solutions of calcium sulfate and of sodium chloride under partial pressures of carbon dioxide ranging from 0.1 to 1.0 atm.; from these results the activity coefficients of calcium bicarbonate have been derived. The concentrations of calcium sulfate and carbonate in the solutions saturated with both gypsum and calcite afford no indication of any alteration in the nature of either of these solid phases under these conditions.

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THE SOLUBILITY OF MAGNESIUM CARBONATE (NESQUEHONITE) IN WATER AT 25° AND PRESSURES OF CARBON DIOXIDE UP TO ONE ATMOSPHERE[1]

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The measurements presented in this paper were made with a view to securing more reliable data than were then available[3] on the solubility of magnesium carbonate (nesquehonite, $MgCO_3{\cdot}3H_2O$) in water at 25°, for a range of partial pressures of carbon dioxide extending downward from one atmosphere, and on the limiting pressure at which magnesium hydroxide becomes the stable solid phase in equilibrium with the solution. Such data are of interest in connection with the control of the conditioning of many natural waters and the preparation of pure magnesia, and are a necessary preliminary step toward the solution of the puzzling problem of the mode of formation of dolomite.

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[1] From the dissertation presented by W. D. Kline to the Graduate School of Yale University, June, 1923, in candidacy for the degree of Doctor of Philosophy.

[2] Loomis Fellow, 1921–1922; du Pont Fellow, 1922–1923.

[3] (a) Engel, *Ann. chim. phys.*, **13**, 344 (1888), determined the equilibrium between $MgCO_3{\cdot}3H_2O$, water and (1) CO_2 at pressures of 0.5–6 atm. at 12°; (2) CO_2 at 1 atm. and several temperatures up to 50°. (b) Leather and Sen, *Memoirs Dept. Agric. India* Chem. Series 3, No. 8 (1914); sundry measurements, not very reliable. (c) Mitchell, *J. Chem. Soc.*, **123**, 1887 (1923), measured the solubility at 25° at pressures of 6–21 atm. of CO_2. (d) Haehnel, *J. prakt. Chem.*, **108**, 61 (1924), made measurements at 18° and pressures 2–56 atm. of CO_2; and at 34 atm. over the temperature range 0–60°. Since, however, the solubility at 18° becomes constant at pressures exceeding 18 atm., this is evidence of a new solid phase, bicarbonate presumably; hence the temperature coefficient of solubility at 34 atm. does not apply to our solid phase. (e) *Cf.* also Johnston, This Journal, **37**, 2001 (1915).

In order to compare these several results with ours, they were recalculated in terms of moles per kilo of water by assuming that (a) the solution may be regarded as all bicarbonate; (b) the temperature coefficient of specific gravity of a solution of $Na(HCO_3)$ (given for 18° in "International Critical Tables") is the same as that of water; (c) the ratio of specific gravity of equimolal solutions of $Mg(HCO_3)_2$ and $NaHCO_3$ is the same as that of equimolal solutions of $MgCl_2$ and NaCl. The solubility at 25° was interpolated by means of a plot of log m against $1/T$.

The equations developed in the preceding paper for solutions saturated with calcium carbonate apply equally to magnesium carbonate if for K_c we substitute $K_M = (\mathrm{Mg}^{++})(\mathrm{CO_3}^{--})$; so that in this case $f(m)$, which is evaluated as $P^{1/3}/m$, is equal to $\alpha\sqrt[3]{K_2/K_1K_M\gamma\lambda c}$.

The form of magnesium carbonate stable in contact with its aqueous solution at 25° is the trihydrate, nesquehonite, $MgCO_3{\cdot}3H_2O$. Numerous basic carbonates have been reported in the literature, but it is doubtful whether any of these correspond to a definite crystalline compound. That some of them at least are indefinite mixtures has been shown by microscopic[4] and by x-ray[5] methods; the probability that all are likewise indefinite may be inferred from a consideration of the factors which determine the stability of hydroxide and of carbonate in aqueous solution. For with decreasing partial pressure of carbon dioxide there corresponds an increase in the ratio $(\mathrm{OH}^-)/(\mathrm{CO_3}^-)$ and, owing to the fact that magnesium hydroxide is much less soluble than the carbonate, there is a pressure below which the hydroxide becomes the stable solid phase; this limiting pressure was in a previous paper[3e] estimated at about 0.00037 atm. of carbon dioxide, slightly greater than the proportion ordinarily present in air. It is therefore likely that in the precipitation of magnesium carbonate some proportion of hydroxide will also appear unless care is taken to keep the effective concentration of $\mathrm{CO_3}^{--}$ high and of OH^- correspondingly low. In any case, if there be any range of carbon dioxide pressure within which a basic carbonate is stable at 25°, this range must lie between the zones of stability of the normal carbonate and the hydroxide; no definite indication of this was observed in the present work.

Experimental

Kahlbaum's magnesium carbonate trihydrate was used as the solid phase in this work, since its analysis and its solubility proved to be identical with those of material prepared with special precautions to obviate contamination by magnesium hydroxide and by double carbonates of magnesium with the alkali metals. Equilibrium was established in three to five days by bubbling mixtures of carbon dioxide and air in constant proportions through conductivity water in contact with the finely divided solid in the manner used for studying the solutions of alkali carbonates;[6] the methods there described were employed in analyzing gas phase and solution. In the determination of total base no attempt was made to correct for incomplete saturation of the titration mixture with carbon dioxide, as the correction was apparently less than the general experimental error. In the determination of bicarbonate, made on 15–20 g.

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[4] E. S. Larsen, *Am. Mineralogist*, **2**, 3 (1917).

[5] G. R. Levi, *Ann. chim. appl.*, **14**, 265 (1924).

[6] Walker, Bray and Johnston, This Journal, **49**, 1235 (1927).

of the equilibrated solution, the excess of baryta added was limited to 20 milli-equivalents; otherwise the end-point, on titration with acid, was uncertain owing to the gradual re-solution of the magnesium hydroxide precipitated by the excess of baryta.

Table I lists the mean analytical results in the first three columns, respectively, the partial pressure of carbon dioxide, P, and the millimolality (millimoles per kilo water) of magnesium, m_1, and of bicarbonate, m_2. The figures in the fourth column are derived from the relation $[CO_3^-] = m_3 = m_1 - {}^1/_2\, m_2$; the ionic strength ($\mu$) in the fifth column is from the data in Cols. 2, 3 and 4; and the values of $[OH^-]$, in the last column, as will be described later.

TABLE I

OBSERVED MEAN MOLALITIES OF SOLUTIONS IN EQUILIBRIUM WITH A SERIES OF PRESSURES OF CARBON DIOXIDE AT 25°

P	$[Mg^{++}] \times 10^3$, m_1	$[HCO_3^-] \times 10^3$, m_2	$[CO_3^{--}] \times 10^3$, m_3	μ	$[OH^-] \times 10^5$, m_4	Solid phase
0.000107	4.33	4.88	1.89	0.0149	3.84	$Mg(OH)_2$
.000113	4.45	5.01	1.95	.0153	3.73	
.000170	5.77	7.45	2.05	.0194	3.69	
.000179	5.93	7.63	2.12	.0199	3.59	
.000197	6.58	7.95	2.61	.0224	3.40	
.000210	7.08	8.06	3.05	.0243	3.23	
.000233	7.80	8.37	3.61	.0270	3.03	
.000251	8.07	8.55	3.80	.0280	2.87	
.000310	10.13	11.84	4.21	.0346	3.22	
.000376	12.96	14.04	5.94	.0448	3.14	
.000380	13.55	14.32	6.39	.0470		
.000510	14.37	17.10	5.82	.0489		$MgCO_3 \cdot 3H_2O$
.000680	15.12	18.72	5.76	.0511		
.000845	15.66	19.90	5.71	.0527		
.000887	15.93	20.46	5.70	.0535		
.000930	16.24	21.19	5.65	.0544		
.00160	18.59	26.98	5.10	.0609		
.00334	22.10	35.48	4.36	.0707		
.00690	25.07	44.68	2.73	.0779		
.0150	31.27	60.22	1.16	.0950		
.0432	46.01	89.98	1.02	.1390		
.1116	62.66	123.6	0.85	.1889		
.9684	213.5	426.9	..	.6405		

From these data it is obvious that with increase of partial pressure the molality of carbonate increases to a well-defined maximum, when P is about 0.00038 atm., and then decreases more gradually. Corresponding to this it was observed that the appearance of the crystals of $MgCO_3 \cdot 3H_2O$ remained unchanged throughout the course of the experiment at all of the pressures greater than 0.00038; but that at lower pressures the solid phase appeared to become very fine-grained—indicating therefore a change from carbonate to hydroxide, the duration of the experiments being insufficient to ensure complete conversion of the solid phase from carbonate to hydroxide. Accordingly we shall take the transition pressure (P_{tr}) as 0.0004 atm. at 25°, and consider separately the two regions in which carbonate or hydroxide, respectively, is the stable solid phase.

Evaluation of K_M, the Activity-Product Constant of $MgCO_3{\cdot}3H_2O$.—By definition $K_M = (Mg^{++})(CO_3^{--}) = m_1m_3\alpha_1\alpha_3$, where m_1 and m_3 represent gross molalities, and α_1 and α_3 the activity coefficients. When the experimental values of log m_1m_3 for pressures above 0.0004 are plotted against $\mu^{1/2}$ they lie—particularly at the more dilute end—on a smooth curve with diminishing curvature, becoming a straight line with the slope 4 (in accordance with the Debye–Hückel theory); the point at which this line cuts the axis $\mu^{1/2} = 0$ (where accordingly α_1 and α_3 are each unity) corresponds to $K_M = 1.1 \times 10^{-5}$.

It may also be evaluated from a plot of log $m_1m_2^2/P$ against $\mu^{1/2}$, extrapolated finally as a straight line of slope 3; the intersection with the axis corresponds to log K_M + log φ_0, φ_0 being 310.[7] This leads to $K_M = 0.8 \times 10^{-5}$; but we would assign a greater weight to the other value, because this second function is very sensitive. Accordingly we shall adopt for K_M at 25° the value 1×10^{-5}.

Evaluation of K_H, the Activity-Product Constant of $Mg(OH)_2$.—With a knowledge of K_M and of the transition pressure P_{tr} we may evaluate K_H from the relation

$$K_H = \frac{K_W^2}{\gamma\lambda c K_1 K_2} \times \frac{K_M}{P_{tr}}$$

which is readily derived by combining[8] the equations of the preceding paper with the definitions $K_H = (Mg^{++})(OH^-)^2$, $K_W = (H^+)(OH^-)$. Substituting the values of the several coefficients, we obtain

$$K_H = 2.20 \times 10^{-10} \times \frac{1 \times 10^{-5}}{0.0004} = 5.5 \times 10^{-12}$$

This also may be evaluated in another way. The molality of hydroxyl ion (m_4) is calculated in each case from m_2, P and the appropriate constants;[9] the resulting values are listed in the last column of Table I. When log $m_1m_4^2$ is plotted against $\mu^{1/2}$ and extrapolated, as before, on an initial slope of 3, we find an intercept corresponding to $K_H = 2.7 \times 10^{-12}$.

These two values agree as well as could be expected under the circumstances; we consider the higher to be the more reliable. This constant has been given as 12×10^{-12} at 18°, derived from conductivity measure-

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[7] *Cf.* preceding paper and ref. 6.

[8] This equation was developed, in slightly different notation, in ref. 3 e.

[9] As discussed in ref. 6; $[OH^-] = 8.42 \times 10^{-7}[HCO_3^-]/P$.

ments of saturated solutions of magnesium hydroxide[10] and from hydrogen electrode determinations;[11] that it is higher than ours is to be ascribed in part to the difference of temperature (the solubility of magnesium hydroxide is thought to decrease with increase of temperature) and to the method of calculation, but may be largely due to the fact that such direct determinations tend to be high unless carbon dioxide is rigorously excluded from the solution. It may be added that Greenfield and Buswell,[12] from observations of the $P_{\rm H}$ at which magnesium hydroxide is precipitated by alkali, conclude that K_H should be slightly less than 12×10^{-12}.

The general agreement of these values corroborates the view that there is at 25° no definite stable basic carbonate with a field between that of hydroxide and that of normal carbonate, for by substituting the values of K_H and K_M in the expression given above, we derive a value of P_{tr} of the same order as that observed; whereas the assumption of any basic carbonate (for instance, $MgCO_3{\cdot}Mg(OH)_2$ or $3MgCO_3{\cdot}Mg(OH)_2{\cdot}3H_2O$), leads to a calculated transition pressure so much larger as to be irreconcilable with that observed.

Summary

The equilibrium in solutions of magnesium carbonate at 25° has been investigated over a range of pressures of carbon dioxide from 1 to 0.0001 atmosphere. The carbonate is stable down to 0.004 atm., below which the hydroxide is stable; no indication of definite basic carbonates was observed. The activity product constant of magnesium carbonate at 25° is taken as 1×10^{-5}; that of magnesium hydroxide similarly as 5×10^{-12}. Interpolated values of the molality of magnesium in the solution saturated with the carbonate at 25° for a series of values of the partial pressure (in atm.) of carbon dioxide are appended.

P	[Mg]	P	[Mg]	P	[Mg]
0.001	0.0178	0.3	0.117	2	0.287
.01	.0270	.5	.152	5	.384
.05	.0489	.7	.181	10	.471
.1	.0660	1.0	.217	15	.526

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[10] Dupré and Bialas, *Z. angew. Chem.*, **16**, 55 (1903).

[11] Gjaldbaek, *Z. anorg. allgem. Chem.*, **144**, 145, 269 (1924).

[12] Greenfield and Buswell, THIS JOURNAL, **44**, 1435 (1922).