ART. XXXI.—*Contribution to the Chemistry of the Mineral Springs of Onondaga, New York;* by CHARLES A. GOESSMANN, Ph.D., Chemist to the Salt Company of Onondaga.

SOME of the characteristics of the Brines of Onondaga, N. Y., have already been illustrated by a series of analyses in two previous reports elsewhere published.[1]

The following pages may be considered as a continuation of the discussion on subjects of similar import, since I propose to treat here of certain peculiar features of the locality where these brines are found.

The majority of the wells, from which the supply of brine for the Onondaga Salt Works has been hitherto obtained, are located in a half circle around the southern and eastern shores of Onondaga Lake, north and west of the city of Syracuse. This entire district consists mainly of low lands, which are yet partly in a marshy state. They have been reclaimed in the course of time from the original lake bed, by natural and artificial drainage, and extend from one to one and half miles south of the lake. They are everywhere bounded by more or less abruptly rising grounds. These embankments, toward the east and west, at the southern end of the lake basin terminate, in several places, in hills of a hundred feet and upward in height, consisting chiefly of sand and gravel. In other quite frequent instances may be seen the outcroppings of the red and blue shale of the Onondaga Salt Group at a considerable elevation above the level of the lake. The Onondaga red and blue shale, in a crumpled condition, forms a clay of corresponding color; its present outcrops seem to have been originally covered with the same diluvial detritus which is spread so extensively over the northwestern part of the State. The shales of the Onondaga Salt Group underlie, also, the lowlands at the southern termination of the lake, dipping apparently at a rapid rate toward the center of the valley or its proximity, and are supposed (Beck) to form a natural underground basin in which the brine accumulates. This pre-

[1] Report on the Brines of Onondaga, by C. A. Goessmann. Syracuse, N. Y., December 6, 1862.

Report on the Manufactory of Solar Salt, &c., by the same. Syracuse N. Y., December, 1863.

sumed basin is no doubt, filled in its lower portions with the same *debris* which covers the surrounding hills. Layers of sand, coarse gravel, loamy soil and hard pan are found here quite frequently, alternating with each other. Upon the deposit, within the low lands (mainly along the banks of the Onondaga Creek), rests a considerable amount of alluvial material of a loamy nature, sometimes rich in pebbles. Trunks of trees and hickory nuts, in a tolerable state of preservation, have been found at a depth of from twenty-five to thirty feet. These formations, particularly near the outcrops of the Onondaga shales, or at the termination of their surface drainage, are frequently found to be filled with an abundance of water of a peculiar saline character.

These waters sometimes contain only mere traces of chlorids, while in those from other similar localities in their vicinity a considerable amount of chlorid of sodium may be observed.

Among the questions to which these facts give rise, the following appeared to me of great interest:

First: Is there any relation between the chemical composition of the spring waters peculiar to the locality, and the brines?

Second: What chemical changes may result from their union, should their composition materially differ.

Third: Do the waters of the springs and the brines derive their characteristic qualities from soil or rocks of one and the same kind, though in different conditions; or do they both owe their peculiar chemical composition to entirely different sources; and if so, where are these sources located?

We may, for instance, suppose—adopting to some extent a view which has been advocated with much propriety in similar connections—that in the course of time an increased amount of percolation, or a certain order in the stratification, or a difference in the nature of the various layers, or particular advantages in drainage in general, may have favored a more rapid extraction of the more soluble compounds as chlorid of sodium, etc., in one locality than another. In fact, the well known and interesting discovery by A. Eaton,[1] of pseudomorphs of chlorid of sodium found in layers of a hardened clayish deposit—somewhat remote from the present brine-supplying district—contends strongly in favor of a previous gradual extraction of larger quantities of more soluble saline compounds (chlorid of sodium in particular) from the rocks and soil of the surrounding country.

The existing deficiency[2] of properly detailed geological records of numerous wells sunk at former periods is a deplorable fact, which seriously interferes with the discussions of the questions above proposed. For venturing at all, under such disad-

[1] W. Haidinger. Mittheilungen, etc., November 12, 1846. Wien. This Journal, xv, January, 1829.

[2] We are indebted to the Hon. George Geddes for a very valuable map of the outlines of the geology of Onondaga County.

vantageous circumstances, on the third question, I trust I may be justified by the course I shall adopt, viz: presenting merely a few facts which have come within my observation. Future local geological investigations must decide upon their value.

In entering upon considerations of the above questions I selected two springs from an elevation several miles distant from the brine-bearing district, two in its immediate vicinity and a sample of average brine of the Syracuse district.

The samples were as follows:

a, From a well at the north of a hill where, formerly, numbers of pseudomorphs of chlorid of sodium had been found; the well terminated in a hard clayish shale.

b, From a well situated midway between the former and the brine-furnishing locality; the well terminated in the red clay of the Onondaga Salt Group. Both wells were at least from forty to fifty feet above the level of the lake.

c, From a spring within the brine-producing district, at a height of about ten feet above the level of the lake.

d, From a spring in close proximity to *c*, and at the same elevation.

e, A brine from the vicinity of springs *c* and *d*.

a. Water from a well (47 feet deep) on Willow street near the corner of Catharine street, in the city of Syracuse.

The well from which this water was collected is situated in the vicinity of one of those spots (James street height) where, some years ago, while workmen were engaged in grading James street, a considerable number of pseudomorphs of chlorid of sodium were found. Serpentine was also discoverd not far off. Two prominent hills, of which the most conspicuous is known as "Prospect Hill," intervene between that locality and the quite abrupt descent of the high grounds around the east and southwest side of the former lake bed—our present brine-furnishing district. In sinking this well, (Nov., 1863,) a layer of gravel-bearing loamy soil of ten feet thick was passed, then twelve feet of crumbled green shale, and lastly twenty-five feet of a hard light green clayish shale. The water usually stands fourteen feet. The ground perforated by this well is probably fifty feet above the level of the lake, and about two and a half miles from the nearest salt well.

One thousand parts of this water contained—

Calcium, - - - -	0·2302 parts.
Magnesium, - - -	0·0359
Sodium, - - - -	0·0101
Silica, - - - -	0·0050
Chlorine, - - - -	0·0156
Sulphuric acid, - - -	0·3442
Free carbonic acid, - - -	(not determined)

1000 parts of this water left at 200° to 212° F., 0·8906 parts of solid residue; one gallon would consequently leave 3·36525 grams or 51·9849 grains.

b. Water taken from a well sunk from the top of Prospect Hill, to a depth of seventy-five feet, i. e., the level of Salina street at the corner of Lock street. Prospect Hill lies about midway between the well which furnished the water for Analysis *a*, and the northwestern termination of the high embankment (30 or 40 feet) around the eastern and southeastern shores of Onondaga Lake and its adjoining low lands. Prospect Hill consists mainly of gravel and is covered with numerous boulders, and underlaid with the red clay of the Onondaga Salt Group. The gravel is here and there interspersed with layers of cemented gravel (hard pan) and of a red loamy soil. These layers are of varying extent and apparently without any order of succession. The water subjected to analysis was taken from the first quantities drawn from the well soon after its completion (April, 1863). Quantitative tests for carbonic acid and iron, being under existing circumstances of no value, were omitted.

One thousand parts of this water contained—

Calcium, - - - -	0.52838
Magnesium, - - -	0·03954
Sodium, - - - -	0·00821
Sulphuric acid - - -	1·02660
Chlorine, - - - -	0·01268
Silica, - - - -	0·00450
Iron, - - - -	(not determined)
Free carbonic acid, - - -	" "

1000 parts of this water left, at 200° to 212° F., 2·0080 parts of solid residue. The residue from one gallon would therefore be 118·8602 grains.

c. This water was taken from a spring near the Syracuse Pump House, on the bank of Onondaga Creek, upon grounds which had at one time been occupied by vats for the manufacture of Solar Salt. The spring issues from an embankment near the place where the Onondaga Creek has forced its way through the southern enclosure of the low lands around the south shore of Onondaga Lake. This vicinity is rich in springs of similar character.

This peculiar water was found at a depth of from forty to fifty feet, where loamy soil or hard-pan had intervened between it and the brine proper. Brine had, no doubt, more or less access to some of these springs, if only by surface percolation. The spring which furnished me with the sample for this analysis was somewhat protected by a tight barrel in which it was purposely enclosed; and the barrel was several times emptied before collecting the sample for examination, (Sept., 1863).

One thousand parts of this water contained—

Calcium, - - - -	0·35265
Magnesium, - - -	0·07620
Sodium, - - - -	4·50454
Sulphuric acid, - - -	0·64379
Chlorine, - - - -	6·95266
Silica, - - - -	0·00490
Free carbonic acid, - - -	(not determined)
Carbonate of protoxyd of iron (traces),	" "
Bromine (traces), - - -	" "

1000 grams left, at 200° to 212° F., 13·0340 grams of solid residue; one gallon would consequently leave 49·2405 grams, or 760·7309 grains.

d. This sample of water was taken from a spring about twenty-five to thirty feet distant from the last one, *c.* The spring is enclosed in a tight wooden tank of 10 to 12 feet deep, and issues at the foot of an embankment from thirty to forty feet high. Its elevation above the level of the lake corresponds nearly with that of the spring *c.*

1000 parts of this water contained in solution—

Calcium, - - - -	0·28147
Magnesium, - - -	0·07700
Sodium, - - - -	4·01378
Silica and alumina, - -	0·01770
Sulphuric acid, - - -	0·48150
Chlorine, - - - -	5·30918
Bromine, - - - -	0·00232
Free carbonic acid, - - -	(not determined)
Carbonate of protoxyd of iron, -	" "

1000 parts of this water left, at from 200° to 212° F., 11·7382 parts of solid residue. One gallon would therefore leave 685·07402 grains of residue. This residue contained in combination, 0·1150 parts of carbonic acid.

e. The brine for this analysis was taken from a salt well in the vicinity of *c* and *d*, (July 30, 1863).

Calcium, - - - -	2·25005
Magnesium, - - -	0·36799
Sodium, - - - -	61·06500
Potassium, - - - -	0·05720
Iron, - - - -	0·02123
Chlorine, - - - -	96·36355
Bromine,[4] - - - -	0·02080
Sulphuric acid, - - -	3·39550
Free carbonic acid, - -	(not determined)

1000 grams of this brine contained 164·243 grams of saline

[4] Iodine, traces.

residue; one U. S. gallon[5] would therefore contain 9586·9891 grains.

The brines of Onondaga, though differing somewhat in concentration, vary but slightly in regard to the relative proportions of their component parts; and the analytical statement just made, will be found to meet all practical requirements.

In 1000 parts of	Willow st. well.	Prospect Hill well.	Mineral water.	Mineral water.	Syracuse brine.
are contained	*a.*	*b.*	*c.*	*d.*	*e.*
Calcium,	0·2302	0·5284	0·3526	0·2815	2·2500
Magnesium,	0·0359	0·0395	0·0762	0·0770	0·3679
Sodium,	0·0101	0·0082	4·5045	4·0137	61·0650
Potassium,*	....	....	....	....	0·0572
Sulphuric acid,	0·3442	1·0266	0·6437	0·4815	3·3955
Chlorine,	0·0156	0·0127	6·9526	6·3092	96·3635
Bromine,*	....	....	....	0·00232†	0·0208
Silica,*	0·0050	0·0045	0·0049	0·0177†	....
Carbonic acid,*	....	....	....	0·1150‡	....

* In all cases where no figures are given no quantitative tests have been made.
† Silica and alumina. ‡ Combined in the residue left at 200° to 212° F.

Although, unquestionably, much significance must be conceded to the fact that the same group of elements form the most prominent features of the analytical results, there nevertheless existed some doubts whether a mere succession of extractions of the same strata or the same kind of rocks, etc., would suffice to explain satisfactorily the peculiar nature of the various liquids; a view which appears still more conspicuous when these component parts are arranged in the combinations most likely to be present in each of the waters.

Having arrived at this point, I preferred to institute some inquiry in regard to the action of certain compounds toward each other under circumstances similar to those I should be obliged to take into consideration if a discussion of the second question should promise encouraging results; and in this connection I would call particular attention to the earlier statements of C. B. J. Karsten,[6] and the results given in the highly interesting publications of T. Sterry Hunt,[7]—the former treating mainly of the nature and changes of the brines—the latter more especially of the chemistry of natural waters in general.

My experiments were in some cases designed to give merely an idea of the degree of certain changes under given circumstances. It appeared to me of importance to ascertain—

[5] One United States gallon is equal to 241 cubic inches or 3778·625 grams or 58318 grains.
[6] C. B. J. Karsten, Salinenkunde, Berlin, 1843.
[7] T. Sterry Hunt, Chemistry of Natural Waters, this Journal, March, July and September, 1865.

I. *How does carbonate of magnesia act upon sulphate of lime in the presence of free carbonic acid?*—To test the degree of this action, I adopted the following course. I mixed in a suitable vessel ten grams of well washed carbonate of magnesia, twenty-five grams of sulphate of lime, (gypsum,) and five hundred cubic centimeters of distilled water; which mixture I afterwards treated for a short time each day during four weeks, with well washed carbonic acid gas, so as to secure a constant supply of bicarbonate of magnesia to the solution of gypsum. The solution thence resulting, after being separated by filtration from the white residue, was equal to four hundred and fifty cubic centimeters. I placed it in a flat glass dish, and left it to gradual evaporation at the ordinary temperature.

After a few days rest the bottom of the vessel began to be covered with a small amount of sediment. No further noteworthy change took place, until the whole liquid gradually formed into a solid crystalline mass, consisting in the main of a net-work of needles. The solution, being tested before its solidification, was of a slightly alkaline reaction; the crystals resulting from its evaporation were transparent, yet crumbled readily to a white powder when exposed to dry air.

One hundred parts of an apparently air-dried sample of the saline mass, contained—

Carbonic acid, - - -	1·6721
Sulphuric acid, - - -	31·4803
Calcium oxyd (lime), - - -	0·7988
Magnesium oxyd (magnesia), -	17·0327

One hundred parts of the same mass, heated to a dull red heat, lost 51·0593 parts of its weight; leaving therefore 48·9407 parts of a white residue.

These analytical results, if considered in connection with the general properties of the original liquid as above stated, and the consequent solid crystalline residue, tend to prove that the solid matter may, with some propriety, be considered as consisting of

Carbonate of lime, - - -	1·4268
Basic hydrated carbonate of magnesia $3(MgO, CO^2)+(MgO, HO)$, -	2·4911
Sulphate of magnesia (MgO, SO^3+7HO),	96·8020

As the whole amount of the saline compound obtained in the experiment just described, was 22·605 grams, we learn that about 14·5 grams of gypsum had been decomposed, while some of the carbonate of lime (or more properly, bi-carbonate) left in the originally diluted liquid, had been separated during the progress of its concentration as carbonate of lime. The apparently slow decomposition of gypsum must be attributed to the limited solubility of that compound. It is not unreasonable

to presume that carbonic acid, under pressure and at common temperature, would alter the degree of action above illustrated.

II. *How does carbonate of magnesia act upon sulphate of lime in the presence of free carbonic acid and chlorid of sodium?*—In this investigation I proceeded thus: I weighed into a glass bottle 31 parts of commercial carbonate of magnesia, 86 parts of gypsum, 58 parts of chlorid of sodium, and 3000 parts of distilled water, and treated the whole mass with carbonic acid gas for several weeks, as described in a former experiment. The filtrate, separated from the undissolved white mass, which mainly consisted of gypsum and carbonate of lime, besides mere traces of carbonate of magnesia, was evaporated to dryness at 180° F., and the residue subsequently extracted with absolute alcohol. The alcoholic extract contained (beside a very small quantity of chlorid of sodium), 0·4370 grams of chlorid of magnesium, while the residue left after the extraction by alcohol contained 0·0570 grams of oxyd of calcium, 0·2243 grams oxyd of magnesium, and 0·6860 grams of sulphuric acid. This proved the presence of 0·6532 grams sulphate of soda, 0·4773 grams sulphate of magnesia, beside 0·1018 grams carbonate of lime, and 0·1236 grams carbonate of magnesia, with part of the chlorid of sodium unchanged. These results indicate,

1. That gypsum, carbonate of magnesia, and carbonic acid in the presence of chlorid of sodium, form chlorid of magnesium, sulphate of soda, and carbonate of lime.

2. That at a certain higher temperature, the sulphate of soda and chlorid of magnesium partly re-transform into sulphate of magnesia and chlorid of sodium.

3. That the solubility of the gypsum governs the degree of decomposition.

(To be continued.)