former way are present in the form in which they occurred in the mother liquor; those in the latter way may be entirely different.

Adsorption is a selective phenomenon. In a solution of a single saline compound the acidic ion may be adsorbed while the basic is left in solution, or vice versa. In a solution of two or more saline compounds, it is conceivable that selective adsorption may take place with respect to both acidic and basic ions. Thus, the ratio between the ions in the adsorbed material may be entirely different from that in the solution from which the material was adsorbed. The same considerations apply likewise to adsorption by nonsaline precipitates. The adsorption of potassium ions by clays has been referred to in a foregoing paragraph. Its adsorption by other precipitates has been made the basis of a process for its extraction from sea water. By such a process, from a solution of sodium chloride and calcium sulphate, calcium ions may be adsorbed in proportionately larger amounts than sodium ions, and chloride than sulphate ions. In the subsequent leaching of the precipitates by a solution of a lower concentration than that in which the precipitates were deposited, the adsorbed ions will in part be forced back into solution. A solution results, then, in which the ratio between the ions has been determined by the coefficients of adsorption of the ions in the respective solutions.

It is proposed that in some such way the natural brines were produced—by the permeation of strata of rock salt or shales containing adsorbed saline materials, by seepage waters. The high concentration of sodium chloride strongly suggests that they have passed through rock salt rather than through shales. The presence

of potassium salts in them further suggests the same conclusion. In this way the presence of natural brines of any or all of the saline substances found therein may be accounted for, and thus may be explained the excess of calcium over sulphate ions.

#### GEOLOGICAL OCCURRENCES OF THE SALINES.

##### NEW YORK.

The salines of New York consist in (a) salt springs, which are small and unimportant; (b) natural brines; and (c) beds of rock salt. The springs and natural brines are regarded as seepage water which has flowed through or over the beds of rock salt.

The rock-salt masses occur in the Salina formation, which is a part of the Upper Silurian. This underlies an area stretching from a region a short distance west of the Hudson River to the western boundaries of the State. It outcrops for a long distance east and west a few miles south of Lake Ontario and extends thence beneath overlying rocks to the southern borders of the State.

Further information concerning the stratigraphy of the Salina formation of western New York may be gained from the log of a shaft sunk at Livonia, in Livingston County. This record was made under the direction of Prof. James Hall, geologist, and is quoted from Merrill.<sup>1</sup>

##### *Synopsis of record.*

| Beginning at depth of—      | Thickness and character of stratum penetrated.            |
|-----------------------------|---|
| 380 feet <sup>2</sup> ..... | 6 feet bluish-gray shale.                                 |
| 386 feet.....               | 29 feet compact dark-blue shale.                          |
| 415 feet.....               | 1 foot hard gray limestone.                               |
| 416 feet.....               | 11 feet hard medium dark-blue shale, somewhat calcareous. |
| 427 feet.....               | 2 feet blue-gray limestone.                               |
| 429 feet.....               | 1 foot soft blue-gray shale.                              |
| 430 feet.....               | 1 foot fine pinkish-gray limestone.                       |
| 431 feet.....               | 7 feet blue shale with concretionary layers.              |
| 438 feet.....               | 2 feet hard limestone containing considerable pyrites.    |
| 440 feet.....               | 7 feet soft blue compact, pyritiferous shale.             |
| 447 feet.....               | 20 feet soft blue-gray shale.                             |
| 467 feet.....               | 9 feet dark-blue, slightly pyritiferous shale.            |
| 476 feet.....               | 2 feet concretionary layers with silicified fossils.      |
| 478 feet.....               | 17 feet blue shale, hard and calcareous.                  |
| 495 feet.....               | 27 feet dark-brownish bituminous shale.                   |
| 515 feet.....               | 28 feet dark bluish-gray soft shale.                      |
| 543 feet.....               | 4 feet soft bluish pyritiferous shale.                    |
| 547 feet.....               | 8 feet harder arenaceous and pyritiferous shale.          |
| 555 feet.....               | 5 feet arenaceous shale with layers of impure limestone.  |
| 560 feet.....               | 2 feet light gray limestone.                              |
| 562 feet.....               | 4 feet sandy shale, quite hard.                           |
| 566 feet.....               | 4 feet fine bituminous shale.                             |
| 570 feet.....               | 34 feet soft dark rock.                                   |
| 604 feet.....               | 6 inches hard, sandy dark bluish gray shale.              |
| 604 feet 6 inches.....      | 3 feet 4 inches soft dark-bluish shale.                   |

<sup>1</sup>N. Y. State Museum, Bul. 11, p. 26-31, inclusive.

<sup>2</sup>Beginning of recorded section.

| Beginning at depth of—  | Thickness and character of stratum penetrated.  |
|-------------------------|---|
| 607 feet 10 inches..... | 1 foot 2 inches hard calcareous sandy layer.  |
| 609 feet.....           | 6 feet dark-bluish soft shale.  |
| 615 feet.....           | 11 feet harder dark-blue shale.   |
| 626 feet.....           | 3 feet sandy layer, quite hard.   |
| 629 feet.....           | 21 feet dark-brownish and bluish-gray shale.  |
| 650 feet.....           | 147 feet dark-brown or black shale with bluish or olive layers.   |
| 697 feet.....           | 15 feet very bituminous shale, bottom of Hamilton.  |
| 612 feet.....           | 11 feet black bituminous shale.   |
| 823 feet.....           | 2 feet compact gray limestone.  |
| 825 feet.....           | 4 feet of black bituminous shale.   |
| 829 feet.....           | 22 feet of black shale, very bituminous.  |
| 851 feet.....           | 1 foot bluish-black shale.  |
| 852 feet.....           | 2 feet black impure limestone.  |
| 854 feet.....           | 2 feet blue-black grayish limestone.  |
| 856 feet.....           | 1 foot impure limestone.  |
| 857 feet.....           | 6 feet black shale.   |
| 863 feet.....           | 3 feet black hard shale, bottom of Marcellus.   |
| 866 feet.....           | 22 feet gray limestone with chert.  |
| 888 feet.....           | 66 feet gray limestone containing chert.  |
| 954 feet.....           | 24 feet gray limestone full of chert, very hard.  |
| 978 feet.....           | 20 feet 6 inches gray limestone containing less chert, bottom of Corniferous, gas.  |
| 998 feet 6 inches.....  | 2 feet 6 inches gray limestone, no chert.   |
| 1,001 feet.....         | 5 feet hard green and gray sandstone (Oriskany) containing pebbles and fragments of hydraulic limestone.                          |
| 1,006 feet.....         | 4 feet dark-colored bituminous hydraulic limestone.   |
| 1,010 feet.....         | 14 feet hydraulic limestone, light colored, bottom of water-lime.   |
| 1,024 feet.....         | 6 feet very light gray sandstone.   |
| 1,030 feet.....         | 39 feet hydraulic limestone.  |
| 1,069 feet.....         | 9 feet hard bluish gray shaly rock, with black seams.   |
| 1,078 feet.....         | 9 feet blue gray hard shale, with layers of nodular gypsum.   |
| 1,087 feet.....         | 6 feet fine brownish-gray limestone, with light-blue gypsum in masses from 1 to 4 inches thick.                                   |
| 1,093 feet.....         | 25 feet hydraulic limestone, with gypsum in crystals and nodules.   |
| 1,118 feet.....         | 17 feet dark bluish-gray shales; gypsum in nodules.   |
| 1,135 feet.....         | 3 feet reddish-brown limestone, with dark gypsum in nodules.  |
| 1,138 feet.....         | 45 feet gypsum bed, dark bluish gray marl, intercalated with gypsum in layers and nodules, sometimes 1 or more feet in thickness. |
| 1,183 feet.....         | 9 feet light reddish-gray limestone; gypsum in layers from one-half inch to 1 foot.   |
| 1,192 feet.....         | 5 feet layers of limestone and gypsum.  |
| 1,197 feet.....         | 1 foot of reddish-gray limestone.   |
| 1,198 feet.....         | 3 feet bluish-gray marl, with gypsum in nodular layers.   |
| 1,201 feet.....         | 2 feet red-gray limestone.  |
| 1,203 feet.....         | 2 feet bluish-gray marl.  |
| 1,205 feet.....         | 15 feet limestone.  |
| 1,220 feet.....         | 6 feet bluish marl; gypsum in nodular layers.   |
| 1,226 feet.....         | 7 feet reddish-brown limestone.   |
| 1,233 feet.....         | 1 foot bluish-gray marl, with nodular layers of gypsum.   |
| 1,234 feet.....         | 4 feet reddish-gray limestone.  |
| 1,238 feet.....         | 2 feet yellowish-gray very hard limestone; gypsum in small crystals.  |

| Beginning at depth of— | Thickness and character of stratum penetrated.   |
|------------------------|--|
| 1,240 feet.....        | 1 foot limestone.  |
| 1,241 feet.....        | 8 feet limestone; gypsum in crystals.  |
| 1,249 feet.....        | 6 feet red and yellow limestone with layers of bluish gypsum from 1 to 6 inches thick.   |
| 1,255 feet.....        | 3 feet yellowish-gray limestone.   |
| 1,258 feet.....        | 8 feet bluish-gray marl; gypsum in layers, some of them from 6 to 12 inches <sup>4</sup> thick.  |
| 1,266 feet.....        | 12 feet yellowish and reddish limestone; gypsum in seams and veins, hopper-shaped crystals at 1,274 feet.  |
| 1,278 feet.....        | 7 feet marl; much gypsum in nodules and masses.  |
| 1,285 feet.....        | 2 feet light-brown marl; gypsum abundant in nodules.   |
| 1,287 feet.....        | 9 feet soft light-bluish marl; much gypsum in masses and nodules.  |
| 1,296 feet.....        | 3 feet hard, fine, brownish-gray limestone; gas in small quantity.   |
| 1,299 feet.....        | 1 foot light-gray, soft limestone; gypsum in seams.  |
| 1,300 feet.....        | 11 feet dark-gray hard limestone.  |
| 1,311 feet.....        | 3 feet hard, fine, slightly reddish limestone; gypsum in thin seams.   |
| 1,314 feet.....        | 2 feet yellow-gray bituminous limestone.   |
| 1,316 feet.....        | 1 foot bluish-gray marl.   |
| 1,317 feet.....        | 6 feet light-gray, reddish-gray limestone, hopper-shaped crystals, gypsum in thin seams and veins.   |
| 1,323 feet.....        | 2 feet yellow and light-gray limestone; gypsum in seams and veins.   |
| 1,325 feet.....        | 3 feet of bluish-gray limestone; gypsum in thin veins.   |
| 1,328 feet.....        | 3 feet yellow bituminous limestone; thin veins of light gypsum.  |
| 1,331 feet.....        | 6 feet very hard gray limestone.   |
| 1,337 feet.....        | 2 feet yellowish-gray limestone, white crystallines; gypsum in small thin veins.   |
| 1,339 feet.....        | 4 feet pinkish-gray limestone; gypsum in seams and veins.  |
| 1,343 feet.....        | 11 feet brownish-gray hard limestone.  |
|                        | At 1,348 feet the first salt found was observed in a few thin veins, in some of which the vein matter was of salt, in others the wall matter was crystalline gypsum with which a thin layer of salt was intercalated. The salt was pinkish or cream color; the gypsum was white or pink.   |
| 1,354 feet.....        | 1 foot 6 inches bluish-gray marl; salt and gypsum in veins.  |
| 1,355 feet 6 inches... | 6 inches nodular layer of gypsum.  |
| 1,356 feet.....        | 2 feet dark gray limestone containing a large percentage of salt and crystals in nodules.  |
| 1,358 feet.....        | 2 feet bluish-gray marl with many seams and veins of salt.   |
| 1,360 feet.....        | 6 inches very thinly laminated limestone with salt in seams.   |
| 1,360 feet 6 inches... | 8 feet 6 inches bluish-gray marl, with many cracks filled with white and pinkish crystalline salt; considerable gypsum.  |
|                        | At 1,369 feet at the south end of the shaft a bed of nearly pure coarsely crystalline salt was reached, which on the east wall of shaft showed a dip of 1 foot on the upper line of contact and 4 feet 8 inches on the lower toward the north, the layer being 8 inches thick at the south end and 3 feet at the northeast corner. A small proportion of shale is mixed with the salt. |
| 1,369 feet.....        | 4 feet marl with pink, milk-colored salt in veins and seams; gypsum present, not abundant.   |
| 1,375 feet.....        | 2 feet transparent salt in large fine crystals, mingled with marl.   |



| Beginning at depth of—   | Thickness and character of stratum penetrated.   |
|--------------------------|--|
| 1,377 feet. ....         | 1 foot 6 inches bluish marl, becoming light-blue on exposure; little salt; gypsum abundant.  |
| 1,378 feet 6 inches. . . | 11 feet mixed salt, coarsely crystalline, and marl in flakes and small fragments present throughout the bed.   |
| 1,390 feet. ....         | 13 feet salt.  |
| 1,403 feet. ....         | 3 feet 6 inches dark-gray hard limestone containing much salt in veins, seams, and crystals.   |
| 1,406 feet 6 inches. . . | 2 feet 6 inches gray limestone; soft, pinkish salt in veins and seams.   |
| 1,409 feet. ....         | 1 foot 6 inches very soft bluish marl; pinkish and white salt in seams and veins.  |
| 1,410 feet 6 inches. . . | 15 feet 6 inches white and pink salt in large crystals, with fragments and flakes of marl in varying proportions.  |
| 1,426 feet. ....         | 2 feet dark-gray marl limestone.   |
| 1,428 feet. ....         | 4 feet green marl, with red and pink salt in thin layers.  |
| 1,432 feet. ....         | In this section 408 feet of Salina strata was penetrated below the bottom of the water-lime formation, the bottom of the well being 566 feet below the bottom of the Corniferous. Probably there is as much as 500 feet of Salina strata with salt beds below the bottom of the shaft. It is therefore not certain that more than the upper half of the group is exposed in this section. It is noteworthy that much gypsum overlies the salt. |

The following record was made from the main hoisting shaft (shaft No. 1) of the Retsof Mining Co., Retsof, N. Y., and was obtained through the courtesy of Mr. Frank Rundio.

TABLE V.—*Record of strata in Retsof mine.*

| Formation.                             | Depth of formation. | Total depth. |
|--|---------------------|--------------|
|  | <i>Feet.</i>        | <i>Feet.</i> |
| 1. Shale. ....                         | 133                 | 133          |
| 2. Limestone. ....                     | 8                   | 141          |
| 3. Shale. ....                         | 232                 | 373          |
| 4. Limestone. ....                     | 4                   | 377          |
| 5. Shale. ....                         | 23                  | 400          |
| 6. Limestone. ....                     | 3                   | 403          |
| 7. Corniferous limestone. ....         | 142                 | 545          |
| 8. "Cement" . . . . .                  | 13                  | 558          |
| 9. Sandstone. ....                     | 4                   | 562          |
| 10. "Cement" . . . . .                 | 7                   | 569          |
| 11. Sandstone. ....                    | 14                  | 583          |
| 12. Gypsum. ....                       | 4                   | 587          |
| 13. "Cement" . . . . .                 | 26                  | 613          |
| 14. Gypsum. ....                       | 47                  | 660          |
| 15. Magnesian limestone and sand. .... | 63                  | 723          |
| 16. "Cement" . . . . .                 | 14                  | 737          |
| 17. Blue shale. ....                   | 25                  | 762          |
| 18. "Cement" . . . . .                 | 10                  | 772          |
| 19. Blue shale. ....                   | 12                  | 784          |
| 20. Helderberg "cement" . . . . .      | 17                  | 801          |
| 21. "Mixture" . . . . .                | 31                  | 832          |
| 22. "Cement" . . . . .                 | 10                  | 842          |
| 23. Limestone, "cement," sand. ....    | 15                  | 857          |
| 24. "Cement" . . . . .                 | 6                   | 863          |
| 25. Blue shale. ....                   | 19                  | 882          |
| 26. Red shale. ....                    | 12                  | 894          |
| 27. Blue shale. ....                   | 41                  | 935          |
| 28. Red shale. ....                    | 5                   | 940          |
| 29. Blue shale. ....                   | 12                  | 952          |
| 30. Limestone. ....                    | 12                  | 964          |
| 31. Salt and shale. ....               | 32                  | 996          |
| 32. Rock salt. ....                    | 21                  | (1)          |

<sup>1</sup> Foot of shaft, 1,017 feet.

From data obtainable from a study of the numerous wells and shafts of the Oatka-Genesee district (Wyoming, Livingston, and Genesee Counties) a map has been constructed giving the underground contours of the salt measures of that district.

The stratum with most pronounced characteristics penetrated in the borings for salt is the Corniferous limestone. This contains interspersions of chert and is so unmistakable on account of its greater hardness that it is invariably recognized by the drillers as soon as encountered. For that reason it has been taken as the datum plane of the series, with respect to which the relative positions of the salt strata are determined.

In constructing this map the contours have been located 610 feet below the upper surface of the Corniferous limestone; for the salt beds vary greatly in their thickness and position in the Salina group, and it is necessary to assume a horizon at which the occurrence of salt can be expected. The contour line at the altitude chosen intersects the principal salt beds in nearly every well and shaft.<sup>1</sup>

In the district mentioned salt has been found at depths varying between 550 and 750 feet below the upper level of the Corniferous. There are exceptions to this generalization which put the extremes at 450 and 900 feet below this level. The indications are that the salt measures of western New York have been penetrated to not more than half their depth. The operators, as a rule, have bored only sufficiently deep to reach workable amounts of salt.

At Ithaca and Watkins, in Tompkins and Schuyler Counties, respectively, the southernmost point in New York where salt is being obtained from the Salina beds, salt is found at greater depths than in the more northern parts of the State. At Ithaca a well has been bored to a depth of 3,185 feet. The mouth of the well is 396 feet above sea level. At a depth of 2,244 feet the first salt stratum is encountered, following which are eight other strata of salt distributed through 700 feet of the Salina formation, the last bed being found at a depth of 2,906 feet. Through the final 280 feet no ségregations of salt are encountered.

At Watkins, to the southwest of Ithaca, a well has been bored 3,315 feet in depth; while its total depth is slightly greater than that at Ithaca, its actual depth when referred to sea level is less. Its mouth is 665 feet above sea level. At a depth of 2,005 feet from its mouth the first salt bed is encountered; through the succeeding 815 feet six others are distributed. From a depth of 2,820 feet to the bottom of the well, a distance of about 500 feet, the formation has been found to be barren of salt measures.

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<sup>1</sup> Merrill, loc. cit., p. 32

## OHIO.

In Medina, Wayne, Cuyahoga, and Summit Counties of north-eastern Ohio salt is derived from deposited beds of rock salt. These are found in the Upper Silurian,<sup>1</sup> and as the formations in which they occur are a continuation of those occurring in western New York, it is presumable that these beds of rock salt are continuous with those found in Western New York.

Following is a record of a boring from Trumbull County, Ohio, east of the counties in which salt wells are now in operation.<sup>2</sup> This is doubtless representative of this section of the salt-bearing formation.

TABLE VI.—Record of boring in Trumbull County, Ohio.

| Formation.                             |                  | Depth of formation. | Total depth. |
|--|------------------|---------------------|--------------|
|  |                  | <i>Feet.</i>        | <i>Feet.</i> |
| Drift.....                             |                  | 40                  | 40           |
| Shale.....                             |                  | 60                  | 100          |
| Berea grit.....                        |                  | 160                 | 260          |
| Bedford and Ohio shales.....           |                  | 2,396               | 2,656        |
| Corniferous and Monroe limestones..... |                  | 583                 | 3,239        |
|  |                  | <i>Feet.</i>        |              |
|  | Rock salt.....   | 12                  | } 471 3,710  |
|  | Limestone.....   | 5                   |              |
|  | Rock salt.....   | 2                   |              |
|  | Limestone.....   | 3                   |              |
|  | Rock salt.....   | 10                  |              |
|  | Limestone.....   | 49                  |              |
|  | Rock salt.....   | 29                  |              |
|  | Limestone.....   | 10                  |              |
|  | Rock salt.....   | 52                  |              |
| Salina formation                       | White shale..... | 18                  |              |
|  | Limestone.....   | 36                  |              |
|  | Rock salt.....   | 10                  |              |
|  | Limestone.....   | 50                  |              |
|  | White shale..... | 15                  |              |
|  | Rock salt.....   | 30                  |              |
|  | Limestone.....   | 10                  |              |
|  | Rock salt.....   | 3                   |              |
|  | White shale..... | 90                  |              |
|  | Limestone.....   | 5                   |              |
|  | Blue shale.....  | 32                  |              |

The salt industries of southeastern Ohio, in Meigs and Morgan Counties, derive their brines not from beds of rock salt by dissolving the deposited salt by water pumped into the strata (artificial brines) but from the natural brines occurring in certain pervious strata which lie below the Conemaugh formation.<sup>2</sup> These strata occur at different horizons. As the brines have become exhausted in the upper strata, at a depth of about 300 feet, the wells have been deepened to the lower layers, until a depth of about 1,600 feet has been attained.

<sup>1</sup> Report Geological Survey of Ohio, vol. 1, pt. 1, p. 63 (1873).

<sup>2</sup> Bownocker, loc. cit.

The following brief log of a well in this region conveys an idea of the formations penetrated.<sup>1</sup>

TABLE VII.—*Log of a well in southeast Ohio.*<sup>1</sup>

|                           | Depth of formation. | Total depth. |
|---------------------------|---------------------|--------------|
|                           | <i>Feet.</i>        | <i>Feet.</i> |
| Unrecorded.....           | 58                  | 58           |
| Shale.....                | 492                 | 550          |
| White and gray sand.....  | 320                 | 870          |
| White sand and slate..... | 90                  | 960          |
| Big salt sand.....        | 170                 | 1,130        |
| Sand and white shale..... | 360                 | 1,490        |
| Berea grit.....           | 25                  | 1,515        |

<sup>1</sup> Total depth, 1,590 feet.

The concentration of the brines pumped from the different depths is as follows: 320 feet, 6° Baumé; 710 feet, 9° Baumé; 980 feet, 9° Baumé; 1,550 feet, 16° Baumé.

The strata containing the brines have a dip toward the southeast. At the time of sinking the first wells the brines were under sufficient pressure to raise them to the surface of the ground. As they have been removed, new volumes have taken their places, either flowing downward from more elevated regions or being forced upward from less elevated ones. It is an interesting fact, and perhaps a significant one, that the first Cow Run sand, the first horizon from which the natural brines were here obtained, a short distance to the north is an important source of petroleum.

In the tables below are given the analyses of 31 natural brines, 29 of which are from southern Ohio. The analyses are by T. G. Wormley, and are quoted from the Geological Survey of Ohio (Geolog. II, pp. 601, 602).

TABLE VIII.—*Table of analyses of salts, by T. G. Wormley.*

[Per cent of total solids.]

|                         | 1      | 2      | 3      | 4      | 5      | 6      | 7      | 8      | 9      | 10     |
|-------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Water.....              | 2.900  | 3.100  | 2.500  | 2.800  | 3.400  | 4.000  | 3.250  | 2.150  | 3.300  | 1.900  |
| Insoluble matter.....   | 0.018  | .016   | .008   | .006   | .006   | .004   | .010   | .014   | .010   | .010   |
| Sulphuric acid.....     | Trace. | Trace. |        |        |        |        |        |        | Trace. |        |
| Lime sulphate.....      |        |        |        |        |        |        |        |        |        |        |
| Calcium chloride.....   | 1.431  | 1.487  | 1.232  | 1.076  | .843   | .954   | .976   | 1.343  | 1.354  | 1.387  |
| Magnesium chloride..... | .608   | .633   | .513   | .436   | .359   | .419   | .402   | .608   | .590   | .684   |
| Potassium chloride..... | .152   | .183   | .152   | .137   | .152   | .137   | .095   | .106   | .183   | .212   |
| Sodium chloride.....    | 94.891 | 94.581 | 95.595 | 93.545 | 95.240 | 94.486 | 95.267 | 95.779 | 94.563 | 95.807 |

1. Eureka Furnace, Ohio River.
2. Newcastle Furnace, Ohio River.
3. Clifton, Ohio River.
4. Syracuse, Ohio River.
5. Coal Ridge, Ohio River.
6. Minersville, Ohio River.

7. Valley City, Ohio River.
8. Hartford City, Ohio River.
9. Hocking Valley Coal & Salt Co., Chauncey, Athens County.
10. Havener and Benjamin, Malta, Morgan County.

<sup>1</sup> Bownocker, loc. cit.

TABLE VIII.—Table of analyses of salts, by T. G. Wormley—Continued.

|                         | 11     | 12     | 13     | 14     | 15     | 16     | 17     | 18     | 19     | 20     |
|-------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Water.....              | 2.100  | 2.600  | 2.800  | 1.150  | 1.700  | 1.700  | 2.500  | 2.000  | 1.800  | 1.100  |
| Insoluble matter.....   | .014   | .016   | .020   | .008   | .020   | .054   | .014   | .040   | .017   | .030   |
| Sulphuric acid.....     |        |        |        |        |        |        |        |        |        |        |
| Lime sulphate.....      |        |        |        |        |        |        |        |        |        | .035   |
| Calcium chloride.....   | .843   | 1.787  | 1.630  | .788   | .480   | .480   | 1.110  | 1.087  | .888   | .433   |
| Magnesium chloride..... | .436   | .966   | .757   | .394   | .249   | .231   | .573   | .565   | .445   | .350   |
| Potassium chloride..... | .151   | .182   | .242   | .333   | .511   | .273   | .156   | .090   | .151   | .574   |
| Sodium chloride.....    | 96.456 | 94.449 | 94.551 | 97.327 | 97.040 | 97.262 | 95.647 | 96.218 | 96.699 | 97.478 |

|                         | 21     | 22     | 23     | 24     | 25     | 26     | 27     | 28     | 29     | 30     | 31     |
|-------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Water.....              | 2.100  | 1.100  | 1.000  | 1.800  | 2.000  | 1.700  | 2.800  | 3.150  | 1.300  | 1.100  | 2.000  |
| Insoluble matter.....   | .016   | .009   | .032   | .016   | .010   | .008   | .014   | .116   | .062   | .278   | .012   |
| Sulphuric acid.....     |        |        |        |        |        |        | Trace. |        | 1.833  | 1.797  | Trace. |
| Lime sulphate.....      |        |        | .004   |        |        |        |        |        |        |        |        |
| Calcium chloride.....   | 1.221  | .610   | 1.976  | .788   | .654   | .999   | 1.454  | .732   | .796   | .207   | .677   |
| Magnesium chloride..... | .607   | .103   | .958   | .385   | .309   | .514   | .650   | .436   | .291   | .094   | .240   |
| Potassium chloride..... | .273   | .303   | .151   | .106   | .076   | .151   | .122   | .122   | .122   | .095   | .137   |
| Sodium chloride.....    | 95.783 | 97.875 | 95.879 | 96.905 | 96.951 | 96.628 | 94.960 | 95.444 | 96.596 | 96.429 | 96.934 |

<sup>1</sup> Sulphate of lime.

- |   |  |
|---|--|
| 11. Wm. Sherwood, 3 miles above Malta, Morgan County.             | 19. B. J. Converse, 5 miles above McConnellsville.         |
| 12. John Havener, 3 miles above Malta, Morgan County.             | 20. W. R. Kelly, 3 miles above McConnellsville.            |
| 13. James Moore, 4 miles above Malta, Morgan County.              | 21. W. R. Kelly, $\frac{1}{2}$ mile above McConnellsville. |
| 14. Big Bloom Furnace, 8 miles above Malta, Morgan County.        | 22. Barnes & Sons, 6 miles below McConnellsville.          |
| 15. Samuel Miller, $\frac{1}{2}$ mile below Malta, Morgan County. | 23. Stansbery, $1\frac{1}{2}$ miles below McConnellsville. |
| 16. C. Wilson, 3 miles below Malta, Morgan County.                | 24. M. Cooper, 5 miles below Zanesville.                   |
| 17. A. Morrison, 9 miles above McConnellsville.                   | 25. O. Ballou, 6 miles below Zanesville.                   |
| 18. J. R. Patterson, 8 miles above McConnellsville.               | 26. Jno. Stevens, 9 miles below Zanesville.                |
|   | 27. South Olive, Noble County.                             |
|   | 28. E. M. Scott, Cambridge, Guernsey County.               |
|   | 29. Saginaw, Mich.   |
|   | 30. Onandaga Salt Co., New York.                           |
|   | 31. Kaawha, W. Va.   |

## MICHIGAN.

In Michigan, as in Ohio, salt is obtained in commercial quantities from two sources, namely, natural brines and rock salt. From the latter salt is obtained both by mining and by solution in fresh water admitted to the beds through borings, or wells, from the surface. The natural brines occur in the Marshall sandstones found in the central part of the State, overlying the formations which contain the rock salt. Along the Saginaw River the saliferous sandstones lie at a depth of about 1,000 feet. In other parts of the State natural brines find their way to the surface either through exposed sections or brine-impregnated rocks or through fissures from the lower-lying strata.

The following record of a well sunk by the Saginaw Plate Glass Co., of West Saginaw, illustrates the stratigraphy of this formation.<sup>1</sup>

<sup>1</sup> Appendix, Geol. Survey, Mich, Ann. Rep., 1903.

|                                   | Formation.                          | Depth<br>of for-<br>mation.<br><i>Fect.</i> | Total<br>depth.<br><i>Fect.</i> |
|-----------------------------------|-------------------------------------|---|---------------------------------|
| Pleistocene:                      |                                     |   |                                 |
|                                   | Fine sand, Algonquin Beach.....     | 5   | 5                               |
|                                   | Red clay.....                       | 20  | 25                              |
|                                   | Blue clay.....                      | 53  | 78                              |
|                                   | Gravel, with water.....             | 2   | 80                              |
|                                   | Hardpan, with coal.....             | 21  | 101                             |
| Saginaw formation:                |                                     |   |                                 |
|                                   | Dark shale, Lower Verne.....        | 14  | 115                             |
|                                   | Shale, light and dark.....          | 7   | 122                             |
|                                   | Blue shale.....                     | 17  | 139                             |
|                                   | Black shale.....                    | 15  | 154                             |
|                                   | Coal, Saginaw seam.....             | 6   | 161                             |
|                                   | White shale, black impressions..... | 4   | 165                             |
|                                   | Dark shale, Saginaw coal.....       | 8   | 173                             |
|                                   | Blue shale.....                     | 5   | 178                             |
|                                   | White and brittle blue shale.....   | $\frac{1}{2}$                               | 178 $\frac{1}{2}$               |
|                                   | Dark-gray shale.....                | 19 $\frac{1}{2}$                            | 198                             |
|                                   | Very dark shale, coal horizon.....  | 13  | 211                             |
|                                   | Dark shale.....                     | 9   | 220                             |
|                                   | Gray shale.....                     | 79  | 299                             |
|                                   | Shale, light and dark.....          | 9   | 308                             |
|                                   | Shales, with siderite.....          | 56  | 364                             |
|                                   | Very dark shale, coal horizon.....  | 12  | 376                             |
|                                   | Blue shale.....                     | 19  | 395                             |
|                                   | Micaceous sandstone.....            | 9   | 404                             |
|                                   | Very dark shale, almost coal.....   | 21  | 425                             |
|                                   | Dark shale.....                     | 49  | 474                             |
| Parma conglomerate and sandstone: |                                     |   |                                 |
|                                   | Transition sandstone.....           | 22  | 498                             |
|                                   | Sand rock.....                      | 23  | 521                             |
|                                   | Conglomeritic sand rock.....        | 14  | 535                             |
| Bayport or Maxville sandstone:    |                                     |   |                                 |
|                                   | Limestone.....                      | 81  | 616                             |
| Michigan series:                  |                                     |   |                                 |
|                                   | Black and dark shale.....           | 35  | 651                             |
|                                   | Gypsum.....                         | 25  | 676                             |
|                                   | Dolomite.....                       | 12  | 688                             |
|                                   | Blue shale.....                     | 58  | 746                             |
|                                   | Gray limestone.....                 | 5   | 751                             |
|                                   | Dark sandy shale.....               | 9   | 760                             |
|                                   | Gray limestone.....                 | 14  | 774                             |
|                                   | Blue limestone.....                 | 21  | 795                             |
|                                   | Sandy shale.....                    | 14  | 809                             |
|                                   | Dolomite.....                       | 11  | 820                             |
|                                   | Upper Marshall sandstone.....       | 78  | 898                             |
| Lower Marshall:                   |                                     |   |                                 |
|                                   | Red clay.....                       | 2   | 900                             |

The density of the solutions from the various strata are given in the following table:

TABLE IX.—*Density of solutions from various strata.*

| Depth of stratum. | Density.       | Depth of stratum.               | Density.       |
|-------------------|----------------|---------------------------------|----------------|
| <i>Feet.</i>      | <i>Sp. gr.</i> | <i>Feet.</i>                    | <i>Sp. gr.</i> |
| 280.....          | 1.005          | 775.....                        | 1.120(?)       |
| 375.....          | 1.006          | 898 (st. 27.5°).....            | 1.193          |
| 476.....          | 1.016          |                                 |                |
| 561.....          | 1.012          | By salimeter <sup>1</sup> ..... | 83°-94°        |
| 620.....          | 1.024          |                                 |                |

<sup>1</sup> The salimeter (or salinometer) is a hydrometer whose graduations represent per cent saturation in sodium chloride.

It will be noted that the density of the brines increases, as a rule, with the depth of the horizon in which they occur.

The natural brines of the Marshall formation of Michigan, like those of Ohio, show a striking freedom from sulphates, with a corresponding large content in calcium chloride. Ammonium salts are also present in the brines. The following result of analysis of the Marshall brine is by F. S. Kedzie.<sup>1</sup>

TABLE X.—*Analysis of Marshall brine.*

| Constituent.            | Grams per liter | Constituent.            | Grams per liter. |
|-------------------------|-----------------|-------------------------|------------------|
| MgSO <sub>4</sub> ..... | 0.77            | NaCl.....               | 229.25           |
| CaCl <sub>2</sub> ..... | 45.02           | LiCO <sub>3</sub> ..... | .15              |
| MgCl <sub>2</sub> ..... | 17.24           | NH <sub>4</sub> Cl..... | .05              |
| MgBr <sub>2</sub> ..... | .35             |                         |                  |

Mr. A. E. Schaefer, chemist of the Saginaw Plate Glass Co., has had the kindness to supply the following results of analysis of a composite brine from the company's wells:

TABLE Xa.—*Analysis of composite brine from Saginaw Plate Glass Co.'s wells.*

| Constituent.            | Per cent. | Constituent.            | Per cent. |
|-------------------------|-----------|-------------------------|-----------|
| NaCl.....               | 18.20     | CaSO <sub>4</sub> ..... | 0.067     |
| CaCl <sub>2</sub> ..... | 3.65      |                         |           |
| MgCl <sub>2</sub> ..... | 1.51      | Density at 15° C.....   | 1.185     |

Rock salt is found in Michigan in the eastern and western extremes of the State. In the Detroit region <sup>2</sup> it occurs in the Monroe formation, though formerly its inclosing strata were referred to the Salina or Onondaga salt group.<sup>3</sup> Here it is penetrated by numerous wells and by the shaft of the Detroit Salt Co.

<sup>1</sup> Loc. cit. With modifications.

<sup>2</sup> The beds of the western borders of the State may be regarded as a continuation of those of the eastern

<sup>3</sup> Geol. Survey, Ohio, 6, 15 (1888). A later restriction of the Monroe formation has excluded the Salina (Cl. Grabau and Sherzer, loc. cit.).

The sequence and formation of the strata overlying and containing the rock salt are given in the following log of a well bored by the Morton Salt Co. at Ecorse, near Detroit.<sup>1</sup>

| Formation.                              | Depth of formation.<br>Feet. | Total depth.<br>Feet. |
|---|------------------------------|-----------------------|
| Pleistocene:                            |                              |                       |
| Surface deposit.....                    | 62                           | 62                    |
| Silurian.                               |                              |                       |
| Monroe above Sylvania:                  |                              |                       |
| Dolomite, light buff; sulphur.....      | 75                           | 137                   |
| Dolomites, bituminous; sulphur.....     | 60                           | 197                   |
| Sylvania:                               |                              |                       |
| Sand.....                               | 65                           | 262                   |
| Dolomite.....                           | 20                           | 282                   |
| Dolomite, siliceous.....                | 35                           | 317                   |
| Sand.....                               | 35                           | 352                   |
| Dolomites, siliceous.....               | 10                           | 362                   |
| Monroe below Sylvania:                  |                              |                       |
| Dolomite, cherty.....                   | 50                           | 412                   |
| Dolomite, dove-colored.....             | 20                           | 432                   |
| Dolomite, bluish.....                   | 30                           | 462                   |
| Dolomite, brown.....                    | 15                           | 477                   |
| Dolomite, light.....                    | 15                           | 492                   |
| Dolomite, dark.....                     | 40                           | 527                   |
| Dolomite, with light gypsum.....        | 25                           | 552                   |
| Beginning of Salina:                    |                              |                       |
| Impure gypsum.....                      | 45                           | 597                   |
| Dolomite.....                           | 20                           | 617                   |
| Dolomite, with anhydrite.....           | 175                          | <sup>2</sup> 792      |
| Salt, blue and brown <sup>3</sup> ..... | 50                           | 842                   |
| Dolomite.....                           | 80                           | 922                   |
| Dolomite, with anhydrite.....           | 10                           | 932                   |
| Anhydrite, with salt.....               | 10                           | 942                   |
| Dolomite.....                           | 5                            | 947                   |
| Salt, gray and white.....               | 15                           | 962                   |
| Dolomite, anhydrite, clay.....          | 100                          | 1,062                 |
| Almost solid anhydrite.....             | 5                            | 1,067                 |
| Dolomite, with anhydrite.....           | 50                           | 1,117                 |
| Salt, dolomite, and anhydrite.....      | 5                            | 1,122                 |
| Salt.....                               | 201                          | 1,323                 |

The following imperfect log was made at the time of drilling a well at the Canfield plant, East Lake, of the Louis Sands Salt Co., of Manistee, Mich., near the shore of Lake Michigan:

<sup>1</sup> Geol. Surv. Mich., Ann. Rept. 1908, p. 97.

<sup>2</sup> First salt at 730 feet.

<sup>3</sup> "This is the most likely to contain potash." Loc. cit.



| Formation.                       | Encountered at depth.<br>Feet. | Formation.                      | Encountered at depth.<br>Feet. |
|----------------------------------|--------------------------------|---------------------------------|--------------------------------|
| Clay.....                        | 104                            | Limestone.....                  | 1, 591½                        |
| Sand.....                        | 107                            | Shale.....                      | 1, 724                         |
| Hardpan, sand, and gravel.....   | 509                            | Limestone.....                  | 1, 745                         |
| Quicksand.....                   | 522                            | Gypsum or "chalk" (?).....      | 1, 772                         |
| Clay, red.....                   | 543                            | Limestone.....                  | 1, 773                         |
| Clay, blue.....                  | 580                            | Shale.....                      | 1, 819                         |
| Soft blue shale.....             | 586                            | Crevice.....                    | 1, 852                         |
| Hard shale.....                  | 588                            | Limestone.....                  | 1, 853                         |
| Sand.....                        | 591                            | Limestone, "honeycomb".....     | 1, 913                         |
| Blue shale.....                  | 595                            | Limestone (shell) and gypsum... | 1, 982                         |
| Limestone, gray.....             | 869                            | Limestone.....                  | 1, 991                         |
| Gypsum (1 to 2 inches).....      | 1, 076                         | Salt (20 feet).....             | 1, 993                         |
| Limestone.....                   | 1, 076                         | Rock (?).....                   | 2, 013                         |
| Gypsum (10 feet).....            | 1, 282                         | Salt (6 feet).....              | 2, 014                         |
| Gypsum and limestone (58 feet).. | 1, 292                         | Rock (?).....                   | 2, 020                         |
| Limestone, brown (106 feet)..... | 1, 350                         | Total depth.....                | 2, 024                         |
| Shale.....                       | 1, 518                         |                                 |                                |

Below are given the records of two wells of the Manistee region. The samples from which the record was made were secured through the courtesy of Mr. George Abair, of the Peters Salt Co., East Lake, Mich. The petrographic determinations were made by Mr. W. H. Fry, mineralogist, of the Bureau of Soils.

All of the samples examined in the preparation of the following sections were obtained by drilling, and consequently many of them were in a rather finely pulverized condition. But in a great number of cases fragments large enough for macroscopic examination were present. In these cases the specimens were determined primarily by macroscopic means. In the cases where all of a given sample was very finely pulverized, the material was mounted in an oil of definite index of refraction and the mineral constituents determined petrographically. The macroscopic examinations were also checked by this microscopic study. Each sample was subjected to the action of both dilute and concentrated hydrochloric acid, and the character of the effervescence used to confirm or modify the results of the previous examination. Great difficulty was encountered in judging whether some particular samples, especially the finely pulverized samples, should be referred to the limestone or the shale group. For instance, it was found practically impossible to determine absolutely whether a particular mount was a calcareous shale or a shaly limestone. However, predominance of one or the other of the materials was considered as sufficient to place the sample in the class of the predominating material, the less abundant material being considered as an impurity and being indicated by its appropriate adjective. Before coming into the writer's hands, the samples had been subjected to a mechanical analysis and all particles less than 0.005 mm. diameter discarded. The amount of these very small particles, however, is not large enough to vitiate the accuracy of the determinations.

*Section of well at Ludington, Mich., Stearns Salt & Lumber Co.*

Petrographic examinations by William H. Fry.

| No. of samples. | Depth in feet.      |                                  |
|-----------------|---------------------|----------------------------------|
| 19.....         | 517 to 520.....     | Calcareous sandstone.            |
| 20.....         | 520 to 533.....     | Calcareous and shaly sandstone.  |
| 21 to 22.....   | 533 to 573.....     | Calcareous shale.                |
| 23 to 24.....   | 573 to 603.....     | Calcareous and sandy shale.      |
| 25.....         | 603 to 608.....     | Calcareous shale.                |
| 26.....         | 608 to 609.....     | Sandy calcareous shale.          |
| 27.....         | 609 to 615.....     | Buff calcareous and sandy shale. |
| 28 to 39.....   | 615 to 838.....     | Calcareous shale.                |
| 40 to 60.....   | 838 to 1,211.....   | Sandy calcareous shale.          |
| 61 to 69.....   | 1,211 to 1,390..... | Calcareous shale.                |
| 70 to 73.....   | 1,390 to 1,463..... | Limestone, impure.               |
| 74 to 90.....   | 1,463 to 1,801..... | Fairly pure limestone.           |
| 91 to 97.....   | 1,801 to 1,935..... | Dolomitic limestone.             |
| 98 to 102.....  | 1,935 to 2,021..... | Calcareous mudstone.             |
| 103 to 115..... | 2,021 to 2,281..... | Limestone.                       |
| 116.....        | 2,281 to 2,290..... | Halite.                          |

*Section of well 500 feet from East Lake station of the plant of the R. G. Peters Salt Co.*

Petrographic examinations by W. H. Fry.

| No.     | Depth in feet. |  |
|---------|----------------|--|
| 1.....  | 593.....       | Blue calcareous shale.                       |
| 2.....  | 597.....       | Calcareous shale.                            |
| 3.....  | 800.....       | Calcareous shale.                            |
| 4.....  | 978.....       | Limestone.                                   |
| 5.....  | 1,325.....     | Limestone.                                   |
| 6.....  | 1,400.....     | Limestone.                                   |
| 7.....  | 1,425.....     | Limestone.                                   |
| 8.....  | 1,450.....     | Limestone.                                   |
| 9.....  | 1,475.....     | Limestone.                                   |
| 10..... | 1,487.....     | Calcareous shale.                            |
| 11..... | 1,500.....     | Limestone.                                   |
| 12..... | 1,595.....     | Limestone.                                   |
| 13..... | 1,605.....     | Limestone.                                   |
| 14..... | 1,638.....     | Limestone containing sponge spicules.        |
| 15..... | 1,645.....     | Calcareous shale containing sponge spicules. |
| 16..... | 1,650.....     | Calcareous shale containing sponge spicules. |
| 17..... | 1,652.....     | Calcareous shale containing sponge spicules. |
| 18..... | 1,656.....     | Calcareous shale.                            |
| 19..... | 1,658.....     | Calcareous shale.                            |
| 20..... | 1,661.....     | Limestone.                                   |
| 21..... | 1,680.....     | Limestone.                                   |
| 22..... | 1,690.....     | Limestone (rather impure).                   |
| 23..... | 1,700.....     | Limestone (very sandy).                      |
| 24..... | 1,762.....     | Limestone (very sandy).                      |
| 25..... | 1,780.....     | Limestone (very sandy).                      |
| 26..... | 1,809.....     | Calcareous sandstone.                        |
| 27..... | 1,810.....     | Calcareous sandstone.                        |
| 28..... | 1,820.....     | Limestone.                                   |
| 29..... | 1,830.....     | Limestone.                                   |
| 30..... | 1,850.....     | Limestone.                                   |
| 31..... | 1,862.....     | Limestone.                                   |
| 32..... | 1,870.....     | Limestone.                                   |
| 33..... | 1,880.....     | Limestone.                                   |
| 34..... | 1,895.....     | Limestone.                                   |

| No.     | Depth in feet. |                                      |
|---------|----------------|--------------------------------------|
| 35..... | 1,920.....     | Limestone.                           |
| 36..... | 1,930.....     | Siliceous and ferruginous limestone. |
| 37..... | 1,940.....     | Siliceous and ferruginous limestone. |
| 38..... | 1,964.....     | Shaly limestone.                     |

## WEST VIRGINIA.

In West Virginia natural brines are obtained in commercially workable quantities in the valleys of the Ohio and Kanawha Rivers. The former region, Mason County, lies closely adjacent to the Pomeroy district of Ohio, and the brines there obtained come from the same formation as do those obtained at Pomeroy. Their origin has been discussed in a foregoing paragraph.

In the latter region, the Kanawha Valley, wells have been bored in Kanawha County, at Malden, and penetrate the saliferous sandstones of the Pottsville series of the Carboniferous.<sup>1</sup>

The strata impregnated with brines here lie at a depth of 600 to 1,000 feet below the surface. The stratigraphy of the area is very well illustrated by the incomplete log of a gas well put down in the locality of the "Burning Spring" on the Kanawha, about 9 miles above Charleston. The record begins at 100 feet below the Lower Kittanning coal.<sup>2</sup>

| Formation.                            | Depth of formation. Feet. | Total depth. Feet. |
|---------------------------------------|---------------------------|--------------------|
| Unrecorded.....                       | 53                        | 53                 |
| Coal, trace.                          |                           |                    |
| Sand, white.....                      | 100                       | 153                |
| Shale, gray.....                      | 8                         | 161                |
| Sand, gray (smell of oil).....        | 40                        | 201                |
| Shale, dark.....                      | 25                        | 226                |
| Sand, white (top of "salt sand")..... | 174                       | 400                |
| Coal.....                             | 6                         | 406                |
| Sand, white (salty).....              | 200                       | 606                |
| Shale, white.....                     | 10                        | 616                |
| Limestone, white (shale).....         | 50                        | 666                |
| Shale, white.....                     | 40                        | 706                |
| Sand, white.....                      | 125                       | 831                |
| Sand, white (salty).....              | 130                       | 961                |
| Shale, black.....                     | 2                         | 963                |
| Sand, white.....                      | 50                        | 1,013              |
| Sand, blue (base of "salt sand")..... | 50                        | 1,063              |
| Limestone, blue (gas).....            | 300                       | 1,363              |
| "Red rock" (sand, shale).....         | 50                        | 1,413              |
| Unrecorded.....                       | 187                       | 1,600              |
| Sand, coarse (light oil).....         | 2                         | 1,602              |
| Shale, blue.....                      | 250                       | 1,852              |
| Shale, black.....                     | 75                        | 1,927              |
| Shale, blue.....                      | 323                       | 2,250              |
| Shale, shelly (gas).....              | 100                       | 2,350              |
| Shale, blue.....                      | 50                        | 2,400              |
| Sand, shelly (gas).....               | 50                        | 2,450              |
| Shale, blue (soft).....               | 92                        | 2,542              |

<sup>1</sup> Harris, Bul. 7, Geol. Survey, La.

<sup>2</sup> W. Va. Geol. Survey, I., 272 (1899), with modifications. By "sand" probably is meant "sandstone."

The Pottsville series, containing the "salt sand" or strata impregnated with brine, is here represented as 837 feet thick.

In the limestone stratum beginning at a depth of 1,063 feet are included thin strata or streaks of sand which are assigned to the so-called "Big Injun" horizon. This sand has been noted in the record of the Beck well, at Pittsburgh, at about the same depth, a fact of especial interest as, seemingly, correlating the saliferous strata of central West Virginia with those of western Pennsylvania.

PENNSYLVANIA.

Natural brines are obtained from certain pervious strata underlying Pittsburgh and vicinity. A remarkably deep well has been bored by the John A. Beck Salt Co., of North Side, Pittsburgh, the driller's record of which is appended. This was secured through the courtesy of Mr. Charles Glass, chemist. While the information to be obtained from the record is of a negative character when looked at from the standpoint of possible sources of potash, it is of especial interest as revealing the character of the rocks underlying the saliferous sandstones.

*Record of Well No. 4—The John A. Beck Salt Co., North Side, Pittsburgh, Pa.*

|                            | Feet. | Total.           |
|----------------------------|-------|------------------|
| Ashes and clay.....        | 20    | 20               |
| Gravel.....                | 49    | 69               |
| Shale.....                 | 30    | 1 99             |
| Sandstone.....             | 40    | 139 <sup>1</sup> |
| Shale.....                 | 81    | 220              |
| Sandstone.....             | 50    | 270              |
| Shale.....                 | 15    | 285              |
| Limestone.....             | 5     | 290              |
| Shale.....                 | 89    | 379              |
| Coal.....                  | 7     | 386              |
| Shale.....                 | 50    | 436              |
| Limestone.....             | 30    | 466              |
| Shale.....                 | 10    | 476              |
| Sandstone.....             | 30    | 506              |
| Shale.....                 | 10    | 516              |
| Limestone.....             | 15    | 531              |
| Sandstone.....             | 45    | 576              |
| Shale.....                 | 124   | 700              |
| Sandstone.....             | 10    | 710              |
| Shale.....                 | 35    | 745              |
| Sandstone "Big Injun"..... | 319   | 1,064            |
| Shale.....                 | 10    | 1,074            |
| Sandstone.....             | 70    | 1,144            |
| Shale.....                 | 15    | 1,159            |
| Sandstone.....             | 20    | 1,179            |
| Shale.....                 | 5     | 1,184            |

<sup>1</sup> Water at 95 feet.

|                      | <i>Feet.</i> | <i>Total.</i>        |
|----------------------|--------------|----------------------|
| Sandstone.....       | 20           | 1, 204               |
| Shale and shell..... | 46           | <sup>1</sup> 1, 395  |
| Salt sand.....       | 95           | <sup>2</sup> 1, 490  |
| Sandstone.....       | 30           | 1, 520               |
| Shale.....           | 10           | 1, 530               |
| Sandstone.....       | 115          | 1, 645               |
| Shale.....           | 5            | 1, 650               |
| Sandstone.....       | 10           | 1, 660               |
| Shale.....           | 50           | 1, 710               |
| Sandstone.....       | 30           | 1, 740               |
| Shale.....           | 20           | 1, 760               |
| Sandstone.....       | 10           | 1, 780               |
| Shale.....           | 5            | 1, 785               |
| Red rock.....        | 5            | 1, 790               |
| Sandstone.....       | 30           | 1, 820               |
| Shale.....           | 35           | 1, 855               |
| Sandstone.....       | 10           | 1, 865               |
| Shale and shell..... | 60           | 1, 925               |
| Sandstone.....       | 23           | 1, 948               |
| Shale and shell..... | 82           | 2, 030               |
| Sandstone.....       | 10           | 2, 040               |
| Shale and shell..... | 310          | 2, 350               |
| Sandstone.....       | 30           | 2, 380               |
| Shale.....           | 110          | 2, 490               |
| Sandstone.....       | 40           | 2, 530               |
| Shale.....           | 35           | 2, 565               |
| Sandstone.....       | 40           | 2, 605               |
| Shale.....           | 195          | 2, 800               |
| Sandstone.....       | 20           | 2, 820               |
| Shale.....           | 580          | 3, 400               |
| Sandstone.....       | 40           | 3, 440               |
| Shale and shell..... | 560          | 4, 000               |
| Sandstone.....       | 40           | 4, 040               |
| Shale and shell..... | 49           | <sup>3</sup> 4, 089½ |

## KANSAS.

In the rocks underlying Kansas are found both strata impregnated with brine and beds of rock salt. In addition to these sources of salt there is a third—the salt marshes.

The natural brines are carried in saliferous shales of the Dakota formation, located near the base of the upper Dakota.<sup>4</sup> They are from 15 to 30 feet thick. At or near their outcroppings the salt marshes have been formed in depressions caused by the erosion of these strata and fed by springs of salt water emerging from them. The marshes in periods of dry weather become whitened by a crystallization of sodium chloride.

In addition to this stratum the Red Beds in the upper Permian are likewise impregnated with brine and likewise supply some of the salt found in the marshes.

<sup>1</sup> 145 feet unaccounted for.

<sup>2</sup> Water at 1,405 feet.

<sup>3</sup> Gas 5 feet in fifth sand.

<sup>4</sup> Quoted from Kirk, Min. Res. Kans., 1893, p. 86.

The rock salt is found in a bed lying between shales of the Permian formation. The latter are the Wellington shales above and the Marion shales and limestones below. Toward the eastward they gradually grow thinner and eventually disappear before the borders of the State are reached. To the South they appear in Oklahoma and their limit is entirely unknown. To the northward their thickness decreases at a rate which would indicate their disappearance before the northern borders of the State are reached. The beds have a southern dip. Their western limits are not known. In the region underlying Anthony the salt bed has a thickness of about 400 feet. At Kanopolis the thickness is 250 feet. From the following record of a boring sunk at Kanopolis may be obtained a very definite idea of the stratigraphy of the formations pierced:<sup>1</sup>

*Material from—*

| Number of feet from surface. |                             |
|------------------------------|-----------------------------|
| 5.....                       | Soil, sandy loam.           |
| 10.....                      | Brown sand.                 |
| 15.....                      | Yellow sand.                |
| 20.....                      | Sand and fine gravel.       |
| 25-35....                    | White sand and fine gravel. |
| 35.....                      | Coarse gravel.              |
| 40.....                      | Yellow clayey sand.         |
| 45-55....                    | Gray soapstone.             |
| 55.....                      | Light-gray soapstone.       |
| 60.....                      | Red shale.                  |
| 65.....                      | Pink shale.                 |
| 70-80....                    | Gray shale.                 |
| 80.....                      | Gray sand and gravel.       |
| 85-115...                    | Gray shale.                 |
| 115-150..                    | Dark-blue shale.            |
| 150-185..                    | Lead-colored shale.         |
| 185.....                     | Red shale.                  |
| 190.....                     | Silica or light shale.      |
| 195-200..                    | Silica or light soft shale. |

*Triassic.*

|           |                     |
|-----------|---------------------|
| 205-245.. | Red rock.           |
| 245.....  | Brown rock.         |
| 250-260.. | Dark-brown rock.    |
| 260-270.. | Brown and red rock. |
| 270-280.. | Dark-red rock.      |
| 280-300.. | Brown and red rock. |
| 305-320.. | Red rock.           |
| 320-335.. | Light-red rock.     |
| 335.....  | Brown and red rock. |
| 340-350.. | Dark-red rock.      |

*Triassic—Continued.*

| Number of feet from surface. |                                      |
|------------------------------|--------------------------------------|
| 350-365..                    | Brown rock.                          |
| 365.....                     | Dark-red rock.                       |
| 370.....                     | Dark-brown rock.                     |
| 375-385..                    | Dark-red rock.                       |
| 385.....                     | Traces of gypsum.                    |
| 390.....                     | Dark-red rock.                       |
| 395.....                     | Very dark red rock.                  |
| 400.....                     | Dark (gypsum) rock.                  |
| 405.....                     | Brown (traces) rock.                 |
| 410.....                     | Blue shale.                          |
| 415-465..                    | Blue shale and gypsum.               |
| 465-475..                    | Blue shale.                          |
| 475-490..                    | Brown shale.                         |
| 490.....                     | Red rock, gypsum.                    |
| 495-510..                    | Brown gypsum.                        |
| 510-530..                    | Brown shale.                         |
| 530.....                     | Gray shale.                          |
| 535-565..                    | Brown shale.                         |
| 565-640..                    | Blue shale.                          |
| 640.....                     | Blue shale, with few scales of salt. |
| 645.....                     | Blue shale and salt mixed.           |
| 655.....                     | Salt.                                |
| 660.....                     | Salt and shale.                      |
| 665.....                     | Shale and salt.                      |
| 670.....                     | Salt.                                |
| 675-860..                    | Salt, bright crystals.               |
| 860.....                     | Slightly mixed with shale.           |
| 865-875..                    | Salt, slightly mixed with shale.     |
| 875-880..                    | Salt and clay.                       |

<sup>1</sup>Kirk, Min. Res. Kans., 1898, p. 94, with modifications.

## LOUISIANA.

The State of Louisiana is underlain by salines in certain known areas of both its northern and southern parts. The deposits have been described in Bulletin 7 of the Geological Survey of Louisiana by G. D. Harris, from whose valuable report the few brief facts here given have been taken.

At Petite Anse, on Averys Island, in southern Louisiana, a salt deposit, which is typical, is found in formations of Quaternary origin. The salt deposits are referred to the Tertiary period and are supposed to rest on the Cretaceous.<sup>1</sup> The areal dimensions of the beds or masses here are undetermined, as likewise their depth.

Below are given brief records of two wells, 1 mile apart, which have been sunk at Petite Anse:

| Formation.                       | Thickness<br>of<br>formation. | Total<br>depth. |
|----------------------------------|-------------------------------|-----------------|
|                                  | <i>Fect.</i>                  | <i>Fect.</i>    |
| Superficial detritus.....        | 330                           | 330             |
| Well No. 1:                      |                               |                 |
| Rock salt.....                   | 2, 263                        | 2, 593          |
| Blue gas sand <sup>2</sup> ..... | 70                            | 2, 663          |
| Rock salt.....                   | ....                          | 2, 729          |
| End of boring.....               | ....                          | 2, 729          |
| Well No. 2:                      |                               |                 |
| Yellowish clay.....              | 500                           | 500             |
| Gravel.....                      | 200                           | 700             |
| Grayish sand.....                | 2, 112                        | 2, 812          |

Neither rock salt nor brines were encountered in this well (No. 2). At a depth of about 1,100 feet a bed of shells was penetrated, and at 1,400, logs of wood were encountered.

These two records are of especial interest as indicating irregularity or discontinuity of the beds of this section.

At Grande Cote, also in southern Louisiana, rock salt is found at a depth of only 145 feet below the surface. The nearness of the salt to the surface in this region is particularly favorable to mining.

The rock salt beds of Louisiana, unlike those of New York and Kansas, are not regarded as the desiccation product of a saline sea. Their peculiar pyramidal or domelike shape, their association with petroleum and gas, and the enormous lifting forces which have accompanied their formation have suggested various theories to account for their origin, one of which, advocated by Harris<sup>3</sup> and attributed by Clarke<sup>4</sup> to Hill and Hager, proposes that the rock salt of Louisiana

<sup>1</sup> Lucas, Trans. Am. Inst. Min. Eng., 29, 462 (1899).

<sup>2</sup> A log of wood was found in this formation.

<sup>3</sup> Harris, loc. cit.

<sup>4</sup> F. W. Clarke, Data of Geochemistry, 2d ed., p. 218.

(and Texas) has been crystallized from rising columns of hot solution and that the growth of crystal masses in forming have exerted pressures sufficient to lift the domes.<sup>1</sup>

Crystallization under the conditions assumed by the theories of Harris can only be the result of a chilling of a hot, saturated solution. As the solubility coefficient of sodium chloride is low, the formation of such huge masses of salt must have involved the movement of enormous volumes of brine. As a source of the brine, hot, volcanic water flowing through and dissolving beds of rock salt suggests itself. The crystallization of sodium chloride from this solution would represent a recrystallization, with a consequent elimination of impurities. "The extreme purity of the salt in these mines, especially when taken in connection with the great depths of the salt," according to Harris, "calls for a selective dissolving agent, and a recrystallization in pure salt masses."

It is too much to assume a "selective dissolving agent." And such an assumption is unnecessary, as the impurities present in known beds of rock salt on this continent are in very small amount. This fact is abundantly substantiated by the various artificial<sup>2</sup> brines examined in this investigation. In fact, the artificial brines should be strictly comparable in composition to the theoretical brines from which the rock salt of the salt domes was built up. The crystallization of salt from such a pure solution would result necessarily in a pure product. Furthermore, the amount crystallized from a given volume of solution through chilling would be so small as compared with the total salt in solution that the composition of the solution would be only slightly altered by the precipitation. There would then be no appreciable segregation of impurities in the mother liquor. Also an accumulation of mother liquor would be impossible, theoretically, as the chilled solution must have been displaced by the succeeding volumes of unchilled solution. A further precipitation of salt and consequent segregation of impurities in the mother liquor would have been impossible under the conditions assumed, as no evaporation or other action leading to a further concentration could have taken place within the strata.

If this theory be accepted, then all hope must be abandoned of finding here any segregation of potassium salts.

If these salt masses did form, as supposed, by crystallization from below, and if through any combination of conditions other salts than sodium chloride were deposited, the order of their deposition should have been, roughly, the reverse of that observed in the Stassfurt deposit. The conditions tending to induce a different order of precipitation would have been high temperature and pressure.

<sup>1</sup> For a presentation of these and other theories, reference is made to Bulletin 7 of the Geological Survey of Louisiana.

<sup>2</sup> Cf., pp. 43 and 53.



A further theory, whose assumptions are less violent, accounts for the formation of salt domes as the result of great pressure on plastic salt masses by the inclosing, less plastic rocks. This theory is attributed by Hahn<sup>1</sup> to Harbort, and is stated by him as "a conclusion that the relatively plastic salt mass has been squeezed upward like a fluid magma under the pressure of organic forces while the normally overlying strata either had been pushed aside or left behind as sluggish and inflexible masses."

The plasticity of salt masses is a known and not an assumed quantity.<sup>2</sup> If at ordinary temperatures this quality is insufficient to account for the fluidity which has been exhibited by the masses comprising the salt domes, it easily may be assumed that the salt was warmed to its melting point by volcanic heat. If sodium chloride fuses with a decrease in volume, the pressure to which it is subjected in the earth's crust would lower its melting point. The association of sulphur, presumably a reduction product of calcium sulphate, with the salt masses further suggests elevated temperatures. The formation of salt domes, then, would be the result of ascending columns of fused sodium chloride. Recrystallization would occur when the surface had been approached, being induced by a lower temperature or a lower pressure, or both. Crystal formation, as suggested by Harris, may have added its forces to the pressure of the ascending molten mass.

#### TECHNOLOGY OF SALT MANUFACTURE.

The following brief statements will cover the essential points in the technology of the manufacture of salt as practiced in the plants visited in New York and Michigan.

In these States operations of two distinct sorts are carried on: The preparation of salt from (1) rock salt and (2) from brines.

(1) The first class includes the mining, crushing, and screening of rock salt. Shafts are sunk to the salt beds and the salt is removed by methods in a general way similar to those in vogue in coal mining.

(2) Brines of two general sorts are used—(a) artificial and (b) natural.

(a) By artificial brines is meant those which are obtained where water is admitted to the salt beds through borings from the surface. Two pipes are sunk, a smaller one inside a larger, through one of which fresh water is admitted and through the other brine is taken out. Gradually a cavity in the salt bed is thus obtained. In the larger cavities the amount of brine pumped out in a given length of time is so small as compared with the total amount of solution in the cavity that the issuing brine is a practically saturated solution.

<sup>1</sup> *Econom. Geol.* 7, 120 (1912).

<sup>2</sup> "Umformung von Carnallit unter allseitigen Druck," Rinne, *Koenen-Festschrift*, 1907, 369; "Plastische Umformung von Steinsalz u. Sylvine," *Neues Jahrbuch F. Min.*, 1904 (I), 114.

Since the fresh water admitted to the cavity is of a lower density than the brine, it lies on top of the brine. More rapid solution then takes place from the upper part of the cavity, and hence of the salt stratum. The composition of the brine thus produced, then, is not necessarily representative of that of the entire stratum.

(b) The term "natural brines" in this report has been restricted to those salt solutions, of various degrees of salinity, which are found in the porous strata of certain regions. Natural brines are obtained from wells sunk to the porous strata. A cavity is formed for the collection of the brine by "shooting" the well with nitroglycerine.

#### PRELIMINARY TREATMENT.

From the wells the brines enter settling tanks, where solid matter—small particles of argillaceous limestone and gypsum—is allowed to settle out. Following this, the brines may be run directly into evaporators, or may be subjected to treatment for the removal of any or all of the pernicious impurities. The practice varies from plant to plant. The impurities removed are solid matter, hydrogen sulphide, iron, calcium, and magnesium.

Hydrogen sulphide is removed either by allowing the brine to stand exposed to the open air or by passing it over weirs or cascades or through long troughs. With the removal of hydrogen sulphide, iron present originally as ferrous salts is oxidized and may be precipitated by hydrolysis or by milk of lime.

Calcium and magnesium are removed partially by precipitation with applications of soda ash. A further and more perfect separation is obtained with sodium phosphate.

#### EVAPORATION.

Evaporation is effected in one of three forms of apparatus or in combination of the three: "English open pans," "grainers," and "vacuum pans." The English open pan is of sheet iron and is supported on brick pillars and arches directly over the fire box and flues of a furnace. "Grainers" are shallow pans of sheet iron or cement, heated by means of steam pipes. "Vacuum pans" are funnel-shaped vessels of insulated sheet iron, covered with a dome-like top and heated with steam coils. These are operated singly or in combinations of two or three, designated, respectively, as the "single," "double," and "triple effect" system. The rate of evaporation is increased by reduced pressure.

The crystallized salt is removed from the open pans and grainers by rakes operated by hand or mechanically and from the vacuum pans by bucket conveyers with perforated bottoms. The mother liquor is removed from the salt on the dripping boards, in drainage bins or in centrifuges.

## MOTHER LIQUORS.

The treatment of mother liquors varies from plant to plant, and is determined as much by the purity of the original brine as by any other factor.

The precipitation of calcium sulphate on the bottom of the open pans and the coils of the grainers and vacuum pans acts as an effective heat insulator and interrupts the evaporation. To remove this coating it is necessary to empty the evaporator. In some plants at this stage the brine is allowed to run into drains and is lost. If the preliminary purification has been only slight, this stage of the operation may be reached quite early, and the amount of salt obtained may represent only a small proportion of that present in the brine. There is then but a slight concentration of the solution. The other extreme is found in those plants where it is the practice to subject the brine to a careful preliminary purification. The mother liquor here is never thrown away, but is allowed to mix with fresh volumes of brine.

It was found to be impracticable to secure accurate information concerning the ratio between the volumes of brine evaporated and the mother liquor resulting, or the degree of concentration. And as the practice varied so widely from plant to plant it was even less practicable to determine the average volumes from all the plants visited.

In general it may be said that where mother liquors are discarded the degree of concentration in them is slight.

The mother liquors from the evaporation of natural brines are subjected frequently to further treatment for the recovery of calcium and magnesium chlorides. For this purpose they are further evaporated to the point where, on cooling, the ultimate possible crystallization of the sodium chloride is accomplished. The mother liquor from this crystallization is evaporated in kettles, heated with steam coils, to the concentration at which, on cooling, the mass solidifies. The water present enters into combination as water of crystallization. The product is a mixture of hydrated calcium and magnesium chlorides, with the calcium chloride in preponderating amount.

For the recovery of bromine the mother liquor is acidified with sulphuric acid and is distilled in the presence of manganese dioxide or potassium or sodium chlorate. The acid is neutralized subsequently with lime and the solution is evaporated for the preparation of the solid calcium chloride. The addition of lime in excess over that requisite to the neutralization of the sulphuric acid gives a final product of an alkaline character.

### SOLAR REFINERIES OF THE PACIFIC COAST.

The sea water is pumped at high tide into one end of a long series of shallow ponds. These are connected with each other, and as the evaporation proceeds the brine flows through the series of ponds, gradually increasing in concentration. Gypsum is deposited during this stage of the process. When the brine has reached a concentration of about  $75^{\circ}$  or  $80^{\circ}$  by the salimeter it is pumped into the so-called lime ponds, and when it approaches saturation ( $100^{\circ}$  by the salimeter), thence into the "salt-making" ponds. Here it is allowed to deposit salt during a summer. At the end of the season the mother liquor is drained or pumped off and the crystallized salt is scraped from the bottom of the pond.

The mother liquor is either discarded or is stored in ponds, and used at times to increase the concentration of brines which have not reached a high enough concentration to deposit salt. The approach of the end of the season, rather than the concentration of the impurities in the mother liquor, is the determining factor in bringing the evaporation to a close.

The mother liquors contain, in addition to their saline constituents, a considerable amount of organic matter consisting of bacteria, the larvæ of a certain fly, and the disintegrated remains of fish. The color of the mother liquors is red.

### THE COLLECTION OF SAMPLES.

The specimens of rock salt and brines whose analyses are reported in this bulletin were collected for the most part during the summer of 1911. Samples of rock salt, natural and artificial brines, and mother liquors from New York and Michigan were taken by Dr. W. C. Phalen, of the United States Geological Survey, and the author; those from Ohio, West Virginia, Kansas, and Louisiana were collected by Dr. Phalen.

Certain other samples of brines from numerous sources, such as the oil or gas wells or borings for oil or gas, were collected by correspondence by the Geological Survey. This collection was made, as was the collection by the Geological Survey during the summer of 1911, for the purposes of a systematic investigation of the salines of the United States occurring east of the Rocky Mountains. The taking of the samples in this manner could not be accomplished in accordance with standardized methods, hence the collection of 1911.

Samples of bitterns from the salt refineries of the Pacific Coast were collected by E. E. Free, a representative of the Bureau of Soils. Specimens of the brines from salt lakes of California, likewise, were obtained by Mr. Free.

Samples of brines and bitters of the 1911 collection were taken, with a very few exceptions, in person, either by Dr. Phalen or by the author. Requisite care was observed to secure a representative sample, where that was desirable. In sampling bitters, portions were taken from the evaporators at points as far as possible from the inlet pipe through which fresh brine was entering. Bitters representing the maximum evaporation were sought.

The specimens of rock salt were taken from the actual working faces of the mines. With one exception the samples were taken by cutting a groove from ceiling to floor, thus getting a sample through the entire depth of the strata worked. The resulting lot of salt was thoroughly mixed and quartered and was thus reduced to a convenient bulk for shipment.

In the field special attention was given those points which had a bearing on the question of the occurrence of potash in the rock salt and brines operated with, such as—

1. The salt wells (or mine shafts), their depth, the character of the strata penetrated.

2. The composition and character of the rock salt and brine.

3. The treatment to which the brine is subjected for the removal of impurities and the resulting alteration in its composition.

4. The evaporation of the brine: The methods employed, the extent to which the evaporation is carried, the impurities separating, the amount of mother liquor produced from a definite amount of brine, and its subsequent treatment; its composition.

#### ANALYTICAL METHODS.

In the analyses, for the most part the methods recommended by the Association of Official Agricultural Chemists for the analysis of mineral waters were employed in the determination of iron and aluminum, calcium, magnesium, sodium, potassium, and sulphuric acid. Certain modifications tending to abbreviate the analytical processes were introduced when found expedient. These methods have been widely circulated in Bulletin 107 and Circular 52 of the Bureau of Chemistry of the United States Department of Agriculture. However, the number of inquiries received at this office concerning the methods of analysis employed warrant their publication. For that reason the methods as modified are introduced here.

#### PREPARATION OF THE SOLUTION.

The sample of brine is allowed to stand until all sediment has settled out. A portion, 10 c. c. in volume, is transferred in a dry, calibrated pipette to a 200 c. c. graduated flask. This is filled to the mark with distilled water. Aliquot portions of this solution are taken for the various determinations, as indicated below.

## DETERMINATION OF DIFFERENT CONSTITUENTS.

*Total salts in solution.*—A convenient volume of the above solution (i. e., of the original brine) is transferred by means of a graduated pipette to a weighed platinum dish. It is evaporated to dryness and the residue is heated to constant weight at 105° C. It is sometimes also advisable to weigh after drying at 180° C.

*Loss on ignition.*—Ignite to low redness the residue obtained as total salts in solution. Cool and weigh.

If the brine on standing has remained colorless, proceed next to the determination of calcium and magnesium. Otherwise analyze for iron and aluminum.

*Iron and aluminum.*—Treat an aliquot portion of the solution with ammonium chloride (to keep magnesia in solution) and heat to boiling. Add ammonium hydroxide, a drop at a time, until it can be very faintly smelled coming off from the solution. Boil the solution until the smell of ammonia has practically disappeared, filter, wash with hot water, dry, burn, and weigh as ferric oxide ( $\text{Fe}_2\text{O}_3$ ) and alumina ( $\text{Al}_2\text{O}_3$ ). Use the filtrate for the determination of calcium and magnesium.

*Iron.*—Treat an aliquot portion of the solution with 2 or 3 c. c. of concentrated sulphuric acid and evaporate to a sirupy consistency. Take up with water, reduce with hydrogen by the addition of zinc, filter, and determine the iron in the filtrate with standard potassium permanganate.

*Calcium and magnesium.*<sup>1</sup>—Treat the filtrate from the iron and aluminum determination (or a new portion of the solution) with ammonium hydroxide and ammonium oxalate and allow to stand overnight. Filter off the liquid, wash twice with hot water by decantation, dissolve the precipitate in hydrochloric acid, and reprecipitate with ammonium hydroxide and a little more ammonium oxalate. Allow to stand overnight and filter and wash on the same paper previously used. Dry the precipitate and transfer to a crucible, ignite and blast in the ordinary way, and finally weigh as calcium oxide. Evaporate the combined filtrates to dryness in platinum and drive off the major part of the ammonium salts by heating. Dissolve the residue in dilute hydrochloric acid and filter. Make the filtrate slightly ammoniacal, add enough sodium phosphate solution, a drop at a time, to precipitate all magnesium and 10 c. c. of concentrated ammonium hydroxide, drop by drop. Cover the beaker and allow to stand overnight; filter, wash with 2.5 per cent of ammonium hydroxide until free from chlorides; dry, blast, and weigh as magnesium pyrophosphate.

<sup>1</sup> Not applicable in the presence of weighable amounts of phosphoric acid.

*Sulphuric acid.*—Acidify with hydrochloric acid another portion of the solution and treat, while boiling, with hot, dilute barium chloride solution. After standing, filter; wash the precipitate of barium sulphate and dry; burn and weigh in the usual manner.

Evaporate the filtrate to dryness and take up with a little water. If the presence of lithium is suspected, moisten a platinum wire, thoroughly cleaned in concentrated hydrochloric acid, with the solution obtained as just indicated, and hold in the blue flame of a Bunsen burner. Examine the flame with a spectroscope for the characteristic red lithium lines. If lithium is found to be present proceed, as follows, to the determination of sodium, potassium, and lithium:

*Sodium, potassium, and lithium.*—Add a solution of barium hydrate or milk of lime and filter off the insoluble magnesium hydrate. Wash thoroughly with hot water the magnesium hydrate precipitate, and combine the filtrate and washings. Treat with ammonia, ammonium carbonate, and a little ammonium oxalate to precipitate calcium and barium. Allow to stand overnight, filter and wash thoroughly. Evaporate the filtrate and washings to dryness, dry in an oven and finally drive off the ammonium salts by gentle heat. Take up the residue with water, filter through a small filter, using as little wash water as possible, evaporate to a small volume, and finally again precipitate with a drop of ammonium hydroxide, and two or three drops of ammonium carbonate and oxalate. If any precipitate appears, which is not usually the case, filter and repeat the same process. In any case, filter the solution from the magnesium hydrate that is precipitated on concentrating the solution. Evaporate the filtrate to dryness and drive off all ammonium salts by heating in platinum to a little below redness. Take up the residue with a little water and run through a small filter, using as little wash water as possible, and again heat in platinum to a point slightly below red heat. By this means all of the magnesium should be removed. Take up the residue with a little water, filter into a weighed platinum dish, add a few drops of hydrochloric acid, and evaporate to dryness. Dry in an oven, heat to a little below redness, cool in a desiccator, and finally weigh the combined chlorides of potassium, sodium, and lithium.

The determination of lithium is then made according to the method of Gooch,<sup>1</sup> as follows:

Dissolve the combined chlorides in water and transfer to a small beaker and again evaporate practically to dryness. Add about 30 c. c. of dehydrated amyl alcohol (boiling point 130° C.) and boil until the temperature rises approximately to the boiling point of the amyl alcohol,

<sup>1</sup> Am. Chem. J., 1887, 9:23.

showing that all of the water has been driven off. Cool slightly and add a drop of hydrochloric acid to reconvert small amounts of lithium hydrate to lithium chloride. Continue the boiling again to drive off all water, until finally the liquid reaches a volume of about 15 c. c. Filter the amyl alcohol into a weighed platinum dish and wash the filter with a little amyl alcohol. Drive off the amyl alcohol from the filter and beaker in the air bath and keep these for the determination of potassium and sodium. Evaporate the contents of the platinum dish to dryness, treat with a little sulphuric acid, and finally ignite and weigh. This gives the weight of the lithium sulphate, from which subtract 0.0017 gram to correct for the solubility of sodium and potassium chlorides in the amyl alcohol. Test the residue with the spectroscope for lithium. If lithium is found with the spectroscope, but is not present in sufficient quantity to weigh, it is reported as a trace. In the analyses reported in this bulletin, lithium is omitted, since, in no case, was it present in sufficient amount to justify quantitative estimation.

Use the contents of the beaker and filter from which the amyl alcohol has been driven for the determination of potassium and sodium. Dissolve the contents of the beaker in hot water, filter and thoroughly wash. Transfer the combined filtrate and washings to a porcelain dish. Add a small amount of chlor-platinic acid solution and evaporate nearly to dryness. Treat the residue with 80 per cent alcohol.

If the alcoholic solution is colored yellow, a sufficient excess of chlor-platinic acid is indicated; otherwise more must be added until the yellow color persists. Filter through a tared Gooch crucible, wash thoroughly with 80 per cent alcohol and with a solution of ammonium chloride which contains 100 grams ammonium chloride per 500 c. c. (a 20 per cent solution) and which has been saturated with potassium chlor-platinate. Wash finally with alcohol and dry to constant weight at 100° to 102° C. Calculate to potassium chloride. An addition of 0.0008 gram of potassium chloride is necessary to correct for its solubility in amyl alcohol.

The weight of the sodium chloride is found by subtracting the combined weights of the lithium chloride and the potassium chloride (corrected) from the total weight of the three chlorides. If the amyl alcohol in the determination of lithium is not evaporated to exactly 15 c. c., the correction will differ from those mentioned.

If the initial qualitative examination for the presence of lithium shows its absence, the operations for its determination are omitted. In that case proceed directly with the addition of the chlor-platinic acid.



*Iodine and bromine, qualitative method.*—The qualitative tests for the presence of iodine and bromine are very much the same as those given by Fresenius. Evaporate an aliquot portion of the alkaline filtrate to dryness on the steam bath. Add 2 or 3 c. c. of water to dissolve the residue and enough absolute alcohol to make the percentage of alcohol about 90. Boil and filter and repeat the treatment of the residue with 90 per cent alcohol once or twice. Add 2 or 3 drops of sodium hydrate solution to the filtrate and evaporate to dryness. Repeat the process of extracting with 90 per cent alcohol on the new residue, and filter the extract from the undissolved portion. Add a drop of sodium hydroxid to the filtrate and evaporate to dryness. Treat the residue with a little distilled water, add dilute sulphuric acid to acid reaction, transfer the liquid to a test tube, add a little carbon bisulphide and 3 or 4 drops of 2 per cent potassium nitrate solution, and vigorously shake the test tube. The presence of iodine is shown by a pink color in the carbon bisulphide. Add chlorine water until the pink color due to the iodine has disappeared, and then add a little more chlorine water. The presence of bromine is shown by an orange color in the carbon bisulphide.

*Iodine and bromine, colorimetric method.*—Evaporate an aliquot portion of the alkaline filtrate to dryness and extract with 90 per cent alcohol as in the qualitative examination just described. Dissolve the residue in a little water, acidify with a little sulphuric acid (1 to 5), using 3 or 4 drops in excess, and transfer to a small flask. Add 4 drops of 2 per cent potassium nitrate solution and about 5 c. c. of carbon bisulphide freshly purified by distillation. Shake until all iodine is extracted. Filter off the acid solution from the carbon bisulphide. Wash the flask, filter, and contents with cold distilled water and transfer the carbon bisulphide (containing the iodine in solution) to a 12 c. c. Nessler tube by means of an additional 5 c. c. of pure carbon bisulphide. Make the contents of the tube up to the mark and match the color with that of other 12 c. c. tubes containing known amounts of iodine dissolved in carbon bisulphide. Prepare the standard tubes by taking measured quantities of a solution of known potassium-iodide content, acidifying with sulphuric acid (1 to 5), add 3 or 4 drops of potassium nitrate, and extract with carbon bisulphide just as in the actual determination.

Use the filtrate from the carbon bisulphide for determining bromine. Add to the filtrates from the iodine standards, different measured quantities of potassium-bromide solution of known strength, the standards being run with the actual determination and conducted in exactly the same way. Transfer the filtrates, both from the actual determination and from the standards to small flasks and add freshly

prepared chlorine water. Usually 2 to 8 c. c. of a saturated solution of chlorine is sufficient. Care must be taken not to add too much chlorine in excess of that necessary to set the bromine free, since a bromo-chloride may be formed with an excess of the reagent, thus spoiling the color reaction.

The best results are obtained by adding approximately the same excess of chlorine to the standards as to the actual determination. This may be accomplished by adding the chlorine water 1 c. c. at a time and shaking between additions. After a little practice one can determine approximately when the chlorine ceases to set bromine free. After all bromine has been thus set free add 5 c. c. of freshly purified carbon bisulphide to each of the flasks and shake thoroughly. Filter off the water solution from the carbon bisulphide through a moistened filter, wash the contents of the filter two or three times with water, and then transfer to a 12 c. c. Nessler tube by means of about 1 c. c. of carbon bisulphide. Repeat this extraction of the filtrate twice, using 3 c.c. of carbon bisulphide each time. The combined carbon bisulphide extracts usually amount to from 11.5 to 12 c. c. If they do not quite reach the 12 c. c. mark, add enough carbon bisulphide to each tube to bring them to the required volume and compare the sample with the standards. In some cases when working with the method near its upper limits the bromine is not all extracted by the amounts of carbon bisulphide recommended. If so, make one or two extra extractions with carbon bisulphide, transfer the extracts to another 12 c. c. tube, and compare the color with some of the lower standards.

*Lithium.*—Lithium has not been reported in the following tables of analytical results. In practically every brine examined its occurrence was in such small amount that its determination by ordinary analytical methods was scarcely practicable. However, all mother liquors have been examined spectroscopically for lithium, rubidium, and caesium, and the amount of lithium in each case has been estimated. The results of the latter investigation will be presented subsequently.

#### CALCULATION OF RESULTS.

Calculations are made to parts per thousand (or per liter) in the respective ions. In calculating the conventional combinations, lithium and potassium are calculated to chloride; the sulphate ion is calculated to calcium, sodium and magnesium sulphate; the bromide ion is calculated to magnesium and sodium bromides; the residual metallic ions are calculated to the chlorides.

## ANALYTICAL RESULTS WITH ARTIFICIAL BRINES.

TABLE XI.—Composition of artificial brines of New York.

[Parts per 1,000.]

| Constituent.                          | Number of sample. |        |       |       |       |        |       |       |        |
|---------------------------------------|-------------------|--------|-------|-------|-------|--------|-------|-------|--------|
|                                       | 1                 | 2      | 3     | 4     | 5     | 6      | 7     | 8     | 9      |
| Ions:                                 |                   |        |       |       |       |        |       |       |        |
| K.....                                | 0.3               |        | 0.8   | 0.5   | 11.8  | 12.0   | 2.0   | 0.4   | 0.2    |
| Na.....                               | 114.0             | 110.6  | 93.8  | 108.0 | 104.4 | 108.4  | 112.8 | 113.0 | 85.3   |
| Ca.....                               | 3.2               | 2.7    | 9.3   | 2.7   | 4.8   | 3.4    | 4.2   | 3.8   | .4     |
| Mg.....                               | .3                | .3     | 1.0   | .5    | 1.6   | 1.4    | 1.6   | .2    | .2     |
| Cl.....                               | 180.4             | 181.1  | 163.5 | 160.7 | 179.1 | 181.9  | 182.2 | 179.5 | 129.4  |
| SO <sub>4</sub> .....                 | 2.3               | 2.4    | .9    | 3.1   | 1.6   | 2.4    | 3.4   | 2.6   | 3.8    |
| Br.....                               |                   |        |       |       | 1.1   | 1.1    | .8    | .7    | .6     |
| Conventional combinations:            |                   |        |       |       |       |        |       |       |        |
| KCl.....                              | .6                | Trace. | 1.5   | 1.0   | 22.5  | 22.9   | 3.8   | .8    | .4     |
| NaCl.....                             | 289.3             | 287.8  | 238.0 | 284.2 | 265.0 | 275.2  | 286.4 | 286.5 | 212.0  |
| CaCl <sub>2</sub> .....               | 6.1               | 4.7    | 24.6  | 3.9   | 11.3  | 6.6    | 7.8   | 7.5   | 1.1    |
| MgCl <sub>2</sub> .....               | 1.2               | 1.2    | 3.9   | 2.0   | .8    | Trace. | 2.4   | .8    | Trace. |
| Na <sub>2</sub> SO <sub>4</sub> ..... |                   |        |       |       |       |        |       |       | 5.6    |
| CaSO <sub>4</sub> .....               | 3.3               | 3.4    | 1.3   | 4.4   | 2.3   | 3.4    | 4.8   | 3.7   | Trace. |
| MgBr <sub>2</sub> .....               |                   |        |       |       | 2.5   | 2.5    | 1.8   |       |        |
| NaBr.....                             |                   |        |       |       |       |        |       | .9    | .8     |

1. Worcester Salt Co., Silver Springs, N. Y. 1911. A. R. Merz, analyst.
2. Rock Glen Salt Co., Rock Glen, N. Y. 1911. A. R. Merz, analyst.
3. Star and Crescent Salt Co., Saltvale, N. Y. 1911. A. R. Merz, analyst.
4. Genessee Salt Co., Piffard, N. Y. 1911. A. R. Merz, analyst.
5. Watkins Salt Co., Watkins, N. Y. Sample obtained through Geological Survey, 1910. R. F. Gardner, analyst.
6. International Salt Co., Watkins, N. Y. Sample obtained through Geological Survey. 1910. R. F. Gardner, analyst.
7. Genessee Salt Co., Genessee, N. Y. Sample obtained through Geological Survey. 1910. R. F. Gardner, analyst.
8. Remington Salt Co., Ithaca, N. Y. Sample obtained through Geological Survey. 1910. R. F. Gardner, analyst.
9. Onondaga Pipe Line Co., Liverpool, N. Y. 1910. R. F. Gardner, analyst.

TABLE XII.—Composition of artificial brines of Ohio.

[Parts per 1,000.]

| Constituent.                          | Number of sample. |        |        |        |        |        |
|---------------------------------------|-------------------|--------|--------|--------|--------|--------|
|                                       | 10                | 11     | 12     | 13     | 14     | 15     |
| Ions:                                 |                   |        |        |        |        |        |
| K.....                                | 0.4               | 0.2    | 0.8    | 0.4    | 1.0    | 3.0    |
| Na.....                               | 123.0             | 117.2  | 126.8  | 122.1  | 128.2  | 122.0  |
| Ca.....                               | 1.0               | .8     | .4     | .6     | Trace. | .2     |
| Mg.....                               | Trace.            | Trace. | .9     | Trace. | Trace. | Trace. |
| Cl.....                               | 189.4             | 176.8  | 195.8  | 184.6  | 189.5  | 189.4  |
| SO <sub>4</sub> .....                 | 2.8               | 6.8    | 4.6    | 6.4    | 9.8    | 1.8    |
| Br.....                               | Trace.            | None.  | Trace. | None.  | .7     | Trace. |
| Conventional combinations:            |                   |        |        |        |        |        |
| KCl.....                              | .8                | .4     | 1.5    | .8     | 1.9    | 5.7    |
| NaCl.....                             | 308.9             | 289.1  | 316.4  | 302.1  | 311.3  | 307.4  |
| CaCl <sub>2</sub> .....               | 2.8               | 2.2    | 1.1    | 1.7    | Trace. | .6     |
| MgCl <sub>2</sub> .....               | Trace.            | Trace. | 3.5    | Trace. | Trace. | Trace. |
| Na <sub>2</sub> SO <sub>4</sub> ..... | 4.1               | 10.1   | 6.8    | 9.5    | 14.5   | 2.7    |
| CaSO <sub>4</sub> .....               | Trace.            | Trace. | Trace. | Trace. | Trace. | Trace. |
| MgBr <sub>2</sub> .....               | Trace.            | None.  | Trace. | None.  | Trace. | Trace. |
| NaBr.....                             |                   |        |        |        | 1.5    |        |

10. Colonial Salt Co., Akron, Ohio. Artificial brine from well No. 6. 1911. R. F. Gardner, analyst.
11. Columbia Chemical Co., Barberton, Ohio. Artificial ("hydraulic") brine. 1911. R. F. Gardner, analyst.
12. Columbia Chemical Co., Barberton, Ohio. Artificial ("cavity") brine. 1911. R. F. Gardner, analyst.
13. Cleveland Salt Co., Cleveland, Ohio. Composite artificial brine from 2 wells. 1911. R. F. Gardner, analyst.
14. Union Salt Co., Cleveland, Ohio. Artificial brine from 1 well. 1911. R. F. Gardner, analyst.
15. Ohio Salt Co., Wadsworth, Ohio. Composite artificial brine from 2 wells. 1911. R. F. Gardner, analyst.

TABLE XIII.—Composition of artificial brines of Michigan.

[Parts per 1,000.]

| Constituent.                      | Number of sample. |        |       |       |       |       |        |        |        |
|-----------------------------------|-------------------|--------|-------|-------|-------|-------|--------|--------|--------|
|                                   | 16                | 17     | 18    | 19    | 20    | 21    | 22     | 51     | 61a    |
| <b>Ions:</b>                      |                   |        |       |       |       |       |        |        |        |
| K.....                            | Trace.            | Trace. | 0.1   | 0.1   | 0.2   | 0.1   | 0.2    | Trace. | 0.1    |
| Na.....                           | 114.5             | 119.2  | 113.7 | 113.4 | 112.3 | 114.4 | 113.4  | 109.9  | 120.8  |
| Ca.....                           | .6                | 1.4    | 1.8   | 2.1   | 1.9   | 1.8   | 1.2    | 1.2    | 2.0    |
| Mg.....                           | 1.0               | .4     | .4    | .4    | .7    | .8    | .6     | 1.4    | .4     |
| Cl.....                           | 179.0             | 185.0  | 176.9 | 176.9 | 175.9 | 178.6 | 178.0  | 173.6  | 188.2  |
| SO <sub>4</sub> .....             | 2.2               | 2.8    | 3.3   | 3.7   | 3.2   | 4.0   | .8     | 2.2    | 3.7    |
| Br.....                           | Trace.            | Trace. |       |       |       |       | Trace. | Trace. | Trace. |
| <b>Conventional combinations:</b> |                   |        |       |       |       |       |        |        |        |
| KCl.....                          | Trace.            | Trace. | .2    | .3    | .3    | .2    | .4     | Trace. | .2     |
| NaCl.....                         | 290.6             | 302.6  | 288.6 | 287.8 | 285.0 | 290.4 | 288.1  | 278.9  | 307.3  |
| CaCl <sub>2</sub> .....           | Trace.            | .6     | 1.1   | 1.7   | 1.7   | .3    | 2.2    | .8     | 1.1    |
| MgCl <sub>2</sub> .....           | 3.6               | 1.6    | 1.6   | 1.6   | 2.7   | 3.1   | 2.4    | 5.5    | 1.6    |
| CaSO <sub>4</sub> .....           | 3.1               | 4.0    | 4.7   | 5.2   | 4.5   | 5.7   | 1.1    | None.  |        |
| MgBr <sub>2</sub> .....           | None.             | Trace. |       |       |       |       | Trace. | 3.1    | 5.2    |

16. Delray Salt Co., Delray, near Detroit, Mich. Artificial brines direct from well. 1911. R. F. Gardner, analyst.

17. Michigan Alkali Co., Detroit, Mich. Artificial brine from well. 1911. R. F. Gardner, analyst.

18. Louis Sands Salt & Lumber Co., Manistee, Mich. Artificial brine from wells. A. R. Merz, analyst.

19. R. G. Peters Salt & Lumber Co., East Lake, near Manistee, Mich. Composite artificial brine from 6 wells; contains hydrogen sulphide. 1911. A. R. Merz, analyst.

20. Filer & Son, Filer City, near Manistee, Mich. Artificial brine from wells. 1911. A. R. Merz, analyst.

21. State Lumber Co., plant No. 2, Manistee, Mich. Composite artificial brine from 2 wells. 1911. A. R. Merz and R. F. Gardner, analysts.

22. Stearns Salt & Lumber Co., Ludington, Mich. Composite artificial brine from 4 wells. 1911. R. F. Gardner, analyst.

51. Louis Sands Salt & Lumber Co., Manistee, Mich. Brine from well, 2,013 feet deep; 113,750 gallons per day. 1910. R. F. Gardner, analyst.

61a. Anchor Salt Co., Ludington, Mich. Brine from settlers. 1910. J. A. Cullen, analyst.

TABLE XIV.—Composition of artificial brines of Michigan and Canada.

[Parts per 1,000.]

| Constituent.                          | Number of sample. |       |        |        |       |       |       |        |
|---------------------------------------|-------------------|-------|--------|--------|-------|-------|-------|--------|
|                                       | 23                | 24    | 25     | 26     | 27    | 28    | 50    | 28a    |
| <b>Ions:</b>                          |                   |       |        |        |       |       |       |        |
| K.....                                | Trace.            | 1.4   | 2.4    | Trace. | 1.4   | 3.8   | .8    | .5     |
| Na.....                               | 120.6             | 78.2  | 123.3  | 121.3  | 110.1 | 119.6 | 120.2 | 119.2  |
| Ca.....                               | .8                | 17.8  | .8     | .6     | 6.4   | 1.4   | 2.0   | 2.3    |
| Mg.....                               | Trace.            | 12.8  | Trace. | Trace. | 3.0   | .9    | .3    | 1.3    |
| Cl.....                               | 183.8             | 182.1 | 189.3  | 185.2  | 190.2 | 191.4 | 188.0 | 191.4  |
| SO <sub>4</sub> .....                 | 4.4               | 4.2   | 4.0    | 3.4    | 3.6   | 2.8   | 3.9   | 3.0    |
| Br.....                               | Trace.            | 1.7   | 0.9    | None.  | None. | 1.0   | None. | Trace. |
| <b>Conventional combinations:</b>     |                   |       |        |        |       |       |       |        |
| KCl.....                              | Trace.            | 2.7   | 4.6    | Trace. | 2.7   | 7.2   | 1.6   | 1.0    |
| NaCl.....                             | 300.9             | 198.5 | 306.4  | 303.8  | 279.4 | 303.5 | 305.8 | 303.2  |
| CaCl <sub>2</sub> .....               | 2.2               | 40.1  | 2.2    | 1.7    | 16.9  | .5    | 1.1   | 3.1    |
| MgCl <sub>2</sub> .....               | Trace.            | 45.5  | Trace. | Trace. | 11.8  | 3.9   | 1.2   | 5.2    |
| Na <sub>2</sub> SO <sub>4</sub> ..... | 6.5               |       | 5.9    | 5.0    |       |       |       |        |
| CaSO <sub>4</sub> .....               | Trace.            | 7.5   | Trace. | Trace. | .9    | 4.0   | 4.5   | 4.2    |
| MgSO <sub>4</sub> .....               |                   |       |        |        |       |       | None. | Trace. |
| MgBr <sub>2</sub> .....               | Trace.            | 3.9   |        | None.  | None. | 1.8   |       |        |
| NaBr.....                             |                   |       | 1.6    |        |       |       |       |        |

23. Diamond Crystal Salt Co., St. Clair, Mich. Brine from a single well. 1911. R. F. Gardner, analyst.

24. Davidson, Wouney Co., Marine City, Mich. Brine from 2 wells. 1911. R. F. Gardner, analyst.

25. Michigan Salt Works, Marine City, Mich. Brine from company's 1 well. 1911. R. F. Gardner, analyst.

26. Worcester Salt Co., Ecorse, near Detroit, Mich. Composite brine from 2 wells. R. F. Gardner, analyst.

27. Western Canada Flour Mills Co., Goderich, Canada. Artificial brine from company's well No. 1. 1911. R. F. Gardner, analyst.

28. Mulkey Salt Co., Detroit, Mich. Composite brine from 3 wells. 1911. R. F. Gardner, analyst.

50. Louis Sands Salt & Lumber Co., Manistee, Mich. Brine from wells. 1910. J. A. Cullen, analyst.

28a. Filer & Son, Filer City, Mich. Brine from hot settlers. 1910. J. A. Cullen, analyst.

TABLE XV.—Composition of artificial brines of Kansas.

[Parts per 1,000.]

| Constituent.                          | Number of sample. |        |        |       |        |        |
|---------------------------------------|-------------------|--------|--------|-------|--------|--------|
|                                       | 141               | 138    | 142    | 149   | 136    | 147    |
| Tons:                                 |                   |        |        |       |        |        |
| K.....                                | 0.1               | 0.4    | 0.8    | 0.2   | 0.5    | Trace. |
| Na.....                               | 120.9             | 132.0  | 144.8  | 116.6 | 116.7  | 100.3  |
| Ca.....                               | 2.0               | Trace. | 2.2    | 1.2   | 2.0    | 3.2    |
| Mg.....                               | .2                | .4     | .8     | .8    | .7     | .8     |
| Cl.....                               | 188.0             | 199.0  | 184.8  | 181.7 | 183.2  | 162.2  |
| SO <sub>4</sub> .....                 | 3.9               | 7.4    | 37.8   | 4.2   | 4.1    | Trace. |
| Br.....                               | None.             | Trace. | Trace. | None. | Trace. | Trace. |
| Conventional combinations:            |                   |        |        |       |        |        |
| KCl.....                              | .2                | 0.8    | 1.5    | 0.4   | 1.0    | Trace. |
| NaCl.....                             | 307.4             | 325.8  | 293.6  | 295.1 | 296.8  | 254.6  |
| CaCl <sub>2</sub> .....               | 1.2               | Trace. | 6.1    | None. | .8     | 8.8    |
| MgCl <sub>2</sub> .....               | .8                | 1.6    | 3.1    | 3.2   | 2.8    | 3.1    |
| Na <sub>2</sub> SO <sub>4</sub> ..... |                   | 11.0   | 55.9   | 1.9   |        | None.  |
| CaSO <sub>4</sub> .....               | 5.5               | Trace. | Trace. | 4.1   | 5.8    | Trace. |
| MgBr <sub>2</sub> .....               | None.             | Trace. | Trace. | None. | Trace. | Trace. |

141. Western Salt Works, Hutchinson, Kans. Composite brine from 3 wells. 1910. J. A. Cullen, analyst.  
 138. Barton Salt Co., Hutchinson, Kans. Composite brine from 3 wells. 1910. R. F. Gardner, analyst.  
 142. Carey Salt Co., Hutchinson, Kans. Composite brine from 4 wells. 1911. R. F. Gardner, analyst.  
 149. Sterling Salt Co., Sterling, Kans. Brine from 1 well. 1911. J. A. Cullen, analyst.  
 136. Hutchinson Salt Co., Hutchinson, Kans. Composite brine from 8 or 9 wells. 1911. J. A. Cullen, analyst.  
 147. Ellsworth Salt Co., Ellsworth, Kans. Brine from well 800 feet deep; 14,000 gallons per day. 1910. R. F. Gardner, analyst.

## ANALYTICAL RESULTS WITH NATURAL BRINES.

TABLE XVI.—Composition of the natural brines of Michigan.

[Parts per 1,000.]

| Constituent.                          | Number of sample. |       |        |       |       |        |   |        |        |       |
|---------------------------------------|-------------------|-------|--------|-------|-------|--------|---|--------|--------|-------|
|                                       | 29                | 30    | 31     | 32    | 33    | 34     | 35  | 36     | 37     | 38    |
| Ions:                                 |                   |       |        |       |       |        |   |        |        |       |
| K.....                                | Trace.            | 0.4   | 1.4    | 0.8   | 1.0   | Trace. | 1.2                                       | Trace. | Trace. | 0.8   |
| Na.....                               | 77.8              | 100.0 | 129.7  | 78.2  | 86.6  | 69.3   | 52.5                                      | 85.5   | 111.5  | 132.6 |
| Ca.....                               | 10.8              | 7.6   | 12.8   | 10.8  | 16.0  | 36.6   | 50.2                                      | 15.8   | 4.2    | 2.8   |
| Mg.....                               | 3.8               | 1.0   | 3.6    | 3.2   | 4.4   | 8.6    | 11.6                                      | 4.0    | 13.2   | .4    |
| Cl.....                               | 145.4             | 155.1 | 155.4  | 145.9 | 172.8 | 196.4  | 205.4                                     | 163.0  | 205.4  | 205.4 |
| SO <sub>4</sub> .....                 | 4.2               | 2.4   | 26.0   | 2.2   | 1.2   | 1.2    | .6  | .6     | 1.8    | 3.6   |
| Br.....                               | .4                | 1.7   | 2.0    | .5    | .4    | 2.2    | Trace.                                    | 2.0    | 2.8    | 1.1   |
| Conventional combinations:            |                   |       |        |       |       |        |   |        |        |       |
| KCl.....                              | Trace.            | .8    | 2.7    | 1.6   | 1.9   | Trace. | 2.3                                       | Trace. | Trace. | 1.5   |
| NaCl.....                             | 197.3             | 239.6 | 242.8  | 198.4 | 219.7 | 175.8  | 133.3                                     | 217.0  | 283.2  | 334.0 |
| CaCl <sub>2</sub> .....               | 24.9              | 18.3  | 35.4   | 27.4  | 42.9  | 99.8   | 138.0                                     | 42.9   | 9.4    | 3.6   |
| MgCl <sub>2</sub> .....               | 13.3              | 3.9   | 6.3    | 9.8   | 15.3  | 32.5   | 45.5                                      | 5.5    | 37.2   | 1.6   |
| Na <sub>2</sub> SO <sub>4</sub> ..... |                   |       | 39.7   |       |       |        |   |        |        |       |
| CaSO <sub>4</sub> .....               | 6.0               | 3.4   | Trace. | 3.1   | 1.7   | 1.7    | .9  | .9     | 2.6    | 5.1   |
| MgBr <sub>2</sub> .....               | .8                |       | 4.0    | 1.2   | .9    | 2.7    | 7.8                                       | 4.6    | 6.5    | 1.4   |
| NaBr.....                             |                   | 2.2   |        |       |       |        | {Fe <sub>2</sub> Cl <sub>6</sub> }<br>2.3 |        |        |       |

29. Bliss, Van Auken Co., Saginaw, Mich. Composite natural brine from 3 wells, 80° by salimeter. 1911. R. F. Gardner, analyst.  
 30. Edward Germain, Saginaw, Mich. Natural brine from well No. 1 (750 feet deep). 1910. R. F. Gardner, analyst.  
 31. Mershon, Eddy, Parker & Co., Saginaw, Mich. Composite natural brine from 2 wells. 1911. R. F. Gardner, analyst.  
 32. S. L. Eastman Flooring Co., Saginaw, Mich. Composite natural brine from 2 wells, 80° by salimeter. 1911. R. F. Gardner, analyst.  
 33. Saginaw Plate Glass Co., Saginaw, Mich. Composite brine from 10 wells. 1911. R. F. Gardner, analyst.  
 34. Dow Chemical Co., Midland, Mich. Composite brine from 12 wells. 1911. R. F. Gardner, analyst.  
 35. Dow Chemical Co., Mount Pleasant, Mich. Composite brine from 5 wells. 1911. R. F. Gardner, analyst.  
 36. Saginaw Salt Co., St. Charles, Mich. Brine from 1 well. 1911. R. F. Gardner, analyst.  
 37. Saginaw Salt Co., St. Charles, Mich. Plant No. 2. Composite natural brine from 2 wells. 1911. R. F. Gardner, analyst.  
 38. Port Huron Salt Co., Port Huron, Mich. Natural brine from a shallow well at plant. 1911. R. F. Gardner, analyst.

TABLE XVII.—Composition of the natural brines of Ohio and West Virginia.

[Parts per 1,000.]

| Constituent.                          | Number of sample. |        |       |       |        |        |        |        |        |        |
|---------------------------------------|-------------------|--------|-------|-------|--------|--------|--------|--------|--------|--------|
|                                       | 39                | 40     | 41    | 42    | 43     | 44     | 45     | 46     | 47     | 48     |
| Ions:                                 |                   |        |       |       |        |        |        |        |        |        |
| K.....                                | 3.2               | 3.2    | 5.8   | 3.9   | 0.2    | 0.2    | 1.0    | Trace. | Trace. | 0.2    |
| Na.....                               | 68.0              | 62.7   | 48.0  | 43.4  | 24.6   | 37.1   | 124.8  | 41.4   | 37.8   | 44.5   |
| Ca.....                               | 29.0              | 30.8   | 45.6  | 48.6  | 2.6    | 3.8    | 1.0    | 1.2    | 2.6    | 8.2    |
| Mg.....                               | 6.4               | 6.4    | 9.8   | 11.2  | 5.8    | 1.0    | 1.6    | .2     | 1.0    | Trace. |
| Cl.....                               | 170.2             | 164.8  | 187.0 | 188.4 | 57.2   | 66.0   | 183.0  | 65.8   | 65.6   | 83.2   |
| SO <sub>4</sub> .....                 | .6                | Trace. | None. | .2    | Trace. | Trace. | 8.0    | Trace. | Trace. | Trace. |
| Br.....                               | .2                | 2.0    | .4    | ..... | .6     | 1.6    | .....  | 1.8    | None.  | None.  |
| Conventional combinations:            |                   |        |       |       |        |        |        |        |        |        |
| KCl.....                              | 6.1               | 6.1    | 11.1  | 7.4   | .4     | .4     | 2.0    | Trace. | Trace. | .4     |
| NaCl.....                             | 172.6             | 159.1  | 121.8 | 109.7 | 62.4   | 92.8   | 289.6  | 104.1  | 95.9   | 113.0  |
| CaCl <sub>2</sub> .....               | 70.3              | 85.2   | 126.1 | 134.2 | 7.2    | 10.5   | 2.8    | 3.2    | 7.2    | 22.7   |
| MgCl <sub>2</sub> .....               | 23.9              | 14.9   | 36.8  | 43.9  | 19.6   | 3.9    | 6.3    | .8     | 3.9    | Trace. |
| Na <sub>2</sub> SO <sub>4</sub> ..... | .....             | .....  | ..... | ..... | .....  | .....  | 11.8   | .....  | .....  | .....  |
| CaSO <sub>4</sub> .....               | 2.0               | Trace. | None. | .3    | Trace. | Trace. | Trace. | Trace. | Trace. | Trace. |
| MgBr <sub>2</sub> .....               | .5                | 4.6    | .8    | ..... | 1.4    | .....  | .....  | .....  | .....  | .....  |
| NaBr.....                             | .....             | .....  | ..... | ..... | .....  | 2.1    | .....  | 2.3    | .....  | .....  |

39. Colonial Salt Co., Akron, Ohio. Natural brine occurring in strata above rock-salt horizon. 1911. R. F. Gardner, analyst.

40. Columbia Chemical Co., Barberton, Ohio. Natural brine occurring above artificial brine horizon. 1911. R. F. Gardner, analyst.

41. Diamond Alkali Co., Fairport Harbor, Ohio. Natural brine, occurring in strata 300 feet above rock-salt horizon. 1911. R. F. Gardner, analyst.

42. Diamond Alkali Co., Fairport Harbor, Ohio. Natural brine. 1911. A. R. Merz, analyst.

43. Dixie Salt Works, Mason, W. Va. Composite natural brine from 4 wells. 1911. R. F. Gardner, analyst.

44. Pomeroy Salt Association, Pomeroy, Ohio. Composite natural brines from 2 wells. 1911. R. F. Gardner, analyst.

45. Pomeroy Salt Association, Pomeroy, Ohio. Natural brine from spring. 1911. R. F. Gardner, analyst.

46. Hartford City Salt Co., Hartford, W. Va. Composite natural brine from 5 wells. 1911. R. F. Gardner, analyst.

47. Liverpool Salt Co., Hartford City, W. Va. Composite brine from 5 wells. 1911. R. F. Gardner, analyst.

48. Pine Oil Co., Sistersville, W. Va. Natural brine from 1 well, 1,250 feet deep. 1910. R. F. Gardner, analyst.

TABLE XVIII.—Composition of natural brines from oil and gas wells of Ohio.

[Parts per 1,000.]

| Constituent.                          | Number of sample. |        |        |       |        |       |       |
|---------------------------------------|-------------------|--------|--------|-------|--------|-------|-------|
|                                       | 166               | 167    | 164    | 165   | 169    | 53b   | 53f   |
| Ions:                                 |                   |        |        |       |        |       |       |
| K.....                                | Trace.            | 0.2    | 0.6    | 0.6   | 4.2    | 5.0   | 3.9   |
| Na.....                               | 52.4              | 32.8   | 34.6   | 39.5  | 62.0   | 139.5 | 58.1  |
| Ca.....                               | Trace.            | 7.0    | 5.8    | 9.4   | 35.4   | 16.6  | 40.6  |
| Mg.....                               | Trace.            | 1.2    | .2     | 1.2   | 7.8    | 4.2   | 1.8   |
| Cl.....                               | 80.2              | 65.6   | 64.2   | 80.2  | 182.2  | 258.8 | 168.6 |
| SO <sub>4</sub> .....                 | .8                | 1.2    | .4     | .2    | 3.2    | 1.8   | 1.1   |
| Br.....                               | Trace.            | Trace. | Trace. | .2    | Trace. | .2    | 2.5   |
| Conventional combinations:            |                   |        |        |       |        |       |       |
| KCl.....                              | Trace.            | 0.4    | 1.1    | 1.1   | 8.0    | 9.5   | 7.5   |
| NaCl.....                             | 132.2             | 83.2   | 87.8   | 100.2 | 157.4  | 354.2 | 147.8 |
| CaCl <sub>2</sub> .....               | Trace.            | 18.0   | 15.5   | 25.7  | 94.3   | 43.7  | 111.3 |
| MgCl <sub>2</sub> .....               | Trace.            | 4.7    | .8     | 3.5   | 30.6   | 15.3  | 5.5   |
| Na <sub>2</sub> SO <sub>4</sub> ..... | 1.2               | None.  | None.  | None. | None.  | None. | ..... |
| CaSO <sub>4</sub> .....               | Trace.            | 1.7    | .6     | .3    | 4.5    | 2.6   | 1.6   |
| MgBr <sub>2</sub> .....               | Trace.            | Trace. | Trace. | .5    | Trace. | .4    | 2.9   |

166. Geo. T. Berlin, Bethel, Ohio. Brine from 1,167 feet; 3 barrels per day. 1910. R. F. Gardner, analyst.

167. Geo. T. Berlin, Bethel, Ohio. Brine from 1,228 feet; 5 barrels per day. 1910. R. F. Gardner, analyst.

164. G. A. Gifford, Center, Ohio. Brine from 1,600 feet; 15 barrels per day. 1910. R. F. Gardner, analyst.

165. G. A. Gifford, Green, Ohio. Brine from 1,560 feet; 18 barrels per day. 1910. R. F. Gardner, analyst.

169. Northeastern Oil and Gas Co., Austinburg, Ohio. Brine from 2,000 feet; about 5 barrels per day.

R. F. Gardner, analyst.

53b. Southern Oil Co., Junction City, Ohio. Brine from 2,700 feet; 48 barrels per day. 1910. R. F. Gardner, analyst.

53f. Southern Oil Co., Vinton County, Ohio. From well 2,100 feet deep; 150 barrels per day. 1910. J. A. Cullen, analyst.

TABLE XIX.—Composition of natural brines of West Virginia.

[Parts per 1,000.]

| Constituent.                          | Number of sample. |        |        |       |        |        |        |        |     |
|---------------------------------------|-------------------|--------|--------|-------|--------|--------|--------|--------|-----|
|                                       | 204               | 60b    | 60m    | 60c   | 60k    | 60f    | 5      | 48     |     |
| <b>Ions:</b>                          |                   |        |        |       |        |        |        |        |     |
| K.....                                | 3.0               | 0.2    | 0.9    | 0.4   | 2.7    | 1.2    | 0.2    | 0.1    |     |
| Na.....                               | 34.7              | 55.9   | 13.9   | 53.8  | 28.0   | 45.5   | 23.6   | 19.3   |     |
| Ca.....                               | 9.5               | 19.0   | 3.9    | 18.4  | 6.8    | 19.6   | 3.9    | 4.4    |     |
| Mg.....                               | 1.5               | 2.6    | 1.0    | 2.9   | .9     | 1.7    | 1.1    | 1.4    |     |
| Cl.....                               | 74.9              | 125.3  | 31.6   | 123.8 | 54.5   | 110.4  | 46.5   | 39.5   |     |
| SO <sub>4</sub> .....                 | Trace.            | .2     | .2     | .2    | .5     | .3     | Trace. | .4     |     |
| Br.....                               | .6                | 1.2    | .5     | 1.2   | .8     | 1.0    | .4     | .7     |     |
| <b>Conventional combinations:</b>     |                   |        |        |       |        |        |        |        |     |
| KCl.....                              | .6                | .4     | 1.8    | .8    | 5.2    | 2.3    | .4     | .2     |     |
| NaCl.....                             | 88.3              | 142.1  | 35.3   | 136.9 | 66.9   | 115.7  | 60.0   | 49.0   |     |
| CaCl <sub>2</sub> .....               | 26.3              | 49.7   | 10.5   | 50.6  | 18.3   | 53.8   | 10.8   | 11.6   |     |
| MgCl <sub>2</sub> .....               | 5.6               | 9.5    | 3.5    | 10.7  | 3.1    | 6.3    | 4.0    | 3.1    |     |
| Na <sub>2</sub> SO <sub>4</sub> ..... |                   |        |        |       |        |        |        |        |     |
| CaSO <sub>4</sub> .....               | Trace.            | .3     | .3     | .3    | .7     | .5     | Trace. | .6     |     |
| MgBr <sub>2</sub> .....               | .7                | 1.4    | .6     | 1.4   | 1.0    | 1.1    | .5     | 1.3    |     |
|                                       |                   | 60g    | 60h    | 205   | 60d    | 60l    | 60n    | 60a    | 60e |
| <b>Ions:</b>                          |                   |        |        |       |        |        |        |        |     |
| K.....                                | 0.7               | 0.4    | Trace. | 0.2   | 0.4    | 0.4    | 4.4    | Trace. |     |
| Na.....                               | 55.1              | 28.5   | 51.3   | 58.6  | 43.2   | 38.2   | 59.0   | 41.5   |     |
| Ca.....                               | 19.8              | 9.0    | 14.4   | 7.0   | 2.0    | 7.2    | 4.2    | 18.0   |     |
| Mg.....                               | 1.5               | 2.1    | 3.4    | 1.2   | 1.0    | 2.2    | 3.0    | 2.6    |     |
| Cl.....                               | 124.5             | 64.4   | 108.3  | 103.5 | 72.0   | 76.4   | 109.0  | 120.1  |     |
| SO <sub>4</sub> .....                 | .4                | Trace. | 6.6    | 3.4   | 1.6    | 2.4    | 2.0    | 2.2    |     |
| Br.....                               | 1.2               | .8     | 1.3    | 1.1   | Trace. | Trace. | .2     | .3     |     |
| <b>Conventional combinations:</b>     |                   |        |        |       |        |        |        |        |     |
| KCl.....                              | 1.4               | .8     | Trace. | .4    | .8     | .8     | 8.4    | Trace. |     |
| NaCl.....                             | 140.2             | 72.5   | 130.3  | 148.8 | 109.6  | 97.0   | 149.8  | 105.3  |     |
| CaCl <sub>2</sub> .....               | 54.4              | 23.0   | 32.1   | 15.5  | 3.6    | 16.9   | 9.4    | 67.0   |     |
| MgCl <sub>2</sub> .....               | 5.2               | 8.0    | 11.8   | 4.3   | 3.9    | 8.6    | 11.0   | 8.6    |     |
| Na <sub>2</sub> SO <sub>4</sub> ..... |                   |        | None.  | None. | None.  | None.  | None.  | None.  |     |
| CaSO <sub>4</sub> .....               | .6                | Trace. | 9.4    | 4.8   | 2.3    | 3.5    | 2.8    | 3.1    |     |
| MgBr <sub>2</sub> .....               | 1.4               | .9     | None.  | .2    | Trace. | Trace. | .4     | .7     |     |

204. South Penn. Oil Co., Jefferson district, Pleasant County, W. Va. Brine from salt sand. 1910. J. A. Cullen, analyst.
- 60h. South Penn. Oil Co., Marion County, W. Va. Well 2,092 feet. "Big Injun" sand. 1910. J. A. Cullen, analyst.
- 60m. South Penn. Oil Co., Wood County, W. Va. Brine from "Cow Run" sand. 1910. J. A. Cullen, analyst.
- 60c. South Penn. Oil Co., Tyler County, W. Va. 1,843 feet; 20 barrels brine; 10 barrels oil per day. "Big Injun" sand. 1910. J. A. Cullen, analyst.
- 60k. South Penn. Oil Co., Ritchie County, W. Va. Brine from salt sand. 1910. J. A. Cullen, analyst.
- 60f. South Penn. Oil Co., Harrison County, W. Va. Well 2,094 feet. Brine from a 50-foot stratum of sand. 1910. J. A. Cullen, analyst.
5. Slagel Salt Co., Mason County, W. Va. Well 1,100 feet. 1910. J. A. Cullen, analyst.
48. J. O. Dickinson & Co., Malden, W. Va. Natural brine from one well, 1,000 feet deep. 1910. R. F. Gardner, analyst.
- 60g. South Penn. Oil Co., Harrison County, W. Va. Well 2,122 feet; from fourth saliferous sand. 1901. J. A. Cullen, analyst.
- 60i. South Penn. Oil Co., Wetzel County, W. Va. Brine from 2,770 feet depth. 1910. J. A. Cullen, analyst.
205. South Penn. Oil Co., Grand district, W. Va. 1910. R. F. Gardner, analyst.
- 60d. South Penn. Oil Co., Freeman's Creek district, Lewis County, W. Va. Brine from T. M. Bode's farm, well No. 2, from a depth of 2,247 feet. 1910. R. F. Gardner, analyst.
- 60l. South Penn. Oil Co., Wood County, Union district, W. Va. Brine from "Big Injun" sand. 1910. R. F. Gardner, analyst.
- 60n. South Penn. Oil Co., Union district, Wood County, W. Va., Brine from Berea sand. 1910. R. F. Gardner, analyst.
- 60a. South Penn. Oil Co., Mannington district, Marion County, W. Va. Brine from 1,858 feet. "Big Injun" sand. J. A. Phillips, oil well No. (3). R. F. Gardner, analyst.
- 60e. South Penn. Oil Co., Ellsworth district, Tyler County, W. Va. Isaiah Baker, oil well No. 4; 1,385 feet below Pittsburgh coal. Penetrates "Big Injun" sand at 1,782 feet. Produces 110 barrels brine and 4 barrels oil per day. 1910. R. F. Gardner, analyst.

TABLE XX.—Composition of natural brines of Pennsylvania.

[Parts per 1,000.]

| Constituent.                          | Number of sample. |       |        |        |               |        |
|---------------------------------------|-------------------|-------|--------|--------|---------------|--------|
|                                       | 12a               | 53c   | 53d    | 168    | 51            | 133    |
| Ions:                                 |                   |       |        |        |               |        |
| K.....                                | Trace.            | 0.9   | 0.6    | Trace. | 0.2           | 0.7    |
| Na.....                               | 27.3              | 28.6  | 38.3   | 27.0   | 2.1           | 26.0   |
| Ca.....                               | 6.9               | 10.7  | 6.0    | 4.0    | Trace.        | 7.0    |
| Mg.....                               | 1.3               | 2.0   | .6     | .6     | Slight trace. | 1.1    |
| Cl.....                               | 57.9              | 68.3  | 70.0   | 50.4   | 3.4           | 56.2   |
| SO <sub>4</sub> .....                 | Trace.            | 1.4   | 2.4    | Trace. | Trace.        | Trace. |
| Br.....                               | .5                | 1.0   | Trace. | Trace. | None.         | .8     |
| Conventional combinations:            |                   |       |        |        |               |        |
| KCl.....                              | Trace.            | 1.8   | 1.1    | Trace. | .4            | 1.4    |
| NaCl.....                             | 69.4              | 72.8  | 97.2   | 68.5   | 5.3           | 66.1   |
| CaCl <sub>2</sub> .....               | 19.1              | 28.0  | 13.8   | 11.1   | Trace.        | 19.4   |
| MgCl <sub>2</sub> .....               | 4.8               | 7.1   | 2.4    | 2.4    | Slight trace. | 4.0    |
| Na <sub>2</sub> SO <sub>4</sub> ..... | .....             | ..... | None.  | None.  | .....         | .....  |
| CaSO <sub>4</sub> .....               | Trace.            | 2.0   | 3.4    | Trace. | Trace.        | Trace. |
| MgBr <sub>2</sub> .....               | .6                | 1.2   | Trace. | Trace. | None.         | .9     |

12a. John A. Beck Salt Co., Pittsburgh, Allegheny County, Pa. Well 1,160 feet, 57,600 gallons in 28 hours. 1910. J. A. Cullen, analyst.

53c. C. Herman, Clarion, Clarion County, Pa. Well 1,187 feet. 1910. J. A. Cullen, analyst.

53d. Southern Oil Co., Butler, Pa. Brine from 1,727 feet, 2 barrels per day. 1910. R. F. Gardner, analyst.

168. H. H. Hemphill, Renfrew, Pa. Brine from Penn Township, Butler County, Pa. From 1,591 feet, 8 barrels per day. 1910. R. F. Gardner, analyst.

51. N. V. V. Franchot (Olean, N. Y.), Indian Creek, McKean County, Pa. Natural brine from 1 well, 1,100 feet deep. 1910. R. F. Gardner, analyst.

133. John A. Beck Salt Co., Pittsburgh, Pa. Composite brine from 4 wells. 1911. J. A. Cullen, analyst.

TABLE XXI.—Composition of natural brines of Oklahoma.

[Parts per 1,000.]

| Constituent.                          | Number of sample. |        |        |       |       |       |       |        |
|---------------------------------------|-------------------|--------|--------|-------|-------|-------|-------|--------|
|                                       | 25r               | 40b    | 52a    | 25c   | 25p   | 25d   | 25v   | 52     |
| Ions:                                 |                   |        |        |       |       |       |       |        |
| K.....                                | 0.8               | 0.2    | 0.2    | 0.5   | 0.3   | 0.5   | 1.1   | 1.2    |
| Na.....                               | 46.2              | 94.9   | 58.9   | 32.1  | 41.6  | 66.0  | 47.2  | 112.8  |
| Ca.....                               | 6.1               | 2.6    | 2.1    | 4.5   | 7.1   | 9.7   | 9.0   | 3.0    |
| Mg.....                               | 2.2               | 1.5    | 1.1    | 2.2   | 2.4   | .7    | 1.3   | 2.2    |
| Cl.....                               | 89.4              | 153.5  | 95.2   | 63.9  | 82.5  | 120.7 | 93.2  | 18.5   |
| SO <sub>4</sub> .....                 | Trace.            | 4.0    | 3.9    | .1    | .7    | .7    | .4    | 3.8    |
| Br.....                               | Trace.            | Trace. | Trace. | .6    | .3    | .4    | .5    | Trace. |
| Conventional combinations:            |                   |        |        |       |       |       |       |        |
| KCl.....                              | 1.6               | .4     | .4     | 1.0   | .6    | 1.0   | 2.2   | 2.4    |
| NaCl.....                             | 117.5             | 241.3  | 149.8  | 81.7  | 105.8 | 167.9 | 120.1 | 287.0  |
| CaCl <sub>2</sub> .....               | 16.9              | 3.4    | 1.4    | 11.9  | 18.9  | 25.8  | 24.4  | 3.9    |
| MgCl <sub>2</sub> .....               | 8.7               | 6.0    | 4.3    | 8.3   | 9.3   | 2.4   | 4.8   | 8.8    |
| Na <sub>2</sub> SO <sub>4</sub> ..... | .....             | .....  | .....  | ..... | ..... | ..... | ..... | .....  |
| CaSO <sub>4</sub> .....               | Trace.            | 5.6    | 5.5    | .3    | 1.0   | 1.0   | .6    | 5.4    |
| MgBr <sub>2</sub> .....               | Trace.            | Trace. | Trace. | .7    | .4    | .5    | .6    | Trace. |

25r. Prairie Oil & Gas Co., Independence, Kans., Cleveland Township, Pawnee County, Okla. Well 1,750 feet; 50 barrels per day. 1910. J. A. Cullen, analyst.

40b. A. Henquenet, (Ferguson) township 78, Blaine County, Okla. From well 5 feet deep. 1910. J. A. Cullen, analyst.

52a. D. A. Thomas, Salton, Harmon County, Okla. Brine (2) from spring. 1910. J. A. Cullen, analyst.

25c. Prairie Oil & Gas Co., township 4, Washington County, Okla. Brine from oil well 925 feet deep; 240 barrels per day. 1910. J. A. Cullen, analyst.

25p. Prairie Oil & Gas Co., Tulsa County, Okla. Brine from oil well 1,557 feet deep; 6 barrels per day. 1910. J. A. Cullen, analyst.

25d. Prairie Oil & Gas Co., township 24, Osage County, Okla. Brine from oil well, 1,565 feet deep; 15 barrels per day. 1910. J. A. Cullen, analyst.

25v. Prairie Oil & Gas Co., Schulten Township, Okmulgee County, Okla. Brine from oil well, 2,007 feet deep; 40 barrels per day. 1910. J. A. Cullen, analyst.

52. D. A. Thomas, Salton, Harmon County, Okla. Brine (1) from spring. 1910. J. A. Cullen, analyst.



TABLE XXI.—Composition of natural brines of Oklahoma—Continued.

| Constituent.                          | Number of sample. |       |       |      |        |      |        |        |        |
|---------------------------------------|-------------------|-------|-------|------|--------|------|--------|--------|--------|
|                                       | 25x.              | 25f.  | 25m.  | 25b. | 25o.   | 25h. | 25s.   | 1a.    | 25n.   |
| Ions:                                 |                   |       |       |      |        |      |        |        |        |
| K.....                                | 1.0               | 0.7   | 0.9   | 0.6  | 1.0    | 0.2  | 0.9    | 1.0    | Trace. |
| Na.....                               | 14.0              | 46.7  | 45.0  | 34.4 | 43.3   | 38.2 | 51.4   | 122.9  | 37.3   |
| Ca.....                               | 1.3               | 7.9   | 8.0   | 4.8  | 6.9    | 3.6  | 13.8   | 2.3    | 13.2   |
| Mg.....                               | .6                | 1.7   | 1.7   | 2.4  | 1.7    | .8   | .6     | 1.3    | 1.0    |
| Cl.....                               | 25.4              | 92.8  | 89.3  | 68.8 | 84.7   | 67.1 | 105.9  | 195.9  | 82.8   |
| SO <sub>4</sub> .....                 | .9                | 1.0   | .8    | .5   | Trace. | .7   | Trace. | 4.4    | 1.0    |
| Br.....                               | Trace.            | .4    | .6    | .5   | .4     | .6   | .5     | Trace. | Trace. |
| Conventional combinations:            |                   |       |       |      |        |      |        |        |        |
| KCl.....                              | 2.0               | 1.4   | 1.8   | 1.2  | 2.0    | 0.4  | 1.8    | 2.0    | Trace. |
| NaCl.....                             | 35.6              | 118.8 | 114.5 | 87.5 | 110.1  | 97.2 | 130.7  | 312.6  | 94.6   |
| CaCl <sub>2</sub> .....               | 2.5               | 20.8  | 21.5  | 12.7 | 19.1   | 9.1  | 38.5   | 1.4    | 35.4   |
| MgCl <sub>2</sub> .....               | 2.1               | 6.3   | 6.3   | 9.1  | 6.3    | 2.8  | 2.1    | 5.1    | 3.9    |
| Na <sub>2</sub> SO <sub>4</sub> ..... |                   |       |       |      |        |      |        |        | None.  |
| CaSO <sub>4</sub> .....               | 1.3               | 1.4   | 1.1   | .7   | Trace. | 1.0  | Trace. | 6.2    | 1.4    |
| MgBr <sub>2</sub> .....               | Trace.            | .5    | .7    | .6   | .5     | .7   | .6     | Trace. | Trace. |

| Constituent.                          | Number of sample. |       |        |        |        |        |        |       |
|---------------------------------------|-------------------|-------|--------|--------|--------|--------|--------|-------|
|                                       | 25l.              | 25q.  | 46a.   | 25t.   | 25a.   | 25w.   | 3f.    | 50.   |
| Ions:                                 |                   |       |        |        |        |        |        |       |
| K.....                                | 1.0               | 0.2   | 0.6    | 0.6    | Trace. | 0.6    | Trace. | 0.4   |
| Na.....                               | 38.4              | 2.5   | 115.1  | 40.9   | 23.9   | 1.9    | 40.0   | 112.1 |
| Ca.....                               | 8.2               | 1.1   | 2.7    | 3.6    | 2.2    | 5.0    | 7.8    | 7.6   |
| Mg.....                               | 2.0               | .2    | 1.9    | 1.4    | .2     | 1.6    | 1.4    | 1.2   |
| Cl.....                               | 80.7              | 6.4   | 185.2  | 71.4   | 40.0   | 43.4   | 79.4   | 185.8 |
| SO <sub>4</sub> .....                 | Trace.            | .1    | 3.3    | 3.4    | 1.6    | 1.6    | Trace. | 3.8   |
| Br.....                               | .4                | None. | Trace. | Trace. | Trace. | Trace. | Trace. | .4    |
| Conventional combinations:            |                   |       |        |        |        |        |        |       |
| KCl.....                              | 2.0               | .4    | 1.2    | 1.1    | Trace. | 1.1    | Trace. | .8    |
| NaCl.....                             | 97.6              | 6.3   | 282.7  | 103.8  | 60.6   | 50.5   | 101.5  | 284.5 |
| CaCl <sub>2</sub> .....               | 22.7              | 2.8   | 3.6    | 6.1    | 4.2    | 11.9   | 21.6   | 16.6  |
| MgCl <sub>2</sub> .....               | 8.0               | .8    | 7.6    | 5.5    | .8     | 6.3    | 5.5    | 3.1   |
| Na <sub>2</sub> SO <sub>4</sub> ..... |                   |       |        | None.  | None.  | None.  | None.  | ..... |
| CaSO <sub>4</sub> .....               | Trace.            | .2    | 4.7    | 4.8    | 2.3    | 2.3    | Trace. | 5.4   |
| MgBr <sub>2</sub> .....               | .5                | None. | Trace. | Trace. | Trace. | Trace. | Trace. | .8    |

25x. Prairie Oil & Gas Co., township 25, Nowata County, Okla. Brine from oil well, 430 feet deep; 4 barrels per day. 1910. J. A. Cullen, analyst.

25f. Prairie Oil & Gas Co., Morris Township, Okmulgee County, Okla. Brine from oil well, 1,587 feet deep; 25 barrels per day. 1910. J. A. Cullen, analyst.

25m. Prairie Oil & Gas Co., Bryan Township, Okmulgee County, Okla. Brine from oil well, 1,674 feet deep; 80 barrels per day. 1910. J. A. Cullen, analyst.

25b. Prairie Oil & Gas Co., township 27, Washington County, Okla. Brine from oil well, 1,305 feet deep; 25 barrels per day. 1910. J. A. Cullen, analyst.

25o. Prairie Oil & Gas Co., Dawson Township, Tulsa County, Okla. Brine from oil well, 1,150 feet deep; 10 barrels per day. 1910. J. A. Cullen, analyst.

25h. Prairie Oil & Gas Co., Muskogee County, Okla. Brine from oil well, 1,569 feet deep; 50 barrels per day. 1910. J. A. Cullen, analyst.

25s. Prairie Oil & Gas Co., Hominy Township, Osage County, Okla. Brine from oil well, 2,375 feet deep; 500 barrels per day. 1910. J. A. Cullen, analyst.

1a. (P. L. Clifton, Pomeroy, Ohio.) Woodard County, Okla. Brine from spring. 1910. J. A. Cullen, analyst.

25n. Prairie Oil & Gas Co., township 21, Tulsa County, Okla. Brine from oil well, 1,148 feet deep; 7 barrels per day. 1910. R. F. Gardner, analyst.

25l. Prairie Oil & Gas Co., township 21, Tulsa County, Okla. Brine from oil well, 1,178 feet deep; 500 barrels per day. 1910. J. A. Cullen, analyst.

25q. Prairie Oil & Gas Co., Hamilton Township, Okmulgee County, Okla. Brine from oil well, 2,222 feet deep; 3 barrels per day. 1910. J. A. Cullen, analyst.

46a. W. H. Chancy, Salton, township 26, Harmon County, Okla. Brine from spring, 1910. J. A. Cullen, analyst.

25t. Prairie Oil & Gas Co., Township 27, Nowata County, Okla. Brine from oil well, 1,240 feet deep; 100 barrels per day. 1910. R. F. Gardner, analyst.

25a. Prairie Oil & Gas Co., Jefferson Township, Washington County, Okla. Brine from oil well, 1,224 feet deep; 30 barrels per day. 1910. R. F. Gardner, analyst.

25w. Prairie Oil & Gas Co., township 25, Nowata County, Okla. Brine from oil well, 1,674 feet deep; 800 barrels per day. 1910. R. F. Gardner, analyst.

3f. (Producers Oil Co., Houston, Tex.) Township 20, Tulsa County, Okla. Brine from oil well, 1,200 feet deep; 200 barrels per day. 1910. R. F. Gardner, analyst.

50. W. H. Chancy, Salton, Okla. Brine from springs. 1910. R. F. Gardner, analyst.

TABLE XXII.—Composition of natural brines of Texas.

[Parts per 1,000.]

| Constituent.                          | Number of sample. |       |        |       |        |        |        |
|---------------------------------------|-------------------|-------|--------|-------|--------|--------|--------|
|                                       | 39a               | 3h    | 3c     | 3b    | 156    | 49     | 59     |
| Ions:                                 |                   |       |        |       |        |        |        |
| K.....                                | 0.3               | 0.6   | 3.4    | 3.2   | Trace. | 0.2    | Trace. |
| Na.....                               | 118.2             | 47.6  | 62.7   | 20.0  | 4.0    | 114.4  | 10.8   |
| Ca.....                               | 2.1               | 13.4  | 5.2    | 3.4   | .2     | 1.8    | .8     |
| Mg.....                               | .7                | 2.0   | Trace. | 1.4   | .4     | 1.0    | .9     |
| Cl.....                               | 188.7             | 102.6 | 104.4  | 42.8  | 6.0    | 179.4  | 20.6   |
| SO <sub>4</sub> .....                 | Trace.            | 1.1   | 6.0    | 1.2   | 2.2    | 3.6    | Trace. |
| Br.....                               | Trace.            | .8    | Trace. | None. | Trace. | Trace. | Trace. |
| Conventional combinations:            |                   |       |        |       |        |        |        |
| KCl.....                              | .6                | 1.2   | 6.5    | 6.1   | Trace. | .4     | Trace. |
| NaCl.....                             | 300.7             | 121.1 | 159.2  | 50.7  | 7.3    | 290.3  | 27.4   |
| CaCl <sub>2</sub> .....               | 5.9               | 35.3  | 7.5    | 8.0   | .6     | .8     | 2.2    |
| MgCl <sub>2</sub> .....               | 2.8               | 7.5   | Trace. | 5.5   | 1.6    | 3.8    | 3.5    |
| Na <sub>2</sub> SO <sub>4</sub> ..... |                   |       | None.  | None. | 3.3    |        | None.  |
| CaSO <sub>4</sub> .....               | Trace.            | 1.6   | 8.5    | 1.7   | Trace. | 5.1    | Trace. |
| MgBr <sub>2</sub> .....               | Trace.            | .9    | Trace. | None. | None.  | Trace. | Trace. |

39a. Grand Saline Salt Co., Grand Saline, Tex. Natural brine from well, 418 feet deep, ready for the evaporators. 1910. J. A. Cullen, analyst.

3h. Producers Oil Co., Houston, Wichita County, Tex. Brine from oil well, 1,800 feet deep;  $\frac{1}{2}$  barrel per day. 1910. J. A. Cullen, analyst.

3c. Producers Oil Co., Herman Lease, Hardin County, Tex. Brine from oil well, 1,198 feet deep; 75 barrels per day. 1910. R. F. Gardner, analyst.

3b. Producers Oil Co., Sour Lake Township, Hardin County, Tex. Brine from oil well, 1,350 feet deep; 50 barrels per day. 1910. R. F. Gardner, analyst.

156. Edwards Bros., Midland, Crane County, Tex. Brine from 70 feet depth. 1910. R. F. Gardner, analyst.

49. Grand Saline Salt Co., Saline, Tex. Natural brine direct from well. 1910. R. F. Gardner, analyst.

59. Palestine Salt Co., Palestine, Anderson County, Tex. Brine from a depth of 300 feet. 1910. R. F. Gardner, analyst.

TABLE XXIII.—Composition of miscellaneous natural brines.

[Parts per 1,000.]

| Constituent.                          | Number of sample. |        |        |       |        |        |        |        |        |
|---------------------------------------|-------------------|--------|--------|-------|--------|--------|--------|--------|--------|
|                                       | 160               | 53     | 161    | 8     | 173    | 63     | 171    | 158    | 172    |
| Ions:                                 |                   |        |        |       |        |        |        |        |        |
| K.....                                | Trace.            | 0.1    | Trace. | 1.5   | 0.4    | 0.8    | Trace. | 0.6    | 0.6    |
| Na.....                               | 0.2               | 15.5   | 16.5   | 114.6 | 1.3    | 4.4    | 100.3  | 2.4    | 47.6   |
| Ca.....                               | .6                | 1.2    | .8     | 2.3   | .2     | .4     | Trace. | Trace. | Trace. |
| Mg.....                               | Trace.            | 1.8    | 1.6    | .3    | Trace. | Trace. | 1.2    | Trace. | Trace. |
| Cl.....                               | 1.4               | 28.2   | 31.2   | 180.6 | 2.0    | 6.4    | 154.4  | 2.0    | 72.4   |
| SO <sub>4</sub> .....                 | Trace.            | 4.2    | .2     | 3.7   | 3.2    | 2.2    | 4.6    | 2.2    | 1.6    |
| Br.....                               | Trace.            | None.  | Trace. | None. | Trace. | None.  | None.  | None.  | Trace. |
| Conventional combinations:            |                   |        |        |       |        |        |        |        |        |
| KCl.....                              | Trace.            | .2     | Trace. | 2.9   | .8     | 1.5    | Trace. | 1.1    | 1.1    |
| NaCl.....                             | .5                | 34.2   | 41.8   | 291.5 | 2.0    | 8.3    | 24.9   | 2.8    | 118.7  |
| CaCl <sub>2</sub> .....               | 1.7               | 3.3    | 1.9    | 2.2   | .6     | 1.1    | Trace. | Trace. | Trace. |
| MgCl <sub>2</sub> .....               | Trace.            | 7.1    | 6.3    | 1.2   | Trace. | Trace. | 4.7    | Trace. | Trace. |
| Na <sub>2</sub> SO <sub>4</sub> ..... | None.             | 6.2    | None.  |       | 4.7    | 3.3    | 6.8    | 3.3    | 2.4    |
| CaSO <sub>4</sub> .....               | Trace.            | Trace. | .3     | 5.2   | Trace. | Trace. | Trace. | Trace. | Trace. |
| MgBr <sub>2</sub> .....               | Trace.            | None.  | Trace. | None. | Trace. | None.  | None.  | None.  | Trace. |

160. J. W. Samuels, Georgetown, Ky. Brine from 80 feet. 1910. R. F. Gardner, analyst.

53. New Domain Oil & Gas Co. (Lexington, Ky.), Griffin, Wayne County, Ky. Natural brine from well, 300 feet deep; above oil sand. 1910. R. F. Gardner, analyst.

161. E. W. Shaw, Clinton County, Ill. Schaffly oil well No. 1. Brine from 1,052 feet; 75 barrels per day. 1910. R. F. Gardner, analyst.

8. Mathieson Alkali Works, Saltville Township, Smyth County, Va. Well about 1,000 feet. 1910. J. A. Cullen, analyst.

173. S. S. Hunter, New Mansfield, De Soto County, La. Brine from 830 feet; 4,000,000 cubic feet per day. Pressure 380 pounds. 1910. R. F. Gardner, analyst.

63. S. S. Hunter, Shreveport, La. Brine from oil well, Caddo oil fields. 1910. R. F. Gardner, analyst.

171. Union Ice & Salt Co., Hutchinson, Kans. Brine from 700 feet. 1910. R. F. Gardner, analyst.

158. M. J. Munn, Overton County, Tenn. Water which followed a flow of oil. "Has been flowing since 1866." 1910. R. F. Gardner, analyst.

172. Evangeline oil field, Evangeline, La. Brine from oil well. 1910. R. F. Gardner, analyst.

## ANALYTICAL RESULTS WITH BITTERNs FROM ARTIFICIAL BRINES.

TABLE XXIV.—Composition of bitterns from artificial brines of New York.

[Parts per 1,000.]

| Constituent.               | Number of sample. |       |       |       |       |       |       |
|----------------------------|-------------------|-------|-------|-------|-------|-------|-------|
|                            | 54                | 55    | 56    | 57    | 58    | 59    | 60    |
| Ions:                      |                   |       |       |       |       |       |       |
| K.....                     | 1.7               | 2.8   | 1.9   | 9.4   | 1.8   | 1.3   | 2.2   |
| Na.....                    | 110.1             | 100.3 | 106.7 | 73.7  | 93.7  | 114.2 | 108.9 |
| Ca.....                    | 11.4              | 19.9  | 13.5  | 20.2  | 25.2  | 6.4   | 7.6   |
| Mg.....                    | 1.0               | 1.8   | 1.5   | 1.6   | 2.6   | 1.9   | 1.9   |
| Cl.....                    | 193.1             | 197.2 | 193.5 | 135.0 | 197.5 | 192.8 | 187.5 |
| SO <sub>4</sub> .....      | .7                | .5    | .8    | 2.2   | .4    | 1.2   | 1.3   |
| Conventional combinations: |                   |       |       |       |       |       |       |
| KCl.....                   | 3.2               | 5.3   | 3.6   | 17.9  | 3.4   | 2.5   | 4.2   |
| NaCl.....                  | 279.2             | 255.1 | 270.8 | 144.7 | 238.0 | 289.7 | 276.3 |
| CaCl <sub>2</sub> .....    | 30.7              | 54.5  | 36.5  | 53.4  | 69.1  | 16.3  | 19.7  |
| MgCl <sub>2</sub> .....    | 3.9               | 7.1   | 5.9   | 6.3   | 10.2  | 7.5   | 7.4   |
| CaSO <sub>4</sub> .....    | 1.0               | .7    | 1.1   | 3.1   | .6    | 1.7   | 1.8   |
| MgBr <sub>2</sub> .....    |                   |       |       | 74.7  |       |       |       |

| Constituent.               | Number of sample. |        |       |       |       |       |        |
|----------------------------|-------------------|--------|-------|-------|-------|-------|--------|
|                            | 61                | 62     | 63    | 64    | 65    | 66    | 67     |
| Ions:                      |                   |        |       |       |       |       |        |
| K.....                     | Trace.            | Trace. | 1.0   | 0.2   | 0.6   | 0.2   | 0.6    |
| Na.....                    | 117.0             | 109.6  | 109.1 | 114.9 | 111.4 | 73.2  | 112.0  |
| Ca.....                    | 4.8               | 4.0    | 10.3  | 5.4   | 8.2   | 5.3   | .8     |
| Mg.....                    | 2.2               | .8     | 1.6   | .8    | .6    | .7    | .8     |
| Cl.....                    | 187.9             | 172.9  | 191.1 | 185.4 | 185.6 | 122.8 | 173.4  |
| SO <sub>4</sub> .....      | 3.6               | 4.6    | .6    | 2.4   | 2.0   | 1.1   | 1.2    |
| Br.....                    | 1.1               | .9     |       | .8    | 2.0   |       | .6     |
| Conventional combinations: |                   |        |       |       |       |       |        |
| KCl.....                   | Trace.            | Trace. | 1.9   | .4    | 1.1   | .4    | 1.1    |
| NaCl.....                  | 296.8             | 277.1  | 276.9 | 290.0 | 280.8 | 185.8 | 284.4  |
| CaCl <sub>2</sub> .....    | 9.1               | 4.2    | 27.7  | 12.2  | 20.5  | 13.3  | .8     |
| MgCl <sub>2</sub> .....    | 3.1               | 3.1    | 6.3   | 3.1   | 2.4   | 2.7   | Trace. |
| CaSO <sub>4</sub> .....    | 5.1               | 7.1    | .9    | 3.4   | 2.8   | 1.6   | 1.7    |
| NaBr.....                  |                   | 1.3    |       | 1.0   | 2.8   |       |        |
| MgBr <sub>2</sub> .....    | 2.5               |        |       |       |       |       | 1.4    |

54. Worcester Salt Co., Silver Springs, N. Y. Bittern from vacuum pans. 1911. A. R. Merz, analyst.
55. Worcester Salt Co., Silver Springs, N. Y. 1911. Bittern from grainer No. 6. A. R. Merz, analyst.
56. Rock Glen Salt Co., Rock Glen, N. Y. Bittern, 10 days' evaporation in open pans. 1911. A. R. Merz, analyst.
57. Rock Glen Salt Co., Rock Glen, N. Y. Bittern, 6 weeks' evaporation in grainer, taken at time of run-off. 1910. R. F. Gardner, analyst.
58. Star & Crescent Salt Co., Warsaw, N. Y. Bittern from open pans, taken at time of run-off. Represents an evaporation of 85,000 gallons of original brine to 350 gallons. 1911. A. R. Merz, analyst.
59. Genesee Salt Co., Piffard, N. Y. Bittern from open pans, 36 hours' evaporation. Represents an evaporation of 30,000 gallons to 15,000 gallons. 1911. A. R. Merz, analyst.
60. Genesee Salt Co., Piffard, N. Y. Bittern from grainer, 2 weeks' evaporation. 1911. A. R. Merz, analyst.
61. International Salt Co., Myers, N. Y. Bittern after 22 hours' evaporation. 1911. R. F. Gardner, analyst.
62. International Salt Co., Myers, N. Y. Bittern. 1911. R. F. Gardner, analyst.
63. Remington Salt Co., Ithaca, N. Y. Bittern from evaporators on way to drains. Represents an evaporation of 350 tons of original brine to 25 tons. 1911. A. R. Merz, analyst.
64. Remington Salt Co., Ithaca, N. Y. Bitterns from centrifuges at 9 a. m., first hour of centrifuging. 1911. R. F. Gardner, analyst.
65. Remington Salt Co., Ithaca, N. Y. Bittern from centrifuges at end of centrifuging (7 hours). 1911. R. F. Gardner, analyst.
66. Le Roy Salt Co., Le Roy, N. Y. Bittern from (continuous) run-off. 1911. A. R. Merz, analyst.
67. Solvay Process Co., Syracuse, N. Y. Original brine from 50-foot salt bed. 1910. R. F. Gardner, analyst.

TABLE XXV.—Composition of bitterns from artificial brines of Michigan, East Shore.

[Parts per 1,000.]

| Constituent.                          | Number of sample. |        |       |        |        |       |        |
|---------------------------------------|-------------------|--------|-------|--------|--------|-------|--------|
|                                       | 68                | 69     | 70    | 71     | 72     | 73    | 74     |
| Ions:                                 |                   |        |       |        |        |       |        |
| K.....                                | 0.1               | Trace. | 0.4   | Trace. | Trace. | 2.0   | 1.6    |
| Na.....                               | 120.3             | 121.1  | 115.9 | 117.1  | 121.4  | 104.6 | 118.4  |
| Ca.....                               | 2.0               | 1.9    | 2.2   | 3.4    | .6     | 13.8  | 1.2    |
| Mg.....                               | .2                | .2     | 1.4   | .6     | Trace. | 2.7   | Trace. |
| Cl.....                               | 186.8             | 187.5  | 184.8 | 188.0  | 185.5  | 194.6 | 179.6  |
| SO <sub>4</sub> .....                 | 3.8               | 3.4    | 3.6   | 2.0    | 1.8    | .6    | 4.6    |
| Br.....                               |                   |        | None. | .8     | 2.5    |       | 7.8    |
| Conventional combinations:            |                   |        |       |        |        |       |        |
| KCl.....                              | .2                | Trace. | .8    | Trace. | Trace. | 3.8   | 3.1    |
| NaCl.....                             | 305.3             | 306.9  | 295.0 | 296.5  | 304.2  | 265.9 | 289.9  |
| CaCl <sub>2</sub> .....               | 1.7               | 1.4    | 1.9   | 9.2    | 1.7    | 37.3  | 3.3    |
| MgCl <sub>2</sub> .....               | .8                | .8     | 5.5   | 2.4    | Trace. | 10.6  | Trace. |
| Na <sub>2</sub> SO <sub>4</sub> ..... |                   |        |       |        | 2.7    |       | 6.8    |
| CaSO <sub>4</sub> .....               | 5.4               | 4.8    | 5.1   | 2.8    | Trace. | .9    | Trace. |
| NaBr.....                             |                   |        | None. | 1.0    | 3.2    |       | 10.1   |
| MgBr <sub>2</sub> .....               |                   |        | None. |        |        |       |        |

68. Delray Salt Co., Delray (Detroit), Mich. Bittern; drippings from salt as conveyed from vacuum pans. Probably but slight concentration. 1911. A. R. Merz, analyst.

69. Delray Salt Co. Bittern from grainer, 12 days' evaporation. 1911. A. R. Merz, analyst.

70. Pennsylvania Salt Co., Wyandotte, Mich. Bittern from dripping vats. 1910. R. F. Gardner, analyst.

71. Diamond Crystal Salt Co., St. Clair, Mich. Bittern from grainer, 23 days' evaporation. 1911. R. F. Gardner, analyst.

72. Davidson, Wonsey Co., Marine City, Mich. Bittern; drippings from vacuum pan salt. 1911. R. F. Gardner, analyst.

73. Michigan Salt Works, Marine City, Mich. Bittern from grainer, 6 weeks' evaporation. 1911. A. R. Merz, analyst.

74. Mulkey Salt Co., Detroit, Mich. Bittern, 30 to 35 days' evaporation. 1911. R. F. Gardner, analyst.

TABLE XXVI.—Composition of bitterns from artificial brines of Michigan, West Shore.

[Parts per 1,000.]

| Constituent.               | Number of sample. |       |       |       |       |       |
|----------------------------|-------------------|-------|-------|-------|-------|-------|
|                            | 75                | 76    | 77    | 78    | 79    | 80    |
| Ions:                      |                   |       |       |       |       |       |
| K.....                     | 2.0               | 0.5   | 0.2   | 6.0   | 0.7   |       |
| Na.....                    | 89.7              | 115.1 | 119.1 | 107.6 | 111.1 | 121.4 |
| Ca.....                    | 5.2               | 3.9   | 2.4   | 8.4   | 3.5   | 2.8   |
| Mg.....                    | 15.4              | 3.0   | 1.6   | 3.4   | 4.6   | .3    |
| Cl.....                    | 191.8             | 191.4 | 189.8 | 191.8 | 189.8 | 190.4 |
| SO <sub>4</sub> .....      | 3.2               | 2.3   | 3.4   | 5.0   | 2.3   | 2.4   |
| Br.....                    | Trace.            |       |       | None. |       |       |
| Conventional combinations: |                   |       |       |       |       |       |
| KCl.....                   | 3.8               | 1.0   | .4    | 11.4  | 1.3   |       |
| NaCl.....                  | 227.9             | 292.0 | 302.1 | 273.0 | 282.8 | 307.4 |
| CaCl <sub>2</sub> .....    | 10.8              | 8.0   | 2.8   | 17.4  | 6.9   | 5.0   |
| MgCl <sub>2</sub> .....    | 60.4              | 11.8  | 6.3   | 13.3  | 18.0  | 1.2   |
| CaSO <sub>4</sub> .....    | 4.5               | 3.3   | 4.8   | 7.1   | 3.3   | 3.4   |
| MgBr <sub>2</sub> .....    | Trace.            |       |       | None. |       |       |

75. Filer & Son, Filer City, near Manistee, Mich. Drippings from salt. 1911. R. F. Gardner, analyst.

76. Peters Salt & Lumber Co., East Lake, Manistee, Mich. Bittern from grainer, 19 days' evaporation. 1911. A. R. Merz, analyst.

77. Buckley, Douglas Lumber Co., Manistee, Mich. Bittern from grainer, 4 weeks' evaporation. 1911. A. R. Merz, analyst.

78. Same bittern, 17 days' evaporation. 1911. R. F. Gardner, analyst.

79. Louis Sands Lumber Co., Manistee, Mich. Bittern from grainer, 3 weeks' evaporation. 1911. A. R. Merz, analyst.

80. Stearns Salt & Lumber Co., Ludington, Mich. Bittern from grainer. 1911. A. R. Merz, analyst.

TABLE XXVII.—Composition of bitterns from artificial brines from Canada and Ohio.

[Parts per 1,000.]

| Constituent.                      | Number of sample. |        |        |        |        |
|-----------------------------------|-------------------|--------|--------|--------|--------|
|                                   | 80                | 81     | 82     | 83     | 84     |
| <b>Ions:</b>                      |                   |        |        |        |        |
| K.....                            | 1.4               | 2.8    | 1.2    | 0.7    | 1.8    |
| Na.....                           | 115.7             | 108.4  | 100.1  | 103.7  | 97.6   |
| Ca.....                           | 4.6               | 12.8   | 16.3   | 16.5   | 12.0   |
| Mg.....                           | 2.4               | 1.6    | 3.7    | 1.3    | 2.4    |
| Cl.....                           | 191.6             | 193.0  | 194.5  | 192.3  | 187.8  |
| SO <sub>4</sub> .....             | 3.2               | 5.0    | .7     | 1.1    | 1.8    |
| Br.....                           | None.             | Trace. | Trace. | Trace. | Trace. |
| <b>Conventional combinations:</b> |                   |        |        |        |        |
| KCl.....                          | 2.7               | 5.4    | 2.3    | 1.3    | 3.4    |
| NaCl.....                         | 293.7             | 275.2  | 254.6  | 263.4  | 263.0  |
| CaCl <sub>2</sub> .....           | 11.9              | 29.6   | 44.3   | 44.3   | 31.0   |
| MgCl <sub>2</sub> .....           | 6.1               | 6.3    | 14.5   | 5.1    | 9.4    |
| CaSO <sub>4</sub> .....           | 4.5               | 7.1    | 1.0    | 1.6    | 2.6    |
| MgBr <sub>2</sub> .....           | None.             | Trace. | Trace. | Trace. | Trace. |

80. Western Canada Flour Mills Co., Goderich, Canada. Bittern; 5 weeks' evaporation. 1911. R. F. Gardner, analyst.

81. Colonial Salt Co., Akron, Ohio. Bittern from grainer; 5½ months' evaporation. 1911. R. F. Gardner, analyst.

82. Union Salt Co., Cleveland, Ohio. Bittern from grainer; 5 days' evaporation. 1911. A. R. Merz, analyst.

83. Ohio Salt Co., Wadsworth, Ohio. Bittern; 35 days' evaporation. 1911. A. R. Merz, analyst.

84. Ohio Salt Co., Wadsworth, Ohio. Bittern, from vacuum pan at boot. 1911. A. R. Merz and R. F. Gardner, analysts.

TABLE XXVIII.—Composition of bitterns from artificial brines of Kansas.

[Parts per 1,000.]

| Constituent.          | Number of sample. |        |        |        |        | Constituent.                          | Number of sample. |        |        |        |        |
|-----------------------|-------------------|--------|--------|--------|--------|---------------------------------------|-------------------|--------|--------|--------|--------|
|                       | 85                | 86     | 87     | 148    | 139    |                                       | 85                | 86     | 87     | 148    | 139    |
| <b>Ions:</b>          |                   |        |        |        |        | <b>Conventional combinations:</b>     |                   |        |        |        |        |
| K.....                | 1.0               | Trace. | 0.2    | 1.4    | 0.4    | KCl.....                              | 2.0               | Trace. | 0.4    | 2.7    | 0.8    |
| Na.....               | 90.4              | 118.2  | 101.1  | 116.6  | 117.8  | NaCl.....                             | 229.3             | 293.4  | 242.9  | 296.6  | 299.6  |
| Ca.....               | 1.4               | .8     | .4     | 2.5    | 2.3    | CaCl <sub>2</sub> .....               | Trace.            | 2.2    | 1.1    | 3.1    | 2.5    |
| Mg.....               | 15.8              | 2.4    | 11.6   | 1.6    | 1.6    | MgCl <sub>2</sub> .....               | 57.2              | 9.4    | 45.5   | 6.3    | 5.3    |
| Cl.....               | 182.5             | 186.2  | 182.0  | 189.4  | 188.5  | Na <sub>2</sub> SO <sub>4</sub> ..... |                   | 8.0    | 16.6   |        |        |
| SO <sub>4</sub> ..... | 3.4               | 5.4    | 11.2   | 3.4    | 3.4    | CaSO <sub>4</sub> .....               | 4.8               | Trace. | Trace. | 4.8    | 4.8    |
| Br.....               | .9                | Trace. | Trace. | Trace. | Trace. | MgBr <sub>2</sub> .....               | 2.1               | Trace. | Trace. | Trace. | Trace. |

85. Western Salt Works (Hutchinson Salt Co.), Hutchinson, Kans. Bittern from open pan; after 25 days' evaporation. 1911. R. F. Gardner, analyst.

86. Sterling Salt Co., Sterling, Kans. Bittern from grainer; after 30 days' evaporation. 1911. R. F. Gardner, analyst.

87. Orient Salt Co., Anthony, Kans. Bittern from grainer; after 8 days' evaporation. 1911. R. F. Gardner, analyst.

148. Ellsworth Salt Co., Ellsworth, Kans. Bittern from grainer. 1911. J. A. Cullen, analyst.

149. Barton Salt Co., Hutchinson, Kans. Bittern from grainer after 24 days' evaporation. 1911. J. A. Cullen, analyst.

## ANALYTICAL RESULTS WITH BITTERN FROM NATURAL BRINES.

TABLE XXIX.—Composition of bitterns from natural brines of Michigan.

[Parts per 1,000.]

| Constituent.                          | Number of sample. |        |       |       |                    |        |                                 |                    |        |        |
|---------------------------------------|-------------------|--------|-------|-------|--------------------|--------|---------------------------------|--------------------|--------|--------|
|                                       | 88                | 89     | 90    | 91    | 92                 | 93     | 94                              | 95                 | 96     | 97     |
| <b>Ions:</b>                          |                   |        |       |       |                    |        |                                 |                    |        |        |
| K.....                                | 1.3               | 1.6    | 4.2   | 2.6   | 0.3                | 10.2   | 1.2                             | 0.2                | Trace. | Trace. |
| Na.....                               | 66.1              | 83.3   | 78.2  | 76.1  | 1.0                | 42.1   | 52.5                            | 1.1                | 60.9   | 119.9  |
| Ca.....                               | 40.6              | 32.4   | 36.4  | 32.8  | 18.9               | 192.6  | 50.2                            | 18.4               | .6     | 1.8    |
| Mg.....                               | 11.5              | 9.6    | 11.0  | 9.6   | 4.6                | 35.2   | 11.6                            | 3.4                | .4     | Trace. |
| Cl.....                               | 207.7             | 198.4  | 202.2 | 195.8 | 43.9               | 427.8  | 205.4                           | 42.6               | 91.5   | 184.2  |
| SO <sub>4</sub> .....                 | .4                | Trace. | .8    | 1.4   | None.              | None.  | .6                              | None.              | 3.6    | 4.8    |
| Br.....                               |                   | 4.4    | 3.3   | 2.2   | 1.1                | Trace. | Trace.                          | None.              | 4.3    | Trace. |
| <b>Conventional combinations:</b>     |                   |        |       |       |                    |        |                                 |                    |        |        |
| KCl.....                              | 2.5               | 3.1    | 8.0   | 5.0   | .6                 | 19.5   | 2.3                             | .4                 | Trace. | Trace. |
| NaCl.....                             | 167.5             | 211.6  | 198.4 | 193.0 | 2.5                | 106.9  | 133.3                           | .3                 | 147.2  | 293.6  |
| CaCl <sub>2</sub> .....               | 111.8             | 89.6   | 99.8  | 89.1  | 51.4               | 532.6  | 133.0                           | 50.6               | 1.7    | 5.0    |
| MgCl <sub>2</sub> .....               | 45.1              | 15.3   | 19.3  | 26.3  | 12.5               | 18.4   | 45.5                            | 13.3               | 1.6    | Trace. |
| Na <sub>2</sub> SO <sub>4</sub> ..... |                   |        |       |       |                    |        |                                 | CaHCO <sub>3</sub> |        |        |
| CaSO <sub>4</sub> .....               | .6                | Trace. | 1.1   | 2.0   | None.              | None.  | .9                              | None.              | 5.3    | 7.1    |
| MgSO <sub>4</sub> .....               |                   |        |       |       | {CaCO <sub>3</sub> |        | {F <sub>2</sub> Cl <sub>2</sub> |                    |        |        |
| MgBr <sub>2</sub> .....               |                   | 10.1   | 9.5   | 5.1   | .9                 | Trace. | Trace.                          | None.              |        |        |
| NaBr.....                             |                   |        |       |       | {H <sub>2</sub> O  |        |                                 | {H <sub>2</sub> O  | 5.5    |        |
|                                       |                   |        |       |       | 29.6               |        |                                 | 35.0               |        |        |

88. Hine &amp; Co., Bay City, Mich. Bittern from grainer; 5 days' evaporation. 1911. A. R. Merz, analyst.

89. Bliss, Van Auken Co., Saginaw, Mich. Bittern from grainer; 5 days' evaporation. 1911. R. F. Gardner, analyst.

90. Edward Germain, Saginaw, Mich. Bittern from grainer; 14 days' evaporation. 1911. R. F. Gardner, analyst.

91. Mershon, Eddy, Parker Co., Saginaw, Mich. Bittern from grainer; 4 days' evaporation. 1911. R. F. Gardner, analyst.

92. Saginaw Chemical Works (Saginaw Plate Glass Co.), Saginaw, Mich. Solid calcium chloride. Results in per cent. Contains also trace of barium and strontium. 1911. R. F. Gardner, analyst.

93. Saginaw Chemical Works (Saginaw Plate Glass Co.), Saginaw, Mich. Bittern, which had been evaporated to 8.5 per cent of the volume of the original brine, before the final evaporation for the preparation of calcium chloride. Sample was taken while hot. On cooling, a crystalline solid separated, which contained 1.1 per cent potassium, or 2.3 per cent potassium chloride. 1911. R. F. Gardner, analyst.

94. Dow Chemical Co., Mount Pleasant, Mich. Bittern after removal of bromine. Contaminated with iron compounds. 1911. R. F. Gardner, analyst.

95. Van Schaack Calcium Works, Mount Pleasant, Mich. Solid calcium chloride. Results in per cent. 1911. R. F. Gardner, analyst.

96. Saginaw Salt Co., St. Charles, Mich. Bittern; 4 days' evaporation. 1911. R. F. Gardner, analyst.

97. Port Huron Salt Co., Port Huron, Mich. Bittern from grainer; 2 weeks' evaporation. 1911. R. F. Gardner, analyst.

## TABLE XXX.—Composition of mother liquors from natural brines of Michigan and Ohio.

[Parts per 1,000.]

| Constituent.                          | 75    | 74     | 170    | 118   | 98    | 99                | 5a     |
|---------------------------------------|-------|--------|--------|-------|-------|-------------------|--------|
| <b>Tons:</b>                          |       |        |        |       |       |                   |        |
| K.....                                | 8.2   | Trace. | 5.4    | 2.8   | 3.2   | 0.7               | 14.6   |
| Na.....                               | 3.4   | 6.2    | 8.2    | 104.8 | 2.6   | .6                | 8.4    |
| Ca.....                               | 174.0 | 82.0   | 87.2   | 13.5  | 145.2 | 19.5              | 13.0   |
| Mg.....                               | 40.4  | 25.4   | 16.8   | 2.2   | 42.2  | 4.9               | 40.2   |
| Cl.....                               | 433.3 | 223.6  | 219.2  | 192.3 | 348.8 | 50.4              | 375.6  |
| SO <sub>4</sub> .....                 | 3.0   | 3.4    | 1.8    | 3.3   | 5.2   | None.             | Trace. |
| Br.....                               | .5    | .4     | Trace. | .5    | 11.6  |                   | 1.0    |
| <b>Conventional combinations:</b>     |       |        |        |       |       |                   |        |
| KCl.....                              | 15.6  | Trace. | 10.3   | 4.7   | 6.6   | 1.4               | 27.9   |
| NaCl.....                             | 8.6   | 15.7   | 20.8   | 266.6 | 6.7   | 1.6               | 21.24  |
| CaCl <sub>2</sub> .....               | 477.5 | 221.5  | 239.0  | 33.6  | 377.9 | 53.9              | 360.7  |
| MgCl <sub>2</sub> .....               | 155.6 | 97.6   | 65.9   | 8.4   | 158.6 | 19.2              | 158.7  |
| Na <sub>2</sub> SO <sub>4</sub> ..... | None. | None.  | None.  |       |       |                   |        |
| CaSO <sub>4</sub> .....               | 4.3   | 5.3    | 2.6    | 4.7   | 7.3   | None.             | Trace. |
| MgBr <sub>2</sub> .....               | 1.2   | .9     | Trace. | .6    | 13.3  | {H <sub>2</sub> O | 1.1    |
|                                       |       |        |        |       |       | 23.9              |        |

75. Saginaw Plate Glass Co., Saginaw, Mich. Bittern from grainer concentrated to 45° B. 1910. R. F. Gardner, analyst.

74. Saginaw Plate Glass Co., Saginaw, Mich. Bittern, 32½° B. 1910. R. F. Gardner, analyst.

170. W. J. Mason, Saginaw, Mich. 1910. R. F. Gardner, analyst.

118. Ohio Salt Co., Wadsworth, Ohio. Bittern from vacuum pan at boot. 1911. J. A. Cullen, analyst.

98. Pomeroy Salt Association, Pomeroy, Ohio. Bittern before going to bromine still. 1911. A. R. Merz and R. F. Gardner, analysts.

99. Eureka Calcium Works, Pomeroy, Ohio. Calcium chloride. Results in per cent. 1911. R. F. Gardner, analyst.

5a. Slagel Salt Co., Pomeroy, Ohio. Bittern ready for bromine stills; 42° B. at 60° F. Concentrated to one-eighth its original volume. From a well 1,100 feet deep. 1910. J. A. Cullen, analyst.

TABLE XXXI.—Composition of bitterns from natural brines of West Virginia.

[Parts per 1,000.]

| Constituent.                    | Number of sample. |       |                              |       |                              |        |        |        |
|---------------------------------|-------------------|-------|------------------------------|-------|------------------------------|--------|--------|--------|
|                                 | 109               | 101   | 102                          | 103   | 104                          | 13a    | 126    | 132a   |
| Ions:                           |                   |       |                              |       |                              |        |        |        |
| K                               | 0.4               | 2.7   | Trace.                       | 2.9   | 0.8                          | Trace. | 3.2    | Trace. |
| Na                              | 97.3              | 3.3   | 3.7                          | .2    | 2.4                          | 10.2   | 18.9   | Trace. |
| Ca                              | 16.2              | 135.8 | 18.5                         | 143.4 | 19.6                         | 85.0   | 43.4   | 24.56  |
| Mg                              | 4.8               | 48.4  | 5.3                          | 43.4  | 5.1                          | 54.4   | 57.2   | 6.33   |
| Cl                              | 191.2             | 355.2 | 53.9                         | 346.4 | 53.9                         | 318.4  | 268.3  | 62.05  |
| SO <sub>4</sub>                 | 1.8               | 4.8   | None.                        | 3.8   | None.                        | 4.8    | Trace. | 1.56   |
| Br                              | None.             | 11.0  | Trace.                       | 12.2  | None.                        | .8     | 1.9    | None.  |
| Conventional combinations:      |                   |       |                              |       |                              |        |        |        |
| KCl                             | .8                | 5.4   | Trace.                       | 5.8   | 1.5                          | Trace. | 6.1    | Trace. |
| NaCl                            | 246.9             | 8.4   | 9.4                          | .7    | 6.1                          | 25.9   | 48.0   | Trace. |
| CaCl <sub>2</sub>               | 42.6              | 362.5 | 51.2                         | 379.0 | 54.2                         | 229.8  | 120.0  | 68.32  |
| MgCl <sub>2</sub>               | 188.8             | 179.2 | 20.8                         | 162.5 | 20.0                         | 209.3  | 214.4  | 24.37  |
| Na <sub>2</sub> SO <sub>4</sub> |                   |       | { H <sub>2</sub> O }<br>18.6 |       | { H <sub>2</sub> O }<br>18.2 | None.  | None.  |        |
| CaSO <sub>4</sub>               | 2.6               | 6.8   | None.                        | 5.3   | None.                        | 6.8    | Trace. | 2.20   |
| MgBr <sub>2</sub>               | None.             | 12.6  |                              | 14.1  | None.                        | 1.8    | 4.4    |        |
| NaBr                            |                   |       | Trace.                       |       |                              |        |        |        |

109. Hartford City Salt Co., Hartford, W. Va. Bittern. 1910. R. F. Gardner, analyst.

101. Dixie Salt Works, Mason, W. Va.—Bittern before going to bromine stills. 1911. A. R. Merz and R. F. Gardner, analysts.

102. Hartford City Salt Co., Hartford, W. Va. Solid calcium chloride. Results in per cent. 1911. R. F. Gardner, analyst.

103. Liverpool Salt &amp; Coal Co., Hartford, W. Va. Bittern before going to bromine stills. 1911. A. R. Merz and R. F. Gardner, analysts.

104. Liverpool Salt &amp; Coal Co., Hartford, W. Va. Solid calcium chloride. Results in per cent. 1911. R. F. Gardner, analyst.

13a. J. O. Dickinson &amp; Co., Malden, Kanawha County, W. Va. Bittern representing 10 per cent of original brine, 1910. R. F. Gardner, analyst.

126. Hartford City Salt Co. Hartford, W. Va. Bittern just before going to bromine plant. 1911. R. F. Gardner, analyst.

132a. J. O. Dickinson &amp; Co., Malden, W. Va. Solid calcium chloride. Results in per cent. 1911. J. A. Cullen, analyst.

## ANALYTICAL RESULTS—ROCK SALT, MISCELLANEOUS SUBSTANCES, AND SEA-WATER BITTERNs.

TABLE XXXII.—Composition of rock salt from New York, Michigan, Kansas, and Louisiana.

[Per cent.]

| Constituent.                    | Number of sample. |        |        |        |        |        |      |        |        |        |
|---------------------------------|-------------------|--------|--------|--------|--------|--------|------|--------|--------|--------|
|                                 | 105               | 105a   | 106    | 107    | 108    | 109    | 110  | 111    | 112    | 113    |
| Ions:                           |                   |        |        |        |        |        |      |        |        |        |
| K                               | 0.2               | Trace. | Trace. | Trace. | Trace. | Trace. | 0.1  | Trace. | Trace. | Trace. |
| Na                              | 36.0              | 38.9   | 38.0   | 39.0   | 28.9   | 38.4   | 38.6 | 28.4   | 28.4   | 39.1   |
| Ca                              | 1.96              | .2     | 1.0    | Trace. | Trace. | .8     | .4   | .8     | .4     | Trace. |
| Mg                              | .50               | 1.04   | .1     | .2     | .3     | Trace. | .1   | Trace. | .3     | .1     |
| Cl                              | 59.94             | 59.6   | 59.7   | 59.3   | 59.8   | 60.0   | 60.0 | 60.0   | 60.2   | 59.9   |
| SO <sub>4</sub>                 | 1.13              | 1.2    | 1.2    | .5     | 1.0    | .8     | .8   | .8     | .6     | .9     |
| Conventional combinations:      |                   |        |        |        |        |        |      |        |        |        |
| KCl                             | .41               | Trace. | Trace. | Trace. | Trace. | Trace. | .2   | Trace. | Trace. | Trace. |
| NaCl                            | 91.58             | 97.2   | 96.7   | 98.5   | 97.3   | 97.4   | 97.9 | 97.7   | 97.5   | 98.3   |
| CaCl <sub>2</sub>               | 4.16              | .6     | 1.2    | Trace. | Trace. | 1.5    | .3   | 1.2    | .3     | Trace. |
| MgCl <sub>2</sub>               | 1.98              | .4     | .4     | .8     | 1.2    | Trace. | .4   | Trace. | 1.2    | .5     |
| Na <sub>2</sub> SO <sub>4</sub> |                   | 1.8    |        |        | 1.5    |        |      |        |        | 1.2    |
| CaSO <sub>4</sub>               | 1.59              | Trace. | 1.7    | .7     | Trace. | 1.1    | 1.2  | 1.1    | 1.0    | Trace. |

105. Rock salt from near middle of bed at working face. 1911. J. A. Cullen, analyst.

105a. Retsof Mining Co., Retsof, N. Y. Rock salt from near floor at working face, room 24. Bed being removed, 8 feet in thickness. 1911. R. F. Gardner, analyst.

106. Sterling Salt Co., Halite, near Cuylerville, N. Y. Rock-salt dust from beneath main crushers. 1911. R. F. Gardner, analyst.

107. Sterling Salt Co., Halite, near Cuylerville, N. Y. Sample from working face, west side of room No. 1, northwest. Sample taken from roof to floor through full depth of stratum worked. 1911. R. F. Gardner, analyst.

108. Detroit Mining Co., Detroit, Mich. Sample from roof to floor at working face. Representative of stratum being removed. 1911. R. F. Gardner, analyst.

109. Crystal Salt Co., Kanopolis, Kans. 1911. R. F. Gardner, analyst.

110. Royal Salt Co., Kanopolis, Kans. 1911. R. F. Gardner, analyst.

111. Bevis Rock Salt Co., Lyons, Kans. Sample from 16-foot bed. 1911. R. F. Gardner, analyst.

112. Bevis Rock Salt Co., Lyons, Kans. Fine salt screened from coarse. 1911. R. F. Gardner, analyst.

113. Avery Rock Salt Co., Avery Island, La. 1911. R. F. Gardner, analyst.

TABLE XXXIII.—Composition of miscellaneous substances obtained in the manufacture of salt.

[Per cent.]

| Constituent.                          | Number of sample.  |       |        |                    |        |        |                  |                  |
|---------------------------------------|--------------------|-------|--------|--------------------|--------|--------|------------------|------------------|
|                                       | 114                | 115   | 116    | 117                | 118    | 21     | 90               | Y                |
| <b>Ions:</b>                          |                    |       |        |                    |        |        |                  |                  |
| K.....                                | 0.1                | 0.3   | Trace. | 0.4                | Trace. | 1.4    | Trace.           | Trace.           |
| Na.....                               | 19.1               | 1.1   | 119.2  | 2.9                | 31.9   | 51.1   | 13.4             | 26.0             |
| Ca.....                               | 14.2               | 12.9  | 1.4    | 19.0               | 1.1    | 10.8   | 2.0              | 8.6              |
| Mg.....                               | .1                 | None. | .4     | 5.3                | 3.4    | 3.4    | 3.2              | Trace.           |
| Cl.....                               | 51.2               | None. | 185.0  | 59.9               | 45.0   | 107.8  | 31.8             | 40.4             |
| SO <sub>4</sub> .....                 | 5.0                | None. | 2.8    | None.              | 19.6   | 1.4    | 2.4              | 20.0             |
| Br.....                               | None.              | None. | Trace. | None.              | .....  | Trace. | None.            | None.            |
| <b>Conventional combinations:</b>     |                    |       |        |                    |        |        |                  |                  |
| KCl.....                              | .2                 | ..... | Trace. | .8                 | Trace. | 2.7    | Trace.           | Trace.           |
| NaCl.....                             | 42.4               | ..... | 302.6  | 7.3                | 57.2   | 129.7  | 34.0             | 66.0             |
| CaCl <sub>2</sub> .....               | 39.3               | ..... | .6     | 52.6               | .3     | 28.2   | 2.8              | .6               |
| MgCl <sub>2</sub> .....               | .4                 | ..... | 1.6    | 20.8               | 13.5   | 13.3   | 12.6             | Trace.           |
| Na <sub>2</sub> SO <sub>4</sub> ..... | 7.4                | ..... | .....  | .....              | 29.0   | None.  | H <sub>2</sub> O | H <sub>2</sub> O |
| CaSO <sub>4</sub> .....               | None.              | ..... | 4.0    | None.              | Trace. | 2.0    | 47.2             | 5.0              |
| MgSO <sub>4</sub> .....               | { H <sub>2</sub> O | ..... | .....  | { H <sub>2</sub> O | .....  | .....  | 3.4              | 28.4             |
| MgBr <sub>2</sub> .....               | { 10.3             | ..... | .....  | { 18.5             | .....  | .....  | .....            | .....            |
|                                       | None.              | ..... | Trace. | Trace.             | .....  | Trace. | None.            | Trace.           |

114. Bliss, Van Auken Co., Saginaw, Mich. Sludge from grainer floor, removed during cleaning-up process. Results in per cent. 1911. R. F. Gardner, analyst.

115. Dow Chemical Co., Midland, Mich. Refuse from electrolyzing tanks, after removal of chlorine. Results in per cent. 1911. R. F. Gardner, analyst.

116. Saginaw Salt Co., St. Charles, Mich. Solid residue separating from bittern in grainer. Results in per cent. 1911. R. F. Gardner, analyst.

117. Pomeroy Salt Association, Pomeroy, Ohio. Product from bittern. Results in per cent. 1911. R. F. Gardner, analyst.

118. Worcester Salt Co., Silver Springs, N. Y. Salt dust from driers. 1911. R. F. Gardner, analyst.

21. The Slagel Salt Co., Mason City, W. Va. Sediment from settler. 1911. R. F. Gardner, analyst.

90. Port Huron Salt Co., Port Huron, Mich. Sludge from settling tanks. 1911. R. F. Gardner, analyst.

Y. Worcester Salt Co., Silver Springs, N. Y. Dust from salt driers; contains an accumulation of gypsum. 1911. R. F. Gardner, analyst.

TABLE XXXIV.—Composition of bitterns from sea water.<sup>1</sup>

[Parts per 1,000.]

| Constituent.                      | Number of sample. |       |       |       |        |       |       |
|-----------------------------------|-------------------|-------|-------|-------|--------|-------|-------|
|                                   | 119               | 120   | 121   | 122   | 123    | 124   | 125   |
| <b>Ions:</b>                      |                   |       |       |       |        |       |       |
| K.....                            | 8.2               | 13.4  | 13.2  | 14.6  | 21.5   | 35.0  | 11.8  |
| Na.....                           | 72.6              | 62.7  | 60.9  | 24.5  | 4.7    | 93.6  | 51.1  |
| Ca.....                           | 1.2               | 2.2   | .6    | .5    | 1.0    | .2    | 1.1   |
| Mg.....                           | 24.0              | 23.4  | 50.6  | 62.7  | 79.4   | 8.6   | 43.9  |
| Cl.....                           | 179.2             | 176.6 | 179.4 | 183.3 | -220.1 | 180.4 | 190.8 |
| SO <sub>4</sub> .....             | 30.0              | 31.4  | 53.6  | 74.2  | 62.0   | 29.0  | 55.8  |
| Br.....                           | 3.0               | 3.0   | 3.0   | 3.0   | 2.0    | 2.0   | 2.8   |
| <b>Conventional combinations:</b> |                   |       |       |       |        |       |       |
| KCl.....                          | 15.6              | 25.5  | 25.2  | 27.8  | 41.0   | 66.7  | 22.5  |
| NaCl.....                         | 151.2             | 159.1 | 154.6 | 62.1  | 11.9   | 237.6 | 129.7 |
| MgCl <sub>2</sub> .....           | 77.1              | 84.5  | 110.8 | 176.3 | 256.9  | 5.8   | 132.9 |
| CaSO <sub>4</sub> .....           | 4.0               | 7.4   | 2.3   | 1.7   | 3.3    | .6    | 3.7   |
| MgSO <sub>4</sub> .....           | 33.9              | 32.8  | 65.0  | 91.5  | 75.3   | 35.8  | 65.4  |
| MgBr <sub>2</sub> .....           | 3.4               | 3.4   | 3.4   | 3.4   | 2.3    | 2.3   | 3.2   |

<sup>1</sup> Analyses by R. F. Gardner.

119. Leslie Salt Refining Works, San Mateo, Cal. Mother liquor, representative sample from near north-west corner of mother-liquor pond.

120. Leslie Salt Refining Works, San Mateo, Cal. Sample from southeast corner of mother-liquor pond.

121. Leslie Salt Works, San Mateo, Cal. Mother liquor from salt making pond (solar evaporator or "salt garden"); pond has been "making salt" during the summer.

122. Oliver Salt Works, Mcunt Eden, Cal. Mother liquor from slop pond. Represents an accumulation of five years.

123. Oliver Salt Works, Mount Eden, Cal. Mother liquor which has been subjected to some special treatment.

124. California Salt Co., Alvarado, Cal. Mother liquor from "slop" pond. Represents about three years' accumulation, with the abstraction of considerable quantities for "forcing" purposes and the addition of small quantities of other waste liquors.

125. Pioneer Salt Co., San Francisco, Cal. Mother liquor. One year's accumulation.



**THE SEPARATION OF POTASSIUM SALTS FROM SOLUTIONS OF OTHER SALTS.**

An examination of the foregoing tables of analytical results bring out the following general facts:

**ARTIFICIAL BRINES.**

The so-called artificial brines are solutions containing the ions of the metals, sodium, magnesium, calcium, and potassium and of hydrochloric and sulphuric acid. Combining these in accordance with the conventional method, the solutions may be said to contain a large amount of sodium chloride, with smaller amounts of magnesium and calcium chlorides; in addition there are to be found still smaller quantities of calcium sulphate and potassium chloride. While other substances are present, these are the ones which have to be taken into consideration in a discussion of the separation of the potassium salts. Upon the initial evaporation of the solution, sodium chloride and calcium sulphate are the only salts which are precipitated. Portions of the others, of course, are to be found in the crystallized product, being present through occlusion and adsorption. During the crystallization, the solution remains saturated with respect only to sodium chloride and calcium sulphate. It is doubtful if the saturation point of calcium and magnesium chlorides is even remotely approached. Except that which is removed through occlusion and adsorption, both of these substances and potassium chloride remain in solution and become more concentrated. In the separation of potassium salts, then, from an artificial brine, one has to deal with the mother liquor from the sodium chloride crystallization, which is a saturated solution of sodium chloride, contaminated with calcium and magnesium chlorides and some potassium chloride. In general, one has to deal with solutions of chlorides only, though there are certain artificial brines which contain sulphates. In this connection it should be pointed out that the simultaneous occurrence of both calcium and sulphate ions in a solution is limited to the solubility of calcium sulphate in that solution. Solutions containing large amounts of sulphates, then, are found to be low in calcium and those containing considerable calcium are low in sulphates.

**NATURAL BRINES.**

An important difference between the natural and artificial brines is that the former are richer in calcium and magnesium salts. In general the artificial brines are purer solutions of sodium salts than are the natural brines. This is to be expected when we consider their respective origins.

Natural brines containing large proportions of calcium are relatively free from sulphates. The mother liquor from the crystallization of sodium chloride is a saturated solution of sodium chloride,

rich in calcium and magnesium chlorides and containing also bromides, conventionally regarded as magnesium bromide, and potassium chloride. This composition is but slightly altered by the treatment for the recovery of bromine. Occasionally, however, it has been observed that the brines which have been treated for the recovery of bromine, after the neutralization of the sulphuric acid, give an alkaline reaction. This is doubtless due to the fact that an excess of lime has been employed over that requisite for the neutralization of the sulphuric acid.

#### BRINES FROM "SALT GARDENS."

The analysis of sea water shows\* that its composition resembles artificial rather than natural brines. However, a striking difference is found in the sulphate content. Since sea water contains a considerable proportion of sulphate it follows that it must be comparatively free from calcium salts.

The mother liquor remaining after the crystallization of sodium chloride again is a saturated solution of sodium chloride, containing magnesium chloride and sulphate in large amounts, together with lesser amounts of potassium chloride and some bromide and calcium sulphate.

#### MOTHER LIQUORS.

The separation of potash from mother liquors obtained from these three sources represents, therefore, three problems. At least two of these are quite distinct: (1) The separation of potash from a solution containing only chlorides, and (2) from one containing both chlorides and sulphates; or (1) the separation of potassium salts from a solution containing sodium, magnesium, and calcium, and (2) from one containing principally the metals sodium and magnesium.

The recovery of potash from brines and bitterns is a problem of the crystallization of potassium salts from solutions containing other salts; or the crystallization of other salts from solutions containing potassium salts, the latter segregating in the mother liquors. The conditions controlling such separations, for the most part, have already been determined through the application of the phase rule. These will be given, in abstract, in the following paragraphs:

THE SYSTEM: SODIUM CHLORIDE, POTASSIUM CHLORIDE, AND WATER.

At 25° C., 1,000 gram molecular weights (mols) of water will dissolve 44 mols of potassium chloride. From this solution potassium chlorides crystallizes on evaporation; in contact with it, potassium chloride is in equilibrium; there will be neither solution nor crystallization. The solution in equilibrium with the solid phase is known as the "constant solution."

At this temperature an equal volume of water will dissolve 55.5 mols of sodium chloride, and analogous statements may be made concerning the equilibrium between sodium chloride and this solution.

At this temperature an equal volume of water saturated with respect to both sodium and potassium chloride, one with which both of these salts are in equilibrium, contains 44.5 mols sodium chloride and 19.5 mols potassium chloride. On the addition of the sodium chloride to the saturated solution of potassium chloride the solubility of the latter will be depressed from 44 mols to 19.5, and by the addition of potassium chloride to the saturated solution of sodium chloride the solubility of the latter will be depressed from 55.5 mols to 44.5 mols. In other words, there is a mutual depression of the solubility of the two salts. Such a solution of the two salts on evaporation will deposit a mixture of the two, without change in the concentration of the liquid phase, so long as both are present, and obviously no separation can be effected by an evaporation.

From a solution containing a larger proportion of sodium chloride than that mentioned in the case just cited, on evaporation sodium chloride will crystallize and will be the first solid to separate. This will continue until the content of that salt has decreased and that of potassium chloride has increased to the values mentioned. Similar statements can be made for the case where potassium chloride is in the larger proportion. From this it must be concluded that at this temperature (*a*) sodium and potassium chlorides can not be separated by crystallization beyond the point represented by this equilibrium; (*b*) from a solution containing an excess of sodium chloride over that amount existing at the equilibrium point, potassium chloride alone can not be precipitated; (*c*) from a solution containing potassium chloride in excess, that salt may be obtained by crystallization (evaporation) until the equilibrium point is reached.

These statements are true for the temperature of 25° C. The solubility of sodium chloride in water is but slightly affected by changes in temperature. At 0° C., 100 parts of water dissolve 35.7 parts of sodium chlorid, and at 109.7° C., 40.4 parts of sodium chloride. The solubility of potassium chloride is more affected—from the solubility of 28.5 parts of potassium chloride in 100 parts of water at 0° C. to 58.5 parts at 107.65° C.

It is improbable that any point is reached below the boiling point where a very much closer separation of these two salts can be effected by crystallization. The statements made for 25° C. may be considered to apply in a general way for temperatures below the boiling point of the solution.

Since the temperature coefficient of solubility of potassium chloride is greater than that of sodium chloride, it should be possible to effect

a partial separation by chilling a solution saturated with both at or near its boiling point. On chilling, both would precipitate, but the potassium chloride in preponderating amount.

*Application.*—Only sodium and potassium chlorides are present. The conditions here defined are probably never realized experimentally, but are more or less remotely approached in the case of the mother liquors produced in those salt refineries where it is the practice to subject the brines coming from the wells to a preliminary treatment for the removal of both calcium and magnesium salts. This is done, as has been pointed out, by adding to the brines milk of lime, soda ash, and sodium phosphate, in the order named. However, it has been said, if the impurities whose removal is sought are not entirely eliminated, the effect of this treatment on the composition of the mother liquor is ultimately nullified by the fact that the special initial purification of the brine makes possible a more extended condensation or evaporation, so that the final result is a much smaller volume of mother liquor of the same effective composition as that obtained by the evaporation of the unpurified brines. In practice, the result of the careful purification of the brine is to obviate the necessity of throwing away mother liquors at all; they are allowed to mingle with the incoming fresh portions of brine. Should potassium chloride be found in such a brine, the point ultimately would be reached where it would begin to separate with the sodium chloride. The conditions governing their crystallization are those just considered in the theoretical discussion of the system, sodium chloride, potassium chloride, and water. In such a solution the potassium salts segregate, with the exception of that lost through the imperfect separation of the mother liquor from the crystallized sodium chloride, until it has reached a concentration of 19.5 mols per 1,000 of water, at 25° C.<sup>1</sup>, or of 37 mols per 1,000 mols water at 83° C.<sup>2</sup> No further segregation of potassium salts is possible, nor is a further separation of the two salts by a single crystallization possible. Either evaporation to dryness to produce a "manure salt" or the application of some specially designed method of separation would have to be employed.

#### THE SYSTEM: SODIUM SULPHATE, POTASSIUM SULPHATE, AND WATER.

Sodium chloride, we have seen, has but a slight temperature coefficient of solubility. At 0° C. its solubility in 100 parts of water is 37.5 parts, and at 109.7° it is 40.4 parts, a difference of only 4.7 parts. Potassium chloride has a solubility at 0° C. of 28.5 parts, and at 107.65° C., 58.5 parts, a range of 30 parts. In sulphate solution, the solubility coefficients are changed; that of the sodium salt is increased and of the potassium salt decreased. At 0° C.,

<sup>1</sup> Cf. Table XXXVII.

<sup>2</sup> Cf. Table XXXVIII.

100 parts of water dissolved 8.5 parts of potassium sulphate and at 102.25°, 26.75 parts, representing a range of solubility of 18.25 parts. At 0° C., 100 parts of water dissolve 4.8 parts of sodium sulphate, and at 103.5°, 42.2, a range of 37.6 parts, from which it is seen that the solubility of sodium sulphate varies with temperature much more than does the sodium chloride or the potassium sulphate; and at 0° C. sodium sulphate is less soluble than potassium sulphate, while at or near the boiling point of the solution it is much more soluble.

From a solution of sodium sulphate alone may be precipitated at temperatures below 34°C. the decahydrate, Glaubers salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) and above that temperature, anhydrous sodium sulphate ( $\text{Na}_2\text{SO}_4$ ). From a solution of potassium sulphate the anhydrous salt is deposited over the entire range of temperatures between the freezing point and the boiling point of the solution.

Included in Table XXXIV are the data for the invariant points of the system—sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), potassium sulphate ( $\text{K}_2\text{SO}_4$ ), and water, as determined at 25° C. by Meyerhoffer and Saunders.<sup>1</sup>

TABLE XXXIV.—*Equilibria between sodium chloride, potassium chloride, sodium sulphate, potassium sulphate, and water at 25° C.*

| Solids.  |  | Mols per 1,000 mols H <sub>2</sub> O. |                    |                                   |                                  |         |
|--|--|---------------------------------------|--------------------|-----------------------------------|----------------------------------|---------|
|  |  | Na <sub>2</sub> Cl <sub>2</sub> .     | K <sub>2</sub> Cl. | Na <sub>2</sub> SO <sub>4</sub> . | K <sub>2</sub> SO <sub>4</sub> . | Fig. 2. |
| NaCl.....  | .....  | 55.5                                  | .....              | .....                             | .....                            | A.      |
| KCl.....   | .....  | .....                                 | 44                 | .....                             | .....                            | B.      |
| Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O..... | .....  | .....                                 | .....              | 35.5                              | .....                            | C.      |
| K <sub>2</sub> SO <sub>4</sub> .....                     | .....  | .....                                 | .....              | .....                             | 12                               | D.      |
| NaCl.....  | KCl.....   | 44.5                                  | 19.5               | .....                             | .....                            | E.      |
| NaCl.....  | Na <sub>2</sub> SO <sub>4</sub> .....                    | 51                                    | .....              | 12.5                              | .....                            | F.      |
| KCl.....   | K <sub>2</sub> SO <sub>4</sub> .....                     | .....                                 | 42                 | .....                             | 1.5                              | G.      |
| Glazerite.....   | Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O..... | .....                                 | .....              | 35                                | 10                               | H.      |
| Glazerite.....   | K <sub>2</sub> SO <sub>4</sub> .....                     | .....                                 | .....              | 8.5                               | 14                               | I.      |
| Na <sub>2</sub> SO <sub>4</sub> .....                    | Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O..... | 25                                    | .....              | 38                                | .....                            | J.      |
| Glazerite.....   | NaCl.....  | 54                                    | .....              | 3.5                               | 10.5                             | K.      |
| Glazerite.....   | Na <sub>2</sub> SO <sub>4</sub> .....                    | 20                                    | .....              | 28                                | 10                               | L.      |
| Glazerite.....   | NaCl.....  | 54                                    | .....              | 4.5                               | 10                               | M.      |
| Glazerite.....   | KCl.....   | 15                                    | 33.5               | .....                             | 3                                | N.      |
| Glazerite.....   | KCl.....   | 44                                    | 20                 | .....                             | 4.5                              | O.      |

From this table it is seen what solids are deposited at the invariant points and likewise the compositions of the solutions in equilibrium therewith. These data are plotted in figure 1. Two invariant points are possible and are indicated in the figure by H and I.

Solutions of nonvolatile substances upon evaporation invariably tend to become more concentrated with respect to the total number of molecules present. The more concentrated a solution is the lower is its vapor tension. Evaporation then results in a solution of the lowest possible vapor tension. This solution is the final

<sup>1</sup> Zt. phys. Chem. 23, 453 (1899).

“constant solution.” By observing the vapor tension, or the concentrations in molecules of the various constant solutions possible in a system, it is a simple matter to determine the path, so to speak, which the successive concentrations obtainable on evaporation will describe (“Kristallisationswege”). This will lie along the curves of equilibria, will pass toward the invariant points of decreasing vapor tensions (increasing concentration), and will end at the invariant point of the least vapor tension (greatest concentration).

From the system, sodium sulphate, potassium sulphate, and water, the initial solid to separate on evaporation may be one of three—sodium sulphate decahydrate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  (or, at higher temperatures, the anhydrous form) potassium sulphate,  $\text{K}_2\text{SO}_4$ , and glazerite or Penny’s double salt,  $\text{K}_3\text{Na}(\text{SO}_4)_2$ , depending on the

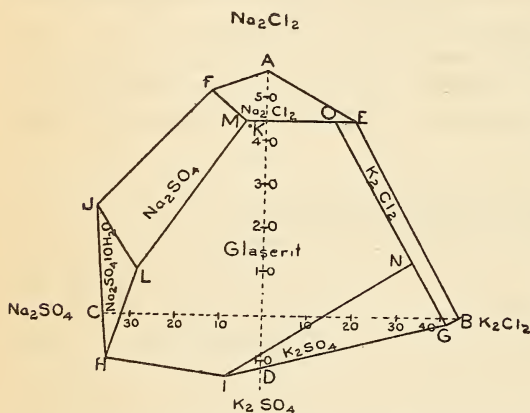


FIG. 1.—Diagram showing the equilibria in the system: Sodium chloride, potassium chloride, sodium sulphate, potassium sulphate, and water.

relative concentrations of the two saline components. If the concentrations are such that sodium sulphate precipitates first, it will continue to separate as a solid until a concentration is reached represented by the point H (fig. 1), when glazerite appears as a solid and sodium sulphate and glazerite will continue to separate until complete desiccation is attained. This point represents a higher concentration than

does I, the only other invariant point possible in this system.

If, however, the original concentration is such that potassium sulphate is the first solid to appear, then, as desiccation proceeds, this salt will form until a concentration is reached represented by a point I. On further desiccation no more potassium sulphate is formed, but glazerite alone precipitates until the concentration represented by H is attained, at which, as stated above, sodium sulphate decahydrate and glazerite will both separate, without change in the concentration of the solution, until complete desiccation is attained.

These statements apply at  $25^\circ\text{C}$ . and lower temperatures. At higher temperatures practically the same relations obtain, except that the decahydrate disappears above  $34^\circ\text{C}$ . and the anhydrous sodium sulphate is the stable form.

*Application.*—It follows from the foregoing that a complete separation of potassium from sodium when the two are in solution as sulphate can not be effected by crystallization alone. Since sodium would always be present in excess over potassium, the field described would be approached from the sodium sulphate region. The only products of the evaporation, then, would be sodium sulphate, followed by a mixture of sodium sulphate and glazerite.

THE SYSTEM: SODIUM CHLORIDE, POTASSIUM CHLORIDE, SODIUM SULPHATE, POTASSIUM SULPHATE, AND WATER.

The invariant points for this system are likewise given in Table XXXV; the numbers refer to figure 1. Glazerite is the solid which occurs over the greater part of the range covered by the data plotted in this diagram. It may occur singly with any one of the other solids possible, and at the triple points is always one of the solids present. If a solution saturated with respect to any of the saline components is evaporated, a concentration is soon reached at which glazerite also separates. Its separation continues to the point of complete desiccation.

Below  $4.4^{\circ}$  the line terminating at M swings to the right so that the decahydrate and potassium chloride fields become concurrent along the line ON. At concentrations represented by points along this line the decahydrate and potassium chloride will crystallize together. At  $4^{\circ}.4$ , and above that point, M swings back to the left and the glazerite field again becomes interposed.

*Application.*—The field over which these solids are precipitable would be approached, in practice, from the sodium side, since sodium in all commercial brines and concentrates therefrom is in excess over potassium. The path of concentration would probably have its origin in the sodium sulphate decahydrate field (this field representing lower concentrations than the anhydrous sodium sulphate field) and would merge with the line HL, along which sodium sulphate decahydrate and glazerite would be in equilibrium with the solution. Following this line in the direction of decreasing vapor tension, or increasing concentration, the path would reach the triple point L, where the three solids, the two sodium sulphates and glazerite would precipitate. On further evaporation the anhydrous form of sodium sulphate and glazerite would precipitate over a range in concentrations represented by the line LM and limited by M. At this point the three solids, sodium sulphate, glazerite, and sodium chloride, are the solid phases. The diagram shows that there is no point where the vapor tension is lower; further evaporation, therefore, would result in the continued precipitation of these solids until complete desiccation had been attained.

If it be assumed that the solution is saturated with sodium chloride, it is evident from the diagram that the point M is reached along the line FM, with the simultaneous depositing of sodium chloride and anhydrous sulphate until glazerite commences to separate also.

Potassium salts, then, can not be segregated in such a solution beyond a concentration of 10 mols potassium sulphate per 1,000 mols water, its concentration at the points M and L. At these concentrations its precipitation as glazerite begins and is continuous to the end of the evaporation.

THE SYSTEM: SODIUM CHLORIDE, POTASSIUM CHLORIDE, SODIUM SULPHATE, POTASSIUM SULPHATE, MAGNESIUM CHLORIDE, MAGNESIUM SULPHATE, AND WATER.

The equilibria, or constant solutions, for the system containing the magnesium ion in addition to those components assumed to be present in the foregoing case considered, have been determined by van't Hoff and his coworkers.<sup>1</sup> These points are given in Table XXXV. The solid phases are named and the compositions in mols of the components per thousand mols of solvent of the solution with which the solids are in equilibrium is stated. These values were obtained at a temperature of 25° C. That these points of equilibrium are but slightly displaced by change in temperature is shown by the values obtained for the same system, as given in Table XXXVI. These values were obtained at 83° C.

TABLE XXXV.—Equilibria between sodium chloride, potassium chloride, magnesium chloride, sodium sulphate, potassium sulphate, magnesium sulphate, and water at 25° C. Sodium chloride present in excess.

| Solids: NaCl and—                    |                                      |                                      | Mols per 1,000 mols H <sub>2</sub> O. |                                  |                     |                     |                                   |
|--------------------------------------|--------------------------------------|--------------------------------------|---------------------------------------|----------------------------------|---------------------|---------------------|-----------------------------------|
|                                      |                                      |                                      | Na <sub>2</sub> Cl <sub>2</sub> .     | K <sub>2</sub> Cl <sub>2</sub> . | MgCl <sub>2</sub> . | MgSO <sub>4</sub> . | Na <sub>2</sub> SO <sub>4</sub> . |
| MgCl <sub>2</sub> .6H <sub>2</sub> O |                                      |                                      | 1                                     |                                  | 106                 |                     |                                   |
| KCl                                  |                                      |                                      | 44.5                                  | 19.5                             |                     |                     |                                   |
| Na <sub>2</sub> SO <sub>4</sub>      |                                      |                                      | 51                                    |                                  |                     |                     | 12.5                              |
| MgCl <sub>2</sub> .6H <sub>2</sub> O | Carnallite                           |                                      | 1                                     | .5                               | 105                 |                     |                                   |
| KCl                                  | Carnallite                           |                                      | 2                                     | 5.5                              | 70.5                |                     |                                   |
| KCl                                  | Glazerite                            |                                      | 44                                    | 20                               |                     |                     | 4.5                               |
| Na <sub>2</sub> SO <sub>4</sub>      | Glazerite                            |                                      | 44                                    | 10.5                             |                     |                     | 14.5                              |
| Na <sub>2</sub> SO <sub>4</sub>      | Astrakanite                          |                                      | 46                                    |                                  |                     | 16.5                | 3                                 |
| MgSO <sub>4</sub> .7H <sub>2</sub> O | Astrakanite                          |                                      | 26                                    |                                  | 7                   | 34                  |                                   |
| MgSO <sub>4</sub> .7H <sub>2</sub> O | MgSO <sub>4</sub> .6H <sub>2</sub> O |                                      | 4                                     |                                  | 67.5                | 12                  |                                   |
| MgSO <sub>4</sub> .6H <sub>2</sub> O | Kieserite                            |                                      | 2.5                                   |                                  | 79                  | 9.5                 |                                   |
| Kieserite                            | MgCl <sub>2</sub> .6H <sub>2</sub> O |                                      | 1                                     |                                  | 101                 | 5                   |                                   |
| KCl                                  | Glazerite                            | Schönite                             | 23                                    | 14                               | 21.5                | 14                  |                                   |
| KCl                                  | Schönite                             | Leonite                              | 19.5                                  | 14.5                             | 25.5                | 14.5                |                                   |
| KCl                                  | Leonite                              | Kainit                               | 9.5                                   | 9.5                              | 47                  | 14.5                |                                   |
| KCl                                  | Kainit                               | Carnallite                           | 2.5                                   | 6                                | 68                  | 5                   |                                   |
| Carnallite                           | Kainit                               | Kieserite                            | 1                                     | 1                                | 85.5                | 8                   |                                   |
| Na <sub>2</sub> SO <sub>4</sub>      | Glazerite                            | Astrakanite                          | 42                                    | 8                                |                     | 16                  | 6                                 |
| Glazerite                            | Astrakanite                          | Schönite                             | 27.5                                  | 10.5                             | 16.5                | 18.5                |                                   |
| Leonite                              | Astrakanite                          | Schönite                             | 22                                    | 10.5                             | 23                  | 19                  |                                   |
| Leonite                              | Astrakanite                          | MgSO <sub>4</sub> .7H <sub>2</sub> O | 10.5                                  | 7.5                              | 42                  | 19                  |                                   |

<sup>1</sup>Zur Bildung der ozeanischen Salzablagerungen, Braunschweig, 1905-1909; Bul. 33, Bureau of Soils, U. S. Dept. of Agr., 1906, et seq. The Soil Solution, Cameron. Chem. Pub. Co., 1911, p. 111 et seq.



VI  
 TABLE XXXIV.—Equilibria between sodium chloride, potassium chloride, magnesium chloride, sodium sulphate, magnesium sulphate, and water at 83° C. Sodium chloride always present in excess.

| Solids: NaCl and—                    |                                      |             | Mols per 1,000 mols H <sub>2</sub> O. |                                  |                     |                     |                                   |
|--------------------------------------|--------------------------------------|-------------|---------------------------------------|----------------------------------|---------------------|---------------------|-----------------------------------|
|                                      |                                      |             | Na <sub>2</sub> Cl <sub>2</sub> .     | K <sub>2</sub> Cl <sub>2</sub> . | MgCl <sub>2</sub> . | MgSO <sub>4</sub> . | Na <sub>2</sub> SO <sub>4</sub> . |
| MgCl <sub>2</sub> .6H <sub>2</sub> O |                                      |             | 1                                     |                                  | 121                 |                     |                                   |
| KCl                                  |                                      |             | 39                                    | 37                               |                     |                     |                                   |
| Na <sub>2</sub> SO <sub>4</sub>      |                                      |             | 56.5                                  |                                  |                     |                     | 8                                 |
| MgCl <sub>2</sub> .6H <sub>2</sub> O | Carnallite                           |             | 1                                     | 2                                | 117                 |                     |                                   |
| KCl                                  | Carnallite                           |             | 1.5                                   | 10                               | 92                  |                     |                                   |
| KCl                                  | Glazerite                            |             | 39.5                                  | 39                               |                     |                     | 4.5                               |
| Na <sub>2</sub> SO <sub>4</sub>      | Glazerite                            |             | 43.5                                  | 21                               |                     |                     | 11.5                              |
| Na <sub>2</sub> SO <sub>4</sub>      | Vanthoffite                          |             | 51                                    |                                  | 4.5                 | 10.5                |                                   |
| Vanthoffite                          | Loewite                              |             | 35                                    |                                  | 22                  | 12.5                |                                   |
| Loewite                              | Kieserite                            |             | 18                                    |                                  | 45                  | 11                  |                                   |
| Kieserite                            | MgCl <sub>2</sub> .6H <sub>2</sub> O |             | 1                                     |                                  | 120                 | 1                   |                                   |
| KCl                                  | Glazerite                            | Langbeinite | 29.5                                  | 33.5                             | 13                  | 10                  |                                   |
| KCl                                  | Carnallite                           | Kieserite   | 2                                     | 12                               | 86.5                | 5                   |                                   |
| KCl                                  | Langbeinite                          | Kieserite   | 11                                    | 15                               | 76                  | 5                   |                                   |
| Glazerite                            | Na <sub>2</sub> SO <sub>4</sub>      | Vanthoffite | 43                                    | 22.5                             |                     | 7.5                 | 5.5                               |
| Loewite                              | Glazerite                            | Vanthoffite | 34.5                                  | 26.5                             | 8.5                 | 17.5                |                                   |
| Loewite                              | Glazerite                            | Langbeinite | 30                                    | 24.5                             | 12                  | 16.5                |                                   |
| Loewite                              | Kieserite                            | Langbeinite | 16                                    | 10.5                             | 42                  | 14                  |                                   |
| Carnallite                           | MgCl <sub>2</sub> .6H <sub>2</sub> O | Kieserite   | 1                                     | 2                                | 116                 | 1                   |                                   |

The formulas corresponding to the mineralogical names of the components obtained are given below:

|             |  |
|-------------|--|
| Astrakanite | = Na <sub>2</sub> SO <sub>4</sub> .MgSO <sub>4</sub> .4H <sub>2</sub> O.   |
| Bischofite  | = MgCl <sub>2</sub> .6H <sub>2</sub> O.                                    |
| Carnallite  | = MgCl <sub>2</sub> .KCl.6H <sub>2</sub> O.                                |
| Glazerite   | = K <sub>2</sub> Na(SO <sub>4</sub> ) <sub>2</sub> .                       |
| Kainite     | = MgSO <sub>4</sub> .KCl.3H <sub>2</sub> O.                                |
| Kieserite   | = MgSO <sub>4</sub> .H <sub>2</sub> O.                                     |
| Langbeinite | = 2MgSO <sub>4</sub> .K <sub>2</sub> SO <sub>4</sub> .                     |
| Leonite     | = MgSO <sub>4</sub> .K <sub>2</sub> SO <sub>4</sub> .4H <sub>2</sub> O.    |
| Loewite     | = 2MgSO <sub>4</sub> .2Na <sub>2</sub> SO <sub>4</sub> .5H <sub>2</sub> O. |
| Schönite    | = MgSO <sub>4</sub> .K <sub>2</sub> SO <sub>4</sub> .6H <sub>2</sub> O.    |
| Tachhydrite | = 2MgCl <sub>2</sub> .CaCl <sub>2</sub> .12H <sub>2</sub> O.               |
| Vanthoffite | = MgSO <sub>4</sub> .3Na <sub>2</sub> SO <sub>4</sub> .                    |
| Sylvine     | = KCl.   |

*Application.*—This system is illustrated by the mother liquor resulting from the evaporation of sea water. In addition to sodium and potassium chlorides the sulphates of these metals and chlorides and sulphates of magnesium are present. Calcium salts are likewise present, in amounts limited by the solubility of calcium sulphate, and tend slightly to complicate the system still further; that is to say, the ratio of calcium to sulphate ions is small. Likewise, the rarer metals, such as lithium and strontium, and the acid radicals, such as bromide, iodide, and borate, are present, but in amounts insufficient to affect the solubility of the other compounds or the physical properties of the solution.

The data obtained from a study of this system (CaSO<sub>4</sub> being absent) are given in Tables XXXV and XXXVI. One compound, potassium sulphate, has been eliminated algebraically from consideration by expressing it in terms of certain other compounds, since it does not, in fact, separate on evaporating such brines.

The vapor tensions of the various "constant solutions" have been determined at definite temperatures. By observing the vapor tensions it is possible to determine the order in which the successive

solid phases will separate on evaporation. In the table below (Table XXXVII) are given the salts and groups of salts that are crystallized from sea water on evaporation, arranged in the order of the vapor tensions of their constant solutions at 25° C., and hence in the order of the sequence of their precipitation at that temperature. It is to be understood that while these data obtain for 25° C., the evaporation of the solution does not have to be effected at that temperature; this may be accomplished at any desired temperature, and the conditions described in

Table XXXVII are arrived at when the temperature of the solution is again brought to 25° C.

The system here is practically the same as that whose data are given in Tables XXXV and XXXVI, except that here the additional component, calcium sulphate, is introduced. As in the foregoing tables, the mineralogical names of the solid phases are given, together with the composition of the solutions with which they are in equilibrium.

The various invariant points may be located on the diagram (fig. 2). If we "place" on the diagram the point representing the concentration of any solution under consideration, by moving in the direction of the points of lower vapor pressure it is possible to trace the path which the concentrations of the solution on evaporation will follow.

Van't Hoff and his collaborators have shown that, on the evaporation of sea water, hydrated calcium sulphate (following calcium carbonate) is the first solid to separate. This is followed, over a wide range, by the crystallization of sodium chloride, which, it is recalled, continues to separate with all the other solids. The next compound to crystallize is magnesium sulphate, which is followed by a mixture

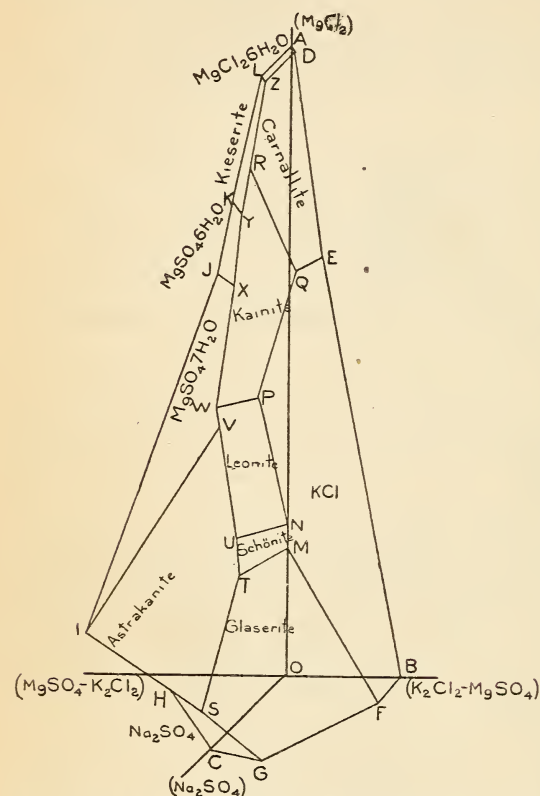


FIG. 2.—Diagram showing the equilibria in the system: Sodium chloride, potassium chloride, magnesium chloride, sodium sulphate, potassium sulphate, magnesium sulphate, and water.

of magnesium sulphate (the heptahydrate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) and kainite ( $\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$ ). This information enables one to determine the concentration of the solution undergoing evaporation as that corresponding to some point on the line WX. The path of concentration must follow this line in the direction of the point of lower vapor tension. From Table XXXVII it is to be seen that the vapor pressure at the point X is lower than that at the point W, from which it is to be concluded that the path leads in the direction of X. At X, an invariant point, a third phase appears, magnesium hexahydrate ( $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ), which, with sodium chloride, the heptahydrate of magnesium sulphate and kainite, comprises the solid phases. Beyond X the heptahydrate ceases to precipitate, and kainite and the hexahydrate crystallize together, until a second invariant point, Y, is reached, beyond which kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ) precipitates instead of the hexahydrate. At R, a third invariant point, carnallite ( $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ ) appears and, together with kainite, kieserite, and sodium chloride, comprises the solid phases. Beyond R kainite no longer occurs, and kieserite and carnallite precipitates together until the fourth invariant point, Z, is reached. There the final products of the evaporation—as is to be seen from Table XXXVII—kieserite, carnallite, sodium chloride, and the magnesium chloride, bischofite ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), are the solid phases. The salts deposited then, from the sea water, or similar solutions, in the order of their crystallizations are: gypsum, sodium chloride, and mixtures of sodium chloride with magnesium sulphate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), with magnesium sulphate and kainite, with kainite and magnesium sulphate hexahydrate ( $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ), with kainite and kieserite, with kieserite and carnallite, and finally with kieserite, carnallite, and bischofite. During these stages of the evaporation the vapor tension of the solution has fallen from some value above 12.2, the vapor tension of the invariant solution at X, to 7.4, the vapor tension of the final solution at Z.

TABLE XXXVII.—Solids obtainable from sea water on evaporation at 25° C., in the order of their crystallization.

| Corresponding point on diagram. | Solids: NaCl and—                               |   |   | Mols per 1,000 mols of $\text{H}_2\text{O}$ . |                         |                 |                 |                          | Vapor pressures in mm. Hg. |                 |
|---------------------------------|---|---|---|---|-------------------------|-----------------|-----------------|--------------------------|----------------------------|-----------------|
|                                 |   |   |   | $\text{Na}_2\text{Cl}_2$                      | $\text{K}_2\text{Cl}_2$ | $\text{MgCl}_2$ | $\text{MgSO}_4$ | $\text{Na}_2\text{SO}_4$ |                            | $\text{CaSO}_4$ |
| S                               | $\text{Na}_2\text{SO}_4$ .....                  | Glazerite.....                                  | Astrakanite...                                  | 42  | 8                       | .....           | 16              | 6                        | 0.06                       | 16.6            |
| T                               | Glazerite.....                                  | Astrakanite.....                                | Schönite.....                                   | 27.5  | 10.5                    | 16.5            | 18.5            | .....                    | .08                        | 16.1            |
| M                               | KCl.....  | Glazerite.....                                  | Schönite.....                                   | 23  | 14                      | 21.5            | 14              | .....                    | .08                        | 15.9            |
| N                               | KCl.....  | Schönite.....                                   | Leonite.....                                    | 19.5  | 14.5                    | 25.5            | 14.5            | .....                    | .09                        | 15.7            |
| U                               | Leonite.....                                    | Astrakanite.....                                | Schönite.....                                   | 22  | 10.5                    | 23              | 19              | .....                    | .08                        | 15.7            |
| V                               | Leonite.....                                    | Astrakanite.....                                | $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ..... | 10.5  | 7.5                     | 42              | 19              | .....                    | .1                         | 14.5            |
| P                               | KCl.....  | Leonite.....                                    | Kainite.....                                    | 9.5   | 9.5                     | 47              | 14.5            | .....                    | .13                        | 13.4            |
| W                               | Leonite.....                                    | Kainite.....                                    | $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ..... | 9.5   | 7.5                     | 45              | 19.5            | .....                    | .09                        | 13.4            |
| Q                               | KCl.....  | Kainite.....                                    | Carnallite.....                                 | 2.5   | 6                       | 68              | 5               | .....                    | .24                        | 12.4            |
| X                               | $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ..... | Kainite.....                                    | $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ..... | 3.5   | 4                       | 65.5            | 13              | .....                    | .2                         | 12.2            |
| Y                               | $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ..... | Kainite.....                                    | Kieserite.....                                  | 1.5   | 2                       | 77              | 10              | .....                    | .21                        | 10.8            |
| R                               | Carnallite.....                                 | Kainite.....                                    | Kieserite.....                                  | 1   | 1                       | 85.5            | 8               | .....                    | .13                        | 9.5             |
| D                               | $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ..... | Carnallite.....                                 | .....   | 1   | .5                      | 105             | .....           | .....                    | .38                        | 7.5             |
| Z                               | Carnallite.....                                 | $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ..... | Kieserite.....                                  | 1   | 5                       | 100             | 5               | .....                    | .15                        | 7.4             |

The sequence in which the solids are deposited at 83° C. is practically the same as for the temperature 25° C.

Certain other solids are deposited over narrow ranges; these are of but minor importance and for that reason their consideration is omitted from this discussion.

The composition and specific gravity (at 40° C.) of sea water and of the mother liquors from the sodium chloride and magnesium sulphate precipitations are given in the subjoined table.<sup>1</sup> The values were determined for unevaporated sea water and for the mother liquors at the point where the respective solids had just begun to precipitate.

TABLE XXXVIII.—*Analysis of sea water and of mother liquors obtained at certain stages in the evaporation of sea water.*

| Solution.                                  | Specific gravity. | NaCl.                      | KCl.                       | MgCl <sub>2</sub> .        | MgSO <sub>4</sub> .        |
|--|-------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| Sea water.....                             | 1.0258            | <i>Per cent.</i><br>2.9424 | <i>Per cent.</i><br>0.0505 | <i>Per cent.</i><br>0.3219 | <i>Per cent.</i><br>0.2477 |
| Mother liquor from NaCl.....               | 1.2100            | 22.2230                    | .4050                      | 2.4420                     | 1.8714                     |
| Mother liquor from MgSO <sub>4</sub> ..... | 1.3200            | 12.1050                    | 2.4970                     | 14.7960                    | 8.6760                     |

THE SYSTEM: SODIUM CHLORIDE, POTASSIUM CHLORIDE, CALCIUM CHLORIDE, MAGNESIUM CHLORIDE, AND WATER.

The further complication of the system just considered by the addition of the calcium ion is, practically speaking, impossible. Calcium and sulphate ions do not exist together in solution beyond a certain small concentration determined by the slight solubility of calcium sulphate. The solubility of calcium sulphate in aqueous solutions has been discussed by Cameron and Bell.<sup>2</sup>

The addition of calcium ions, then, in effect changes the system to one in which the chloride ion is the only anion present. This is not strictly true, as some calcium sulphate will still be present, but in amounts insufficient to displace to any great extent the equilibria of the system.

Some of the invariant points of the system, sodium chloride, potassium chloride, magnesium chloride, calcium chloride, and water, are given in Table XXXIX.

TABLE XXXIX.—*Data for the system: Sodium chloride, potassium chloride, calcium chloride, magnesium chloride, and water at the temperatures indicated.*

| Saturated in NaCl and—                    |                  | Temperature °C. | Mols per 1,000 mols H <sub>2</sub> O. |                     |                                  | Fig. 3. |
|---|------------------|-----------------|---------------------------------------|---------------------|----------------------------------|---------|
|   |                  |                 | CaCl <sub>2</sub> .                   | MgCl <sub>2</sub> . | K <sub>2</sub> Cl <sub>2</sub> . |         |
| CaCl <sub>2</sub> .6H <sub>2</sub> O..... | KCl.....         | 25              | 146                                   | .....               | 11                               | L       |
| CaCl <sub>2</sub> .2H <sub>2</sub> O..... | KCl.....         | 83              | 249                                   | .....               | 11                               | L       |
| Magnesium chloride.....                   | Tachhydrite..... | 25              | 91                                    | 51.5                | 0.5                              | H       |
| Magnesium chloride.....                   | Tachhydrite..... | 83              | 141                                   | 45.5                | 0.5                              | H       |
| CaCl <sub>2</sub> .6H <sub>2</sub> O..... | Tachhydrite..... | 25              | 122                                   | 34.5                | 2                                | J       |
| CaCl <sub>2</sub> .2H <sub>2</sub> O..... | Tachhydrite..... | 83              | 239                                   | 0.5                 | 0.5                              | J       |
| CaCl <sub>2</sub> .H <sub>2</sub> O.....  | Carnallite.....  | 25              | 142                                   | 5                   | 9.5                              | K       |
| CaCl <sub>2</sub> .2H <sub>2</sub> O..... | Carnallite.....  | 83              | 216                                   | 27                  | 10.5                             | K       |

<sup>1</sup> Ann. chim. phys., 27, 92 (1849).

<sup>2</sup> Bul. 33, Bureau of Soils, U. S. Dept. Agr., 1906.

From a consideration of the data in Table XXXIX it becomes evident that there is no concentration within the limits defined at which potassium chloride may be crystallized alone. It crystallizes together with calcium chloride and enters into combination with magnesium chloride to form carnallite, rather than segregating in the mother liquor. On the contrary, where the chlorides of calcium and magnesium are present in amounts exceeding that of the potassium chloride, the latter on evaporation would be largely eliminated from the solution in the manner mentioned. ✕

*Application*—Such a system is typified by the mother liquors resulting from the evaporation of natural brines. Present are the chlorides of sodium, calcium, magnesium, and potassium. The ratio of calcium to sulphate ions is large.<sup>1</sup> In addition to these substances are to be found also small amounts of bromides and, in rarer instances, strontium and other metals of the alkaline and alkaline earth groups. These are present in too small amounts, generally, to affect greatly the solubility of the other components or the physical properties of the solution.

On the evaporation of such a bittern the first solid to separate is sodium chloride. This salt continues to separate throughout the entire evaporation, but its solubility in a concentrated solution of calcium and magnesium chlorides is so low that the amounts in which it is eventually present become negligible. This system is radically different from sea-water bitterns, as sulphates are absent and calcium chloride is present in large amounts. None of the various solids which contain the sulphate radicals are here possible. The equilibria of the system are represented in figure 3, and the data for two temperatures are given in Table XXXIX.

Several concentration paths are possible on evaporation, depending on the relative concentrations of the various components. In practice, both calcium and magnesium would be in such excess over potassium that potassium chloride could not be the solid to separate following sodium chloride. The point J, the point of final desiccation for this system, would be approached from the calcium chloride, the bischofite or the tachydrate field. Potassium chloride (sylvine) would not be deposited unless the concentration relative to that of calcium and magnesium chlorides exceeded that represented by the point K (9.5 mols potassium chloride; 142 mols calcium chloride; 5 mols  $MgCl_2$ ). With the amount of potassium chloride small and constant, the relative amounts of calcium and magnesium chlorides would determine whether the concentration path would have its origin in (a) the bischofite field or (b) the tachydrate field or (c) the calcium chloride field.

<sup>1</sup> If the mother liquor has been treated for the recovery of bromide, the sulphuric acid with which it is acidified before distillation has been removed as calcium sulphate through precipitation with lime.

(a) If in the first, it would follow one of two courses, depending on the ratio between the potassium and calcium chlorides. It would merge with the line AF and would pass toward F, where tachhydrite would appear, and beyond which bischofite would disappear, would move thence toward I, where calcium chloride would appear and together with tachhydrite (and sodium chloride) would continue to deposit until J was reached; or, it would merge with the line DH, along which bischofite and carnallite would crystallize until H was reached, at which tachhydrite would appear as a solid phase and beyond which (toward J) bischofite would cease to come down.

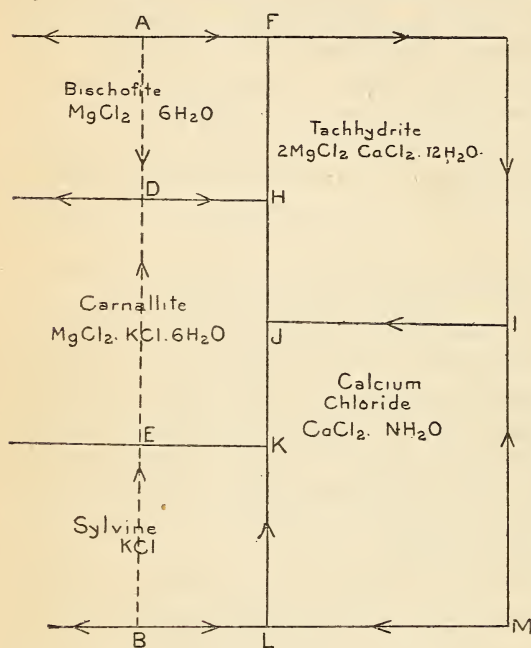


FIG. 3. Diagram showing the equilibria in the system: Sodium chloride, potassium chloride, calcium chloride, magnesium chloride, and water.

carnallite, or with the line MJ; calcium chloride would then be deposited until the concentration became such (as represented by I) that tachhydrite would likewise crystallize. Thence the two (with sodium chloride) would crystallize until J was reached. At J, the four solids, sodium chloride, calcium chloride, tachhydrite, and carnallite, would continue to precipitate until complete desiccation was attained.

In the crystallization of a solution containing chlorides of potassium, calcium, and magnesium, carnallite is invariably present in the final mixture of salts. This compound, however, never separates alone from such a solution, but always with mixtures and compounds

Carnallite and tachhydrite (with sodium chloride) would continue, then, to deposit together until J was reached. (b) If the path had its origin in the tachhydrite field, it would merge either with the line HJ or FJ and would follow these lines in the manner just described. (c) If it had its origin in the calcium chloride field—depending on the ratio between the potassium and magnesium chlorides—it would merge either with the line KJ and follow it, toward J, with the simultaneous crystallization of calcium chloride and carnallite, or with the line MJ; calcium chloride would then be deposited until the concentration became such (as represented by I) that tachhydrite would likewise crystallize. Thence the two (with sodium chloride) would crystallize until J was reached. At J, the four solids, sodium chloride, calcium chloride, tachhydrite, and carnallite, would continue to precipitate until complete desiccation was attained.

of calcium and magnesium chlorides. Its deposition occurs over a wide range, so that a high concentration or segregation of potassium chloride in the solution is impossible.

The concentration of the solution in potassium chloride ( $K_2Cl_2$ ) at H is only 0.5 mol per 1,000 mols water, and at J only 2 to 0.5 mols, depending on the temperature. The formation of a compound or a mixture of compounds rich in potassium chloride or the segregation of the potassium chloride in the mother liquors seems equally impracticable.

As calcium and magnesium chlorides have a commercial value, due to their use in refrigeration and for dressing road surfaces, it is doubtless more profitable to carry the evaporation at once to dryness for the recovery of the solid residue of calcium and magnesium chlorides.

#### THE PREPARATION OF POTASSIUM COMPOUNDS BY COMMERCIAL METHODS.

From the foregoing paragraphs it is seen what compounds of potassium of commercial and manurial value it is possible to obtain from saline mixtures by simple evaporation processes. In addition to these, numerous other processes, some of which are quite involved, have been devised for the separation of potassium salts from saline mixtures and the transformation of less valuable compounds of that element into the more valuable. The more important of the processes, some of which are in actual operation, are given in outline below.

##### PRECIPITATION BY SULPHURIC ACID.

The treatment of mixtures of sodium and potassium chlorides with concentrated sulphuric acid for the separation of potassium compounds has been suggested so frequently that space is given its consideration here. In this brief discussion it is presumed (1) that the salts are treated in concentrated solution; (2) that the solution is saturated practically with respect to both the salts; and (3) that the liberated hydrochloric acid is removed from the solution. The system, then, is made up of the compounds, sodium sulphate, potassium sulphate, and water. The products of crystallization from such a solution have been discussed in a foregoing paragraph. It will be recalled that a deposition of sodium sulphate from such a solution is followed by that of glazerite ( $K_2SO_4 \cdot 3Na_2SO_4$ ) and that the two continue to separate together until complete desiccation has been attained. No separation, therefore, is theoretically possible. This conclusion is based on the further assumption that sulphuric acid is added in an amount sufficient to form the normal salts of

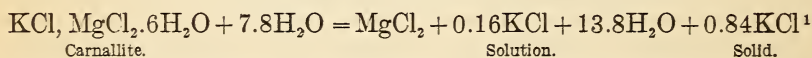
sodium and potassium. The addition of acid in excess over that amount would introduce a new compound, sulphuric acid, and would displace the invariant points.

#### PRECIPITATION BY SODIUM SULPHATE.

The addition of a sulphate in various amounts to the solution of the chlorides of sodium and potassium has been suggested as a method of separation of the potassium salts. Such a procedure would result in a solution representing a system containing both chlorides and sulphates of sodium and potassium. The invariant points of this system are given in Table XXXIV, from which data it is evident that potassium salts alone can not be precipitated or left in solution: Glazerite, over a wide range, is invariably a solid phase.

#### PREPARATION OF POTASSIUM SALTS FROM CARNALLITE.

Potassium chloride can be separated from the double chloride of potassium and magnesium, carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ). Water acts upon this compound, dissolving from it relatively more of the soluble constituent, magnesium chloride, and precipitating potassium chloride, usually in finely crystalline form. This action, at  $25^\circ$ , continues until the concentration of the solution reaches 72.7 mols magnesium chloride and 11.5 mols potassium chloride to 1,000 mols water, or on the percentage basis, 26.8 per cent magnesium chloride and 3.3 per cent potassium chloride. In contact with this solution carnallite is a stable phase; i. e., it is not further acted upon by the solution. The reaction may be expressed by the equation:



From the equation it is evident that if just sufficient water is added to the carnallite to decompose it completely, 84 per cent of the potassium chloride present therein is recovered in the solid form. If the operation be carried out at higher temperatures, the equilibrium point is displaced. More potassium chloride goes into solution which, of course, is reprecipitated on cooling. On the further concentration of the solution by evaporation it is obvious that carnallite will be precipitated. Finally, carnallite and magnesium chloride will precipitate to complete desiccation. At the point where the precipitation of magnesium begins the solution has a potassium chloride content of 0.53 per cent.<sup>2</sup>

In actual practice the process of extracting potassium chloride from carnallite is much less simple than that described, as the carnallite obtained from the mines is far from pure. It contains about

<sup>1</sup> Deutschlands Kalibergbau, 1907. Erdmann, Die Chemie u. Industrie der Kalisalze.

<sup>2</sup> Erdmann, loc. cit.



24 per cent of rock salt, 14 per cent of kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ), and 3 per cent of other impurities, mostly insoluble, leaving less than 60 per cent of carnallite. The potassium chloride resulting from the impure carnallite has to be further purified, not only from magnesium chloride but also from sodium chloride. These are removed by solution. From the impure mother liquor artificial carnallite is prepared, from which potassium chloride is obtained by a repetition of the process.<sup>1</sup>

From the systems represented by the bittern from sea water, the potassium chloride may be separated by eliminating from the systems all the saline components except potassium, sodium, and magnesium chlorides. This is accomplished by a suitable manipulation of concentrations and temperatures to bring about a deposition of the double chloride of potassium and magnesium,  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ , carnallite with, of course, sodium chloride. The process as devised by Ballard and modified by Merle<sup>2</sup> consists in evaporating sea water in the usual way until it has deposited about four-fifths of its sodium chloride content. Its specific gravity at this point is about 1.24. The bittern is diluted with one-tenth its volume of water and is cooled to  $0^\circ \text{F}$ ., whereupon sodium sulphate deposits. The mother liquor from this crystallization is further evaporated by boiling to a density of 1.331, at which a large part of the remaining sodium chloride crystallizes out. On cooling, "the whole of the potash in the form of the double chloride of magnesium and potassium" is precipitated. Potassium chloride is then recovered from the carnallite in the manner described in a previous paragraph.<sup>3</sup>

The solution resulting from the treatment of carnallite, containing all the magnesium and about one-fourth of the potassium, is added to a fresh portion of bittern undergoing treatment.

Meyerhoffer<sup>4</sup> describes a unique method for obtaining potassium chloride from carnallite in accordance with which the carnallite is heated to a temperature of  $167^\circ$ , whereupon three-fourths of the potassium chloride separates as such in the crystalline form, while the magnesium chloride appears as a melt. The potassium chloride is removed from the magnesium chloride in any suitable manner. On cooling to  $115^\circ$  most of the remaining potassium chloride, which has remained in solution in the melt of magnesium chloride, separates in the form of carnallite. The latter may be removed and again treated as described. The magnesium chloride remaining is of a fair degree of purity.

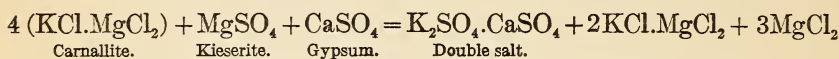
<sup>1</sup> Cf., also Korndorff, D. R. P. 18845; Meyerhoffer, "Purification of Natural Carnallite" (Fusion methods), D. R. P. 92812; 109101.

<sup>2</sup> From Elements of Chemistry, Pt. II, Inorganic Chem., Miller; 3d ed., 1875, p. 355, footnote.

<sup>3</sup> Cf., D. R. P. 19256, to Mineral Salts Production and Moorlands Reclamation Co. (Ltd.), London; Bernhardt, D. R. P. 12498.

<sup>4</sup> D. R. P., 91906.

On the basis of the reaction taking place between potassium chloride and calcium and magnesium sulphates, whereby a double salt of potassium and calcium,  $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ , is formed, Hake<sup>1</sup> has devised a method for the preparation of potassium sulphate in which carnallite is used as the source of the potassium chloride. Carnallite (containing 16 per cent KCl) is dissolved in water to a concentrated solution; to the resulting solution, hot or cold, a fine meal of kieserite and gypsum is added. The reaction ensuing is expressed by the equation (with water of crystallization omitted):



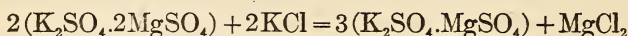
Potassium sulphate is recovered from the double salt of potassium and calcium sulphate by calcining and lixiviating. Calcium sulphate remains as a solid residue.<sup>2</sup>

#### PREPARATION OF "KALIMAGNESIA" OR POTASSIUM-MAGNESIUM SULPHATE.

The preparation of a double salt, potassium-magnesium sulphate,  $K_2SO_4 \cdot MgSO_4$ , known by the trade name of "kalimagnesia," is justified where the raw material started with is the less desirable chloride of potassium, or double chloride, and where it is desired to obtain a product richer in the element potassium than the raw material. The double sulphates of potassium and magnesium occurring in nature are:

|                  |                                      |
|------------------|--------------------------------------|
| Schoenite.....   | $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ . |
| Leonite.....     | $K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ . |
| Langbeinite..... | $K_2SO_4 \cdot 2MgSO_4$ .            |

Of these, leonite is rarely worked commercially because of its unusual and dispersed occurrence. Langbeinite at times is merely sorted mechanically to free it from the other minerals with which it occurs in nature. Chemically, its potassium content may be increased—its magnesium content may be decreased—by treating it with potassium chloride solution. One-fourth of the magnesium is thus removed and the double salt containing one molecule each of potassium and magnesium sulphate is obtained. The reaction may be represented by the equation:



The preparation of *kalimagnesia* from kainite ( $KCl \cdot MgSO_4 \cdot 3H_2O$ ) is the more profitable, since in this operation the less valuable chloride is converted into the more valuable sulphate. The process is simply a recrystallization from water. If the temperature be not too high,

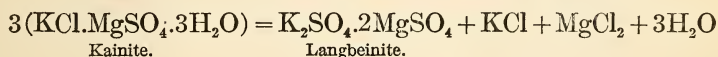
<sup>1</sup> D. R. P., 9108.

<sup>2</sup> Cf. also Ferber, "Preparations of Pure Potassium-Magnesium Sulphate from Carnallite and Kieserite," D. R. P., 5068; Bernhardt, "Utilization of Brines Containing Potassium Compounds," D. R. P., 10821.

the double sulphate precipitates, while the magnesium chloride remains in solution.<sup>1</sup> The reactions in the main proceeds as is indicated by the following equation:



A process in more common practice is one originated by Precht,<sup>2</sup> in accordance with which kainite is heated in a sieve drum to a temperature of 120° to 145°, under a steam pressure of 2 to 7 atmospheres, with magnesium chloride solution (or with liquors from previous treatments) of proper concentration. A finely crystalline precipitate of langbeinite results, which, by means of the sieve, is separated from the coarser impurities (such as rock salt, introduced with the crude kainite). The reaction is represented as follows:



From the mother liquor potassium chloride may be crystallized. The mother liquor resulting from the latter operation, containing principally magnesium chloride, is used for treating fresh portions of kainite. The langbeinite may be converted into kalimagnesia in the manner mentioned.

Kubierschky<sup>3</sup> has prepared langbeinite by boiling the highly concentrated liquors from schoenite with artificial carnallite ( $\text{MgCl}_2.\text{KCl}.6\text{H}_2\text{O}$ ).

The preparation of kalimagnesia finds its most valuable application in the transformations of potassium compounds, entirely as chlorides, into the sulphate compounds. This action may be expressed by the general equation:



This transference is accomplished in practice by adding solid potassium chloride in requisite amount to a solution of magnesium sulphate at 30° C. and of a density of 1.32. The mixture is stirred until the solution shows a content in chloride of 20 to 22 per cent. This composition indicates the point at which the transformation is complete. The resulting precipitate is artificial schönite,  $\text{K}_2\text{SO}_4.\text{MgSO}_4.6\text{H}_2\text{O}$ . The magnesium sulphate solution employed is prepared from kieserite or "bittersalt,"  $\text{MgSO}_4.7\text{H}_2\text{O}$ .

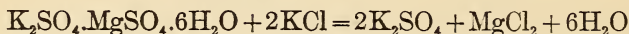
Potassium sulphate, the simple salt, may be produced by modifications of the process just described. Relatively larger amounts of the potassium chloride are necessary, and it is essential that the solution be carefully maintained within certain limiting values of

<sup>1</sup> Cf., also Vorster and Gruneberg, "Utilization of Mother-liquors Resulting in the Preparation of Schönite from Kainite," D. R. P., 28772.

<sup>2</sup> D. R. P., 10637; 13421; 19456.

<sup>3</sup> D. R. P., 222623.

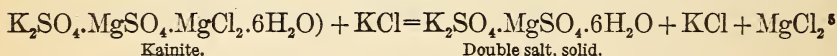
temperature and concentration. It has been found preferable to prepare schoenite as an intermediate compound and convert that into potassium sulphate by treating it with potassium chloride in the proportions of two mols of potassium chloride to one of the schoenite. The reaction takes place in accordance with the equation:



Best results are obtained at a temperature of 60° to 70°. The progress of the reaction may be followed by observing, titrimetrically, the chloride content of the solution. At its completion the chlorine content should be from 18 to 20 per cent. If the temperature is allowed to fall below 55°, potassium chloride separates also.<sup>1</sup> Improvements in the process are proposed by Borsche.<sup>2</sup>

Potassium-magnesium sulphate ( $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ) results, according to Ferber,<sup>3</sup> when purified carnallite is added to a solution of magnesium sulphate (kieserite) of a specific gravity of 1.198 at room temperature until its density reaches 1.270.

For the preparation of potassium-magnesium sulphate and potassium chloride from kainite, Dupré<sup>4</sup> recommends the treatment of the latter with one-third to one-half the equivalent amount of sylvinit (or with an equivalent mixture of potassium and sodium chloride) in hot solution. The ensuing reaction is represented as follows:



Schönite may be prepared, according to a method by Dupré and Hake,<sup>6</sup> by treating kainite with a saturated solution of magnesium chloride at 20° to 25° C. One-third of the potassium of the kainite is carried into solution, the other two-thirds taking the form of schoenite. Schoenite may be prepared also from carnallite and magnesium sulphate.<sup>7</sup> Grüneberg<sup>8</sup> prepares schönite from carnallite, and schoenite from kainite.<sup>9</sup>

#### PREPARATION OF POTASSIUM CHLORIDE AND OTHER POTASSIUM SALTS.

Junger<sup>10</sup> obtains high-grade potassium chloride by treating crude potassium salts low in magnesium, such as sylvinit (potassium chloride and sodium chloride, a natural mixture) and "hartsalz"

<sup>1</sup> See also a process by Grüneberg (D. R. P. 4933).

<sup>2</sup> D. R. P. 2173; Cf. also Nos. 10642, 10701, 11028, 12875, 17795.

<sup>3</sup> D. R. P. 5068.

<sup>4</sup> D. R. P. 53237.

<sup>5</sup> See also process by Bernhardt (D. R. P. 10820) for the preparation of potassium-magnesium sulphate from brines containing potassium compounds.

<sup>6</sup> D. R. P. 6053, 8021.

<sup>7</sup> Cf. D. R. P. 27404, to Consolidirte Alkaliwerke.

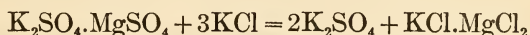
<sup>8</sup> D. R. P. 5607.

<sup>9</sup> D. R. P. 10754, 18947.

<sup>10</sup> D. R. P., 102075.

(containing 20 to 25 per cent kieserite, 55 per cent rock salt, and 2 to 8 per cent anhydrite) with mother liquors obtained in certain stages of the operation. The solution is effected at boiling temperature. On being cooled below zero degrees, potassium chloride precipitates.<sup>1</sup>

Potassium sulphate may be prepared from potassium chloride and schoenite,  $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ , the latter in hot saturated solution, by means of the reaction represented by the equation:

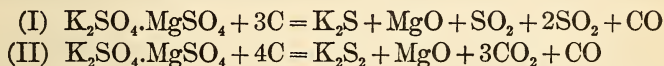


Twice the amount of schönite required by theory must be used, as one-half remains in solution. The temperature should be maintained above 40° C., as below that temperature, KCl, schönite and carnallite crystallize in the order named.<sup>2</sup>

Brunjes<sup>3</sup> has patented a process for the preparation of potassium sulphate from kieserite or kainite and potassium chloride, which depends on the use of alcoholic solution. One equivalent of kainite is added to 1.5 to 2 equivalents potassium chloride or 1 equivalent of kainite to 1 equivalent potassium chloride; this is dissolved in the least possible amount of water—460 to 600 parts. To 1 part of alcohol (by volume) is added 0.25 to 0.5 part of the solution. This results in the precipitation of potassium sulphate. When the alcohol is distilled from the mother liquor, potassium chloride precipitates. On the further evaporation of the remaining solution, pure carnallite precipitates.

In this connection a process by Wibel<sup>4</sup> may be mentioned in which amyl alcohol is used to dissolve calcium and magnesium chlorides from mixtures of sodium, potassium, calcium, and magnesium chlorides and magnesium sulphate.

Precht<sup>5</sup> has devised a method for the preparation of potassium sulphate from potassium magnesium sulphate, whereby (I) the latter is heated with 12.2 per cent of carbon. Potassium sulphide and carbon result. Larger proportions of carbon yield the bisulphide. The reactions may be expressed:



Potassium sulphide is separated from the magnesium by leaching. (II) Potassium sulphate results when potassium-magnesium sulphate

<sup>1</sup> Cf. also Maures, "Extraction of Potassium Chloride from Crude Potassium Salts," D. R. P., 166558 (crystallization method); Meyerhoffer, "Extraction of Potassium Chloride or Potassium Sulphate from Natural Minerals," etc., D. R. P. 98344.

D. R. P. 132474, to Speyerer & Co., relates to the separation of sylvine from naturally occurring mixtures of sylvine, rock salt, and kieserite (known as hartsalz) and from a mixture of sylvine and rock-salt (known as sylvinit); Myerhoffer (D. R. P. 91906); Cf. above.

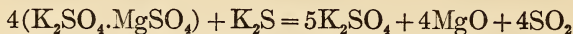
<sup>2</sup> Cf. also Grüneberg, D. R. P. 10753. E. Meyer, D. R. P. 18924.

<sup>3</sup> D. R. P. 11, July, 1877.

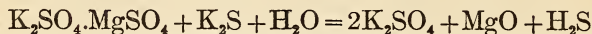
<sup>4</sup> D. R. P. 18226

<sup>5</sup> D. R. P. 15747.

is treated with potassium sulphide, formed as in (I). This is accomplished in two ways: (a) By heating the double salt with dry potassium sulphide, whereupon a reaction ensues which may be represented:



and (b) by heating an aqueous solution of the double salt with potassium sulphide. The reaction which takes place may be expressed as follows:

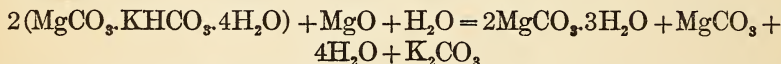


Or, potassium sulphate is obtained as the result of one reaction when the double salt is fused with a smaller amount of carbon—1 to 3 atoms, or 4 to 12 per cent—as indicated in the following equation:



Precht<sup>1</sup> has described an apparatus to be used in the manufacture of potassium sulphate from potassium magnesium sulphate and potassium chloride. Dupré<sup>2</sup> employs ammonia in the separation of potassium sulphate from solutions containing other potassium salts and salts of other metals.<sup>3</sup>

A patent<sup>4</sup> has been granted the Deutsche Solvay-Werke Aktien Gesellschaft covering a process for the preparation of potassium carbonate from the double acid-potassium-magnesium carbonate and magnesia:



and the Salzbergwerke Neu-Stassfurt,<sup>5</sup> covering a process in which potassium carbonate is prepared in an analogous manner, the difference being that potassium hydroxide is employed instead of magnesium oxide.<sup>6</sup>

#### THE POSSIBLE OCCURRENCE OF SEGREGATIONS OF POTASSIUM SALTS IN THE UNITED STATES.

In the search for deposits of potassium salts in the United States two sorts of deposits have been considered, namely, continental and marine.

The former, continental, are those which have resulted from the desiccation of inland seas or lakes; while the latter, marine, are the product of the evaporation of arms of the ocean which have become isolated from the main body of the ocean through the formation of bar reefs. The latter would be analogous to the Stassfurt deposits.

<sup>1</sup> D. R. P., 14534.

<sup>2</sup> D. R. P., 68572.

<sup>3</sup> Cf. also Bernhardt, "Manipulation of Brines which contain Potassium Compounds," D. R. P., 10,821 Recovery of potassium sulphate from magnesium sulphate or schoenite and potassium chloride.

<sup>4</sup> D. R. P., 135329.

<sup>5</sup> D. R. P., 211798.

<sup>6</sup> Cf. also Grun, "Verfahren zur Darstellung hoch prozentigen Pottasche aus Schlempekohle" D. R. P. 210273; Bauer, "Verfahren zur Herstellung hochprozentiger bzw. technisch reiner pottasche aus Schlempekohle" D. R. P., 191105.

## CONTINENTAL.

Among the saline deposits in the United States, theoretically, are deposits of both kinds. These have been (or are being) subjected to scrutiny to discover if therein there may be potassium salts, as well as sodium. The research for continental deposits has been confined to those regions which, it is known, were once covered by inland seas. Such lakes were of sufficiently recent occurrence for their marks to remain on the face of the country where they existed. For deposits of salt to have formed it is not sufficient that these areas were submerged by lakes; it is necessary that the lakes shall have disappeared through desiccation rather than through drainage.

Continental deposits have been sought in the undrained basins of the western part of the United States. As the basins are unfilled by sedimentary or detrital material it was hoped that the saline residues would be found on the floor of the basins. Such has been the case in some instances, while in others there are indications that sufficient detrital matter has been carried into the lowest depressions of the basins to cover any saline matter once deposited there.

The undrained basins of the West may be classified as follows: (1) the Lahontan Basin; (2) the Lake Bonneville Basin; (3) the group of small basins found in southern and central California and southern Nevada; and (4) other basins of slight importance, such as the Salton Basin, formerly of great interest, but now resubmerged; the lake basins of northeastern California and southeastern Oregon and arid basins of New Mexico and small basins bordering the arid area.

## THE LAHONTAN BASIN.

The core of the basin in the northwestern and central part of Nevada, during the Quaternary period of greatest lake expansion, was a single great lake. Its history has been studied by Russell,<sup>1</sup> who gave it the name Lake Lahontan. The basin is nearly a unit, the divides now evident being low or discontinuous. The old lake at present is represented by a few remnants, such as the Pyramid, Winnemucca, and Walker Lakes and by a number of sinks, playas, and saline marshes. The salts now present on its surface, in the form of crusts or brines, are certainly far less than the salts which one reasonably can assume to have been present in the larger lake. Russell accordingly has assumed that the saline material has been buried by alluvial coverings and subsequent investigation has upheld this conclusion. It is reasonably certain that the original saline constituents of the Lahontan Lake water underlie the floor of the present basin, either as crystalline deposits or as salt-impregnated strata of alluvial material.

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<sup>1</sup> Monograph XI, U. S. Geol. Survey.

The rocks of the basin and its drainage area are largely igneous, though for the most part nonpotassic. Consequently it is to be concluded that the salts in the early lake were largely sodium salts and alkaline in character. In the deposition of these salts it is impossible to say from an examination of surface conditions whether the potassium was crystallized at all or, if so, whether in segregated strata or as a crystalline mixture, or whether the mother liquor from the sodium salts deposition, containing the potassium salts, was or was not disseminated through the saline and alluvial strata. These questions can only be settled by boring, a work which the United States Geological Survey is now undertaking. Already a boring several hundred feet deep has been sunk in the Humboldt Basin, a depression of the Lahontan, where the surface conditions indicate that the bottom of the basin may be reached. So far, only alluvial matter has been encountered; and the water obtained from the boring, instead of being a brine, is surprisingly fresh, owing to the probable fact that the boring has reached the underground course of the Carson River.

#### BONNEVILLE BASIN.

In northwestern Utah and extending across the State borders into eastern Nevada is a somewhat smaller basin, recorded by Gilbert <sup>1</sup> as Lake Bonneville. This basin is also a topographic unit and was once occupied by a great Quaternary lake. The last remnant of this lake is found in the present Great Salt Lake, of Utah. The Bonneville basin differs from the Lahontan in that it is set in Paleozoic sediments, instead of rocks of igneous origin. It is to be expected, therefore, that its salines are largely neutral salts rather than alkaline, consisting mainly of the chlorides and sulphates of sodium and magnesium. That such is actually the case is seen from the analysis of the water of Great Salt Lake (cf. Table II).

It is to be expected that potassium salts would have been present in Lake Booneville only in small amounts, and such seems to have been the case from the analysis of water from its remnant—the Great Salt Lake. It is possible that at some previous time the lake may have gone completely to dryness when the saline accumulations of the preceding age were deposited, and that the salts of the present lake represent the accumulation of a more recent age. There is no evidence at hand, however, to substantiate such a supposition.

Desiccation has taken place in the Great Salt Lake to the point of saturation with respect to sodium sulphate and of high concentration in sodium chloride. Crystallization is now taking place in the lake to the extent, at least, that sodium sulphate precipitates during cold weather, forming a crystalline crust on the surface. The crystals doubtless fall to the bottom of the lake, though it has

<sup>1</sup> Monograph I., U. S. Geological Survey.



not been established that there is an accumulation of saline material on the bottom.

Neither the probable geological history of the Bonneville Basin nor the character of the rocks in which it lies offers any indication of the presence of potash, and a negative conclusion may be considered warrantable.

SMALL BASINS OF CENTRAL AND SOUTHERN CALIFORNIA AND SOUTHERN NEVADA.

The region south and southwest of the Lahontan Basin is similarly lacking in seaward drainage. This area likewise was occupied by lakes during an earlier period. The topography of the country is such that it is divided by high and continuous mountains into a number of small basins, each with its individual characteristics. In this area are included the Mojave Desert and Searles, Saline, Amargosa, and Death Valleys. The rim rocks of these basins are varied and have been but little studied. It is known, however, that surrounding them lie rocks of both igneous and sedimentary origin. The basement granites of the Sierra Nevada are exposed in places in the western part of the area, especially toward the south.

Of particular interest among the basins of this group is the Searles Marsh, or Lake, in San Bernardino County, Cal., which has been found in the last stages of desiccation. At present the lake, or dried-up remnant of a lake, covers an area of 11 square miles and is of unknown depth. It is covered by a crust of saline material, beneath which lies a mixture of saline and clayey material. The saline crust has a thickness of 75 to 100 feet and is composed principally of sodium chloride, sulphate, carbonate, and borate. Considerable segregation has taken place in the crust, though the stratification is not at all well defined, and there is no strict demarcation between the saline and clayey strata, but rather a gradual transition from the one to the other.

Various crystalline saline minerals are found intermixed with the loosely defined strata. Among these are halite ( $\text{NaCl}$ ), thenardite ( $\text{Na}_2\text{SO}_4$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), gaylussite ( $\text{Na}_2\text{Ca}(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$ ), borax, hanksite ( $\text{Na}_2\text{K}(\text{SO}_4)_3(\text{CO}_3)_2\text{Cl}$ ), etc. Both the saline and clayey strata are impregnated with brine which contains sulphate, chloride, carbonate and borate of sodium and, in addition, potassium and ammonium salts. At certain levels hydrogen sulphide is also present. The carbonates and borates render the solution alkaline. Its salinity is about 30.34 per cent by weight.

The determination of potassium in 6 samples of the brine from as many different parts of the lake gave an average value of 6.73 per cent  $\text{K}_2\text{O}$  in the total solids; the extreme values were 7.63 and 6.06 per cent. These analyses were made by A. R. Merz of the Cooperative Laboratory, at the Mackay School of Mines, Reno, Nev., and were duplicated by J. G. Smith, of the Bureau of Soils.

TABLE XL.—*Analyses of brine from Searles Lake.*

[Potassium oxide recorded as per cent of total solids.]

| Number of sample. | Total solids, grams per 100 c. c. | K <sub>2</sub> O per cent. |
|-------------------|-----------------------------------|----------------------------|
| 198               | 44.29                             | 7.63                       |
| 199               | 44.69                             | 6.23                       |
| 200               | 43.66                             | 6.89                       |
| 201               | 42.86                             | 6.06                       |
| 202               | 43.96                             | 7.27                       |
| 203               | 43.45                             | 6.57                       |

The following complete analysis of the brine from the Searles Marsh is by W. H. Ross, of the Bureau of Soils. The sample was collected by E. E. Free, of the same bureau, from a well on the marsh designated as A7.

TABLE XLI.—*Results of analysis of brine from Searles Lake.*

[Expressed in percentages of the anhydrous solids.]

| Constituent.          | Quantity. | Constituent.                         | Quantity. | Constituent.                        | Quantity. |
|-----------------------|-----------|--------------------------------------|-----------|-------------------------------------|-----------|
| Na.....               | 33.57     | Mn.....                              | None.     | I.....                              | 0.094     |
| K.....                | 6.06      | Cu.....                              | None.     | SO <sub>4</sub> .....               | 12.96     |
| Li.....               | .01       | Al <sub>2</sub> O <sub>3</sub> ..... | 0.012     | CO <sub>2</sub> .....               | 6.70      |
| Rb.....               | None.     | Fe <sub>2</sub> O <sub>3</sub> ..... | .003      | PO <sub>4</sub> .....               | .30       |
| Ca.....               | None.     | SiO <sub>2</sub> .....               | .023      | NO <sub>3</sub> .....               | None.     |
| NH <sub>4</sub> ..... | None.     | Cl.....                              | 37.02     | AsO <sub>3</sub> .....              | .083      |
| Ca.....               | None.     | Br.....                              | .094      | B <sub>2</sub> O <sub>7</sub> ..... | 3.00      |
| Mg.....               | Trace.    |                                      |           |                                     |           |

Additional results in the following table are expressed in percentages of the original brine by weight. The weight of the total solids was taken after drying at 110° C. and includes some water of hydration and organic matter. This is expressed by the value recorded as loss on ignition.

TABLE XLII.—*Analysis of brine from Searles Lake.*

| Constituent.                 | Quantity.        | Constituent.                        | Quantity.        |
|------------------------------|------------------|-------------------------------------|------------------|
|                              | <i>Per cent.</i> |                                     | <i>Per cent.</i> |
| Total solids, at 110° C..... | 30.34            | Sodium carbonate in solution.....   | 3.04             |
| Loss on ignition.....        | .69              | Sodium bicarbonate in solution..... | .75              |
| Anhydrous solid.....         | 29.65            | Potash, K <sub>2</sub> O.....       | 2.17             |

The system which is represented by the Searles Lake brines—one containing chlorides, sulphates, carbonates, and borates of sodium and potassium—is extremely complex. It can not be accurately foretold, therefore, what the conditions controlling the separation of potassium salts therefrom will prove to be or with what ease or difficulty the separation may be made. Since the carbonates and borates are among the more valuable of the various possible products of the lake, the potassium salts may be produced as a by-product. A study of the system, sodium chloride, sodium sulphate, sodium carbonate, sodium

borate, potassium chloride, potassium sulphate, potassium carbonate, potassium borate, and water, or, in short, the system represented by the water of alkaline lakes and typified by the brine of Searles Lake, is being made in the laboratories of the Bureau of Soils, with a view to the separation of potassium salts from such brines.

Owens Lake, occupying a depression on the extreme western border of this area, is also of interest in view of the fact that its brine has been shown to contain as high as 4.54 per cent of potassium.<sup>1</sup>

It has long been known that the brines of Railroad Valley, Nev., contain a remarkably high percentage of potassium salts. The recent analyses of various samples of these brines, by A. R. Merz, of the Cooperative Laboratory, Reno, Nev., are given in Table XLIII.

TABLE XLIII.—*Analyses of brines from Railroad Valley, Nev.*

[Results in per cent of total solids.]

| Number of sample. <sup>2</sup> | Total solids, grams per 100 c. c. | K <sub>2</sub> O per cent. | Number of sample. | Total solids, grams per 100 c. c. | K <sub>2</sub> O per cent. |
|--------------------------------|-----------------------------------|----------------------------|-------------------|-----------------------------------|----------------------------|
| 1                              | 33.86                             | 9.06                       | 106               | 46.38                             | 6.73                       |
| 2                              | 44.08                             | 9.87                       | 107               | 76.38                             | 5.00                       |
| 3                              | 55.20                             | 12.19                      | 108               | 60.02                             | 3.41                       |
| 4                              | 49.10                             | 10.02                      | 109               | 58.72                             | 2.38                       |
| 5                              | 58.32                             | 7.18                       | 110               | 28.54                             | 3.90                       |
| 6                              | 48.82                             | 11.03                      | 111               | 59.62                             | 6.11                       |
| 7                              | 42.62                             | 8.46                       | 112               | 59.16                             | 5.45                       |
| 26                             | 2.07                              | 5.25                       | 113               | 56.48                             | 6.20                       |
| 23                             | 13.16                             | 4.25                       | 114               | 72.22                             | 4.23                       |
| 30                             | 6.22                              | 6.52                       | 115               | 41.24                             | 1.53                       |
| 43                             | 4.55                              | 5.29                       | 116               | 10.56                             | 6.02                       |
| 45                             | 27.36                             | 5.03                       | 120               | 5.36                              | 6.16                       |
| 48                             | 33.98                             | 3.10                       | 122               | 79.56                             | 12.10                      |
| 54                             | 25.24                             | .89                        | 124               | 68.74                             | 1.90                       |
| 55                             | 22.74                             | 3.28                       | 125               | 45.42                             | 2.94                       |
| 56                             | 53.80                             | 1.22                       | 126               | 56.90                             | 5.04                       |
| 57                             | 7.58                              | 1.65                       | 127               | 76.40                             | 3.68                       |
| 58                             | 33.00                             | 5.87                       | 128               | 62.08                             | 5.65                       |
| 59                             | 27.56                             | 4.10                       | 129               | 55.22                             | 2.73                       |
| 62                             | 24.48                             | 4.68                       | 130               | 20.87                             | 8.54                       |
| 64                             | 27.56                             | 1.05                       | 131               | 83.40                             | 4.53                       |
| 66                             | 12.10                             | 1.65                       | 132               | 40.42                             | 2.06                       |
| 71                             | 59.92                             | 4.35                       | 133               | 12.63                             | 6.14                       |
| 76                             | 4.55                              | 8.53                       | 134               | 13.04                             | 6.23                       |
| 80                             | 58.22                             | 6.85                       | 135               | 68.64                             | 3.39                       |
| 81                             | 56.63                             | 2.98                       | 137               | 14.18                             | 1.81                       |
| 82                             | 55.72                             | 3.67                       | 138               | .97                               | 1.16                       |
| 84                             | 14.09                             | 4.06                       | 139               | 47.18                             | 1.30                       |
| 87                             | 30.46                             | 4.53                       | 143               | 15.74                             | 5.94                       |
| 88                             | 24.03                             | 2.33                       | 144               | 82.46                             | 2.66                       |
| 89                             | 25.58                             | 5.71                       | 145               | 41.34                             | 2.83                       |
| 90                             | 49.48                             | 7.91                       | 146               | 72.06                             | 2.26                       |
| 91                             | 70.97                             | 6.97                       | 148               | 58.22                             | 9.26                       |
| 92                             | 74.72                             | 8.46                       | 149               | 44.22                             | 6.58                       |
| 93                             | 56.37                             | 7.54                       | 152               | 29.80                             | 4.83                       |
| 94                             | 16.68                             | 2.98                       | 153               | 11.62                             | 11.92                      |
| 95                             | 53.00                             | 7.39                       | 154               | 12.09                             | 11.78                      |
| 96                             | 71.64                             | 9.20                       | 155               | 69.00                             | 10.17                      |
| 97                             | 69.12                             | 7.72                       | 156               | 7.86                              | 11.46                      |
| 98                             | 55.16                             | 9.22                       | 158               | 12.82                             | 5.03                       |
| 99                             | 64.96                             | 8.52                       | 159               | 67.92                             | 3.79                       |
| 100                            | 66.62                             | 5.76                       | 162               | 48.92                             | 1.48                       |
| 101                            | 34.48                             | 2.22                       | 163               | 13.99                             | 5.49                       |
| 102                            | 55.18                             | 8.96                       | 164               | 13.97                             | 5.82                       |
| 103                            | 43.24                             | 3.90                       | 165               | 64.62                             | 3.26                       |
| 104                            | 53.96                             | 3.78                       | 166               | 76.58                             | 3.42                       |
| 105                            | 72.64                             | 6.38                       | 168               | 41.10                             | 1.53                       |

<sup>1</sup> Clarke, loc. cit.

<sup>2</sup> Omitted numbers in this table represent samples whose salt content is too low to be of interest.

The potassic brines of this valley, however, are found impregnating the detrital material on the floor of the depression and, like the brines of many such basins, are confined to the upper portion of this material. The composition of these brines in the various parts of the flat are extremely variable, not only in concentration but in the relative porportion of the various salts. From a boring which has reached a depth of over 1,200 feet large volumes of much fresher water are now being obtained.<sup>1</sup>

It appears reasonable to believe that the potassic brines of previous ages may have undergone evaporation in this basin, possibly to the point of deposition of potassium compounds, and that such deposits lie buried beneath the accumulations of detrital material now being explored.

#### OTHER BASINS OF MINOR IMPORTANCE.

The brines of the remnant lakes and the salt crusts of the playas of other basins in the Northwest and Southwest have been examined, and, in brief, their salines have been found to be almost wholly non-potassic in composition. In no instance have potassium compounds been found in commercially interesting amounts.

#### MARINE.

It is strongly indicated that conditions favorable to the segregation of potassium salts have existed in the regions where rock salt now occurs. This is especially true of the saliferous region of New York (and contiguous territory underlain by rock salt) and Kansas.

At first sight analogies drawn between these deposits and those at Stassfurt make it appear improbable that potassic segregations have occurred. The superficial indications are that desiccation took place here only to the point of deposition of sodium chloride and that a heavy influx of fresher water prevented further crystallization.

It is conclusively shown, however, that fresher water conditions were reached in stages. This is evidenced by the interstratification of sodium chloride, calcium sulphate, and clay, dwindling in frequency and thickness as the surface is approached. The deposition of the thick beds of salt, the ones entered by the shafts and wells of those regions, must be regarded as the result of one of the periods of aridity. Whether they mark the period of greatest desiccation and crystallization or whether in some former period desiccation was even more nearly complete and was accompanied by the deposition in strata of

<sup>1</sup> We are advised by Mr. Hoyt S. Gale, of the U. S. Geological Survey, that similar fresh water is being met at about the same depth in the boring he is supervising near Fallon, Nev., in the Lahontan Basin. It may, perhaps, be regarded as a sign of promise indicating that there is no great dissemination of salines in the detrital fill of these basins, and that *per contra*, there are segregated salt layers somewhere below the surface, though at what depth can not be predicted as yet.

potassium-bearing compounds can not be said until the entire saliferous formation has been explored. This should be done by borings, passing through the strata filling the old sea bed at its deepest parts. It is of interest that the strata overlying the rock-salt formations of New York are comparable in a general way to those overlying the Stassfurt deposits. However, this may have no significance, since we know already that the overlying strata in both cases were laid down during periods which marked a decreasing rate of desiccation.

This comparison is brought out by the following tabulation:

TABLE XLIV.—*Comparison between stratigraphy at Stassfurt and New York.*

| Magdeburg-Halberstadt.          |              | New York.                          |              |
|---------------------------------|--------------|------------------------------------|--------------|
| Stratum.                        | Thickness.   | Stratum.                           | Thickness.   |
| Top of Zechstein:               | <i>Feet.</i> | Overlying strata:                  | <i>Feet.</i> |
| Red clay.....                   | 70-100       | Shales to bottom of Marcellus..... | 866          |
| Younger succession:             |              | Limestones.....                    | 221          |
| Youngest rock salt.....         | 160          | Limestones and gypsum.....         | 51           |
| Anhydrite.....                  | 8            | Gypsum.....                        | 45           |
| Red salt clay.....              | 30           | Gypsum and limestone.....          | 205          |
| Younger rock salt.....          | 320-495      | Younger succession:                |              |
| Principal anhydrite.....        | 16           | Limestone with salt and gypsum..   | 11           |
| Older succession:               |              | Salt, gypsum, and limestone.....   | 15           |
| Gray salt clay.....             | 13-33        | Salt.....                          | 1-3          |
| Carnallite stratum.....         | 100-130      | Marl, salt, and gypsum.....        | 4            |
| Kieserite stratum.....          | 70-130       | Salt (with interstratification of  |              |
| Polyhalite stratum.....         | 130-200      | limestone and marl).....           | 51           |
| Older rock salt.....            | 1,000-1,600  | Base:                              |              |
| Base:                           |              | Salina rock, unexplored (esti-     |              |
| Older anhydrite of middle Zech- |              | mated).....                        | 500          |
| stein age.                      |              |                                    |              |

#### THE EXAMINATION OF CERTAIN SALINE CONCENTRATES FOR LITHIUM, RUBIDIUM, AND CAESIUM.

In the investigation of the salines of the United States a collection was made of a number of brines which represented concentrates from large volumes of solution. These should contain accumulations of the rarer elements related to sodium and potassium in their chemical properties and therefore theoretically associated with these in nature. While the search for lithium, rubidium, and caesium, perhaps, can not be said to have logical connection with the search for potash, yet the opportunity afforded for such a research by the large collection of samples from the various bodies of salines of the United States was not one to be overlooked. It is to be regretted that the exigencies of the work made it impracticable to elaborate the methods employed to the extent that smaller amounts of the rare elements looked for could be detected and precise measurements made.

About 40 of these concentrates were examined spectroscopically and compared with standard solutions of lithium chloride. All the solutions examined contained lithium. In a few cases rubidium could be detected. In one case only it appeared probable that caesium

was present, but not definitely. Lithium in some quantity was evidently present in every sample of ocean brine, and in some samples of natural brines from Ohio, Michigan, and West Virginia. The approximation method employed was too inaccurate to justify publication of the quantitative figures obtained, and the exigencies of the potash investigation have not permitted sufficient time for proper analysis. It is of course obviously desirable for a complete understanding of these brines that such data be secured, if time and opportunity occur for further work on them.

#### SUMMARY.

1. In no instance has an artificial or a natural (subterranean) brine been found to contain potassium in such amounts as to warrant its extraction commercially.

2. The concentrates, while containing more potassium than the brines from which they were derived, do not contain sufficient of that substance to warrant attempts at its extraction.

3. The bitters derived from the manufacture of salt from sea water contain potassium in such amounts as to make it appear that they could be evaporated to make the so-called "manure salts" of a sufficiently great potassium content to be valuable commercially.

4. The brine of one desiccated lake of southern California has been found to contain sufficient potassium to make it a possibly valuable commercial source of potash.

5. The theoretical possibilities in separating potassium from various types of brine have been pointed out, and a review has been given of proposed commercial methods.

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