termined for indicator solutions of various hydrogen ion concentrations using the radiometric method developed in the original article.[1]

4. The values of the ionization constant of rosolic acid calculated from the ratio c/c_1, on the assumption that the indicator acid is monobasic, were found to decrease with decreasing alkalinity. When the hydrogen ion concentration was increased from 2.533×10^{-8} to 19.52×10^{-8}, the total salt concentration being 0.0259 N, the value of the ionization constant K_i was found to decrease from 5.65×10^{-8} to 2.89×10^{-8}.

5. It was found that this variation in the constants could be explained by regarding the indicator as a dibasic acid, and it was shown, furthermore, that the intensely colored form of the indicator is formed when the first hydrogen of the indicator acid is replaced by the base.

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THE SOLUBILITY OF MAGNESIUM CARBONATE IN NATURAL WATERS.[2]

BY ROGER C. WELLS.

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Treadwell and Reuter,[3] who determined the solubility of magnesium carbonate in water under given partial pressures of carbon dioxide, found for a partial pressure of "0 mm." of carbon dioxide at 15°, 0.6410 g. magnesium carbonate and 1.9540 g. magnesium bicarbonate per liter. This is equivalent to 0.51 g. magnesium and 2.09 g. carbon dioxide per liter. Cameron and Briggs,[4] however, found only 0.18 g. magnesium and 0.543 g. carbon dioxide per liter at room temperature after passing a current of air through the solution for a very long period. Feeling that more attention should be paid to the nature of the solid phase, I have carried out experiments that show a difference in the behavior of magnesite, the simplest natural variety of magnesium carbonate, and nesquehonite, the trihydrate $MgCO_3.3H_2O$ and, furthermore, find solutions in equilibrium with the latter substance under atmospheric conditions at 20° to contain 0.36 g. magnesium and 1.01 g. carbon dioxide per liter.

As the object of the experiments was to imitate natural conditions, the solutions were exposed to the action of outdoor air over long intervals, in order that they might come into equilibrium with the small amount of carbon dioxide in the atmosphere. The air was filtered through cotton, washed by distilled water and bubbled through the solutions contained in Jena flasks immersed in a thermostat. The thermostat was

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[1] *Loc. cit.*

[2] Published by permission of the Director of the United States Geological Survey.

[3] *Z. anorg. Chem.*, 17, 202 (1898).

[4] *J. Physic. Chem.*, 5, 553 (1901).

not in action over night, but since no large variations of temperature were permitted and since no air was passed then it is believed that no error was introduced from this source.

Magnesite.

This mineral is usually associated with serpentine or rocks containing members of the olivine group. As a rule it is compact and amorphous, possibly a colloid, but a crystalline variety is known whose origin is probably somewhat different from that of the amorphous variety. A specimen of the amorphous variety from Placer County, Colorado, kindly supplied by H. S. Gale, of the United States Geological Survey, and used for the solubility determinations, was found on analysis to have the following composition: SiO_2 0.09, Fe_2O_3 0.11, Al_2O_3 0.09, CaO 0.05, MgO 46.82, CO_2 51.75, H_2O 0.67; sum 99.58%.

Tables I and II show the extent to which this magnesite dissolved in water alone, and in water containing as much sodium chloride as sea water, under atmospheric conditions, during periods that were practicable for laboratory observation.

TABLE I.—SOLUBILITY OF MAGNESITE IN WATER UNDER ATMOSPHERIC CONDITIONS. (GRAMS PER LITER.)

Interval.	Mg.	Free CO_2.	CO_2 as bicarbonate.
One hour at 20°	0.004	0.002	0.018[1]
3 days	0.012	Trace	0.053
25 days	0.013	Trace	0.045
37 days	0.017	Trace	0.055
61 days	0.018	Trace	0.065

TABLE II.—SOLUBILITY OF MAGNESITE UNDER ATMOSPHERIC CONDITIONS IN WATER CONTAINING 27.2 G. NaCl PER LITER. (GRAMS PER LITER.)

Interval.	Mg.	Free CO_2.	CO_2 as bicarbonate.
11 days	0.025	Trace	0.064
35 days	0.028	Trace	0.086

The Trihydrate, $MgCO_3.3H_2O$.

If the excess carbon dioxide is expelled by a current of air at ordinary temperature from a solution containing magnesium bicarbonate and carbon dioxide the precipitate consists of well developed crystals of the trihydrate $MgCO_3.3H_2O$, probably identical with the natural mineral nesquehonite.[2]

Table III shows the rate at which the changes in the solution went on. The state of the carbon dioxide was determined by titration with 0.02 *N* $NaHSO_4$, first with phenolphthalein and then with methyl orange. The total carbon dioxide thus found agreed with that directly determined by

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[1] The distilled water used contained several milligrams of CO_2 per liter to begin with.

[2] Leitmeier, *Z. Kryst.*, 47, 118 (1910). Below 6° the pentahydrate, $MgCO_3.5H_2O$, was obtained.

absorption in soda-lime tubes after expulsion with HCl and boiling. Direct determinations of magnesium were also found to agree with the amounts calculated from the titrations.

TABLE III.—RATE OF EVOLUTION OF CO_2 FROM A SOLUTION CONTAINING $Mg(HCO_3)_2$ + CO_2 AT 20° WITH A GOOD STREAM OF AIR (ABOUT 5 BUBBLES A SECOND).

Time elapsed.	Mg.	Free CO_2. G. per liter.	CO_2 as bicarbonate. G. per liter.	CO_2 as carbonate. G. per liter.	Total CO_2.
Start	0.87	0.37	3.14	....	3.51
1 hour	0.87	0.17	3.10	....	3.27
2 hrs.	0.87	0.10	3.14	....	3.24
3 hrs.	0.87	0.00	3.10	0.02	3.12
5 hrs.	0.87	....	2.96	0.10	3.06
7 hrs.	0.87	....	2.67	0.22	2.89
2 days	0.87	....	2.39	0.37	2.76
3 days	0.87	....	1.83	0.64	2.47
Crystals of $MgCO_3.3H_2O$ appear.					
4 days	0.83	....	1.69	0.66	2.35
14 days	0.61	....	1.45	0.38	1.83
16 days	0.53	....	1.03	0.44	1.47
26 days	0.43	....	0.88	0.35	1.23
47 days	0.39	....	0.84	0.29	1.13
65 days	0.38	....	0.83	0.28	1.11

The solubility of $MgCO_3.3H_2O$ in water under atmospheric conditions was also determined by approaching the point of equilibrium from the side of unsaturation, with the results noted in Table IV. The salt for this purpose was prepared by mixing solutions of magnesium chloride and sodium bicarbonate and washing the precipitate with water. It was proved by analysis to be the trihydrate. Air was bubbled through the solution daily for 4 days followed by a lapse of 10 days when no air was passed; the passage was then resumed daily as noted. The means of the final values of Tables III and IV are: 0.36 g. magnesium and 1.01 g. carbon dioxide per liter.

TABLE IV.—SOLUBILITY OF $MgCO_3.3H_2O$ IN WATER UNDER ATMOSPHERIC CONDITIONS AT 20°. (GRAMS PER LITER.)

Interval.	Mg.	CO_2 as carbonate.	CO_2 as bicarbonate.	Total CO_2.
2 days	0.25	0.36	0.17	0.53
4 days	0.26	0.36	0.21	0.57
13 days	0.28	0.29	0.43	0.72
17 days	0.30	0.31	0.46	0.77
19 days	0.34	0.31	0.61	0.92
22 days	0.35	0.30	0.60	0.90
29 days	0.34	0.32	0.59	0.91

The difference in the solubility of magnesite and the trihydrate $MgCO_3.3H_2O$ is evident from Tables I and IV. Some have supposed the trihydrate to be a basic bicarbonate, $MgOH.HCO_3.2H_2O$. Whether this is so or not, there is a difference in the state of the carbon dioxide in the two solutions; the proportion existing as carbonate increases with the magnesium concentration, although in the more concentrated solutions (Tables III and IV) the bicarbonate ion concentration still exceeds that of the carbonate.

If the trihydrate is regarded as a carbonate its solubility-product may be calculated from the data of Tables III and IV as follows:

Mg = 0.36 g. per liter = 0.015 mole.

CO_2 as carbonate = 0.30 g. per liter = 0.0068 mole CO_3.

The product of the two concentrations just stated gives

$$(Mg)(CO_3) = 0.0_310.$$

This is apparently a maximum value of the solubility product of $MgCO_3.3H_2O$ at 20° since complete dissociation and no hydrolysis are assumed. There appear to be too many uncertainties in the ionic concentrations to attempt to compute a minimum value.

Natural Waters.

It is interesting to note in this connection that the highest concentration of Mg reported in a river water in the United States is 0.077 g. per liter, in the Wabash River near Logansport, Indiana, October, 1906.[1] This water was practically neutral, the HCO_3 reported being 0.276, equivalent to 0.200 g. CO_2 per liter, and NaCl about 1.3 g. per liter.

A slightly higher content of Mg than the above was found in Pyramid Lake, Nevada, in 1884,[2] *viz.*, 0.080 g. Mg per liter, with 0.360 total CO_2, and about 2.5 NaCl. The ocean, however, has 1.30 g. Mg and about 0.10 g. CO_2 per liter.

With the data now at hand, it appears that none of these natural waters is saturated with respect to the trihydrate $MgCO_3.3H_2O$.

On the other hand, either they are all supersaturated with respect to magnesite or else the solubility found for magnesite had not yet reached its maximum value.

Summary.

(1) Under atmospheric conditions it appears possible to attain practically the same state in a solution saturated with $MgCO_3.3H_2O$, whether one starts with a solution containing an excess of magnesium bicarbonate or with the pure trihydrate and water, but the adjustment occurs very slowly. The solution finally contains 0.36 g. magnesium and 1.01 g. carbon dioxide per liter at 20°.

(2) The solubility found for magnesite, however, is much smaller, *viz.*, 0.02 g. magnesium and 0.07 g. carbon dioxide per liter.

(3) Certain natural waters, freely exposed to the atmosphere, appear to be supersaturated with respect to magnesite but none approaches very closely to the point of saturation of the trihydrate $MgCO_3.3H_2O$.

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[1] Dole, U. S. Geological Survey, *Water-Supply Paper*, **236**, 108 (1909).

[2] Clarke, U. S. Geological Survey, *Ibid.*, **364**, 30 (1914).