Magnesium Complex and Ion-Pair in $MgCO_3$–CO_2 Solution System[1]

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pK values of 1.23, 8.08, and 3.24 were obtained for the equilibrium reaction of the complex and ion-pair carbonates of magnesium, $MgHCO_3^+ = Mg^{2+} + HCO_3^-$, $MgHCO_3^+ = H^+ + MgCO_3^0$, and $MgCO_3^0 = Mg^{2+} + CO_3^{2-}$, respectively, by the simultaneous potentiometric estimation of H and Mg ion activities. Standard free energies of formation for $MgHCO_3^+$ and $MgCO_3^0$: −251.10 and −239.63 kcal/mol, respectively.

The accurate definition of Mg in physical and biological systems in equilibrium with bicarbonate and carbonate ions requires a knowledge of the individual Mg species (Mg^{2+}, $MgHCO_3^+$, $MgCO_3^0$) present in solution. However, there are gross inconsistencies in the reported values of the equilibrium constant associated with the different species, and even a question regarding the actual presence of the complex species. These differences reported in the literature are illustrated in Table I. The pK values listed are the negative logarithms of the K's, where $K_1 = (Mg^{2+})(HCO_3^-)/(MgHCO_3^+)$, $K_2 = (MgHCO_3^+)/(MgCO_3^0)(H^+)$, and $K_3 = (Mg^{2+})(CO_3^{2-})/(MgCO_3^0)$, with the parentheses indicating activity.

Greenwald (*4*) questioned Halla and Van Tassel's (*5*) conclusion that $MgHCO_3^+$ is not present, on the basis that the latter's pH measurements were not sensitive enough to detect the complex species. An element of doubt still exists, however, since Halla and Van Tassel's work was done 20 years after Greenwald's (*3*) original investigation, and presumably the mechanics of pH measurements improved considerably over that period. Furthermore, Garrels and Christ (*1*) observed that the relationship between K_1 and the electronegativity of Mg (also Ca) was different from that of the other species, and further noted that the values for K_1 were open to question, since the experimental errors associated with the measurements were large.

Our studies involving magnesium carbonates required a precise knowledge of their various dissociation constants, but the disagreement in the reported data listed earlier cast some doubt on the reliability of the K values. To clarify some of the discrepancies, an improved theoretical model was developed in which K_1, K_2, and K_3 could be estimated simultaneously in the same system from precise measurements of the Mg^{2+} and H^+ activities.

THEORY

The total Mg in solution, Mg_T, may be equated to its component parts by the relation

$$Mg_T = Mg^{2+} + MgHCO_3^+ + MgCO_3^0 \tag{1}$$

assuming the absence of other Mg species of the general form $Mg(HCO_3)_n^{2-n}$ except $MgHCO_3^+$. Using the definition for K_1 and K_2 presented previously, and substituting the component concentration from these constants into Equation 1, together with the appropriate mathematical treatment and rearrangement, yields the relation

$$\frac{([Mg_T]/[Mg^{2+}]) - 1}{[HCO_3^-]\ \dfrac{\gamma_{HCO_3^-}\gamma_{Mg^{2+}}}{\gamma_{MgHCO_3^+}}} = \frac{1}{K_1} + \frac{1}{K_1K_2}\cdot\frac{\gamma_{MgHCO_3^+}}{(H^+)} \tag{2}$$

where the brackets indicate concentration and γ the activity coefficient. All the components of Equation 2 except K_1 and K_2 can be either measured directly or estimated indirectly from the measured parameters. Equation 2 is a first-order linear equation in which $K_1 = 1/\text{intercept}$ and $K_2 = 1/(K_1 \times \text{slope})$. Furthermore, $K_3 = K_1K_2K_{2A}$, where K_{2A} is the second dissociation constant of carbonic acid. In this method, $[Mg_T]$ and $[Mg^{2+}]$ are determined as a function of $[HCO_3^-]$, with the HCO_3^- concentration being varied by changing the partial pressure of CO_2.

An alternative method for estimating K_1 involves the use of a noncarbonate magnesium salt such as $MgCl_2$ instead of MgO or $MgCO_3$, and equilibrating the solution to CO_2 to control the HCO_3^- concentration. By using the charge balance of the ions in solution ($H^+ + 2\ Mg^{2+} + MgHCO_3^+ = Cl^- + HCO_3^-$) and including the definition of K_1 in a manner described by Hostetler (*8*), the solution of K_1 is as follows:

$$K_1 = \frac{\{[Mg_T] - ([H^+] - [HCO_3^-])\}\,[HCO_3^-]\gamma_{Mg^{2+}}\gamma_{HCO_3^-}}{([H^+] - [HCO_3^-])\gamma_{MgHCO_3^+}} \tag{3}$$

In this case, only pH measurements are necessary for calculating K_1. Note also that $[MgHCO_3^+]$ is approximately equal to $[H^+] - [HCO_3^-]$. However, the low pH of the

Table I. Equilibrium Constants Associated with Complex and Ion-Pair of Mg Carbonates at 25° C

Investigator	pK_1	p$(1/K_2)$	pK_3
Halla and Van Tassel (*5*)	Absent	. . .	. . .
Hostetler (*8*)	0.95	7.86[a]	. . .
Greenwald (*3*)[b]	1.16	7.77	3.26[c]
Näsänen (*11*)	3.70	. . .	. . .
Garrels et al. (*2*)	. . .	. . .	3.40
Raaflaub (*12*)	. . .	. . .	2.07[d]

[a] Calculated from pK_3 data of Garrels et al. (*2*). [b] Experiment run at 22° C and $\mu = 0.15$. Correction made to $\mu = 0$. [c] Calculated from pK_1 and p$(1/K_2)$. [d] Experiment run at 20° C and $\mu = 0.10$. Correction made to $\mu = 0$.

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Table II. Experimental and Computational Results for Estimating Apparent $K_{MgHCO_3^+}$ and $K_{MgCO_3^0}$ at Ionic Strength of Approximately 0.04

$[Mg_T] \times 10^2$, M	pH	$P_{CO_2} \times 10^1$, atm	$(Mg^{2+}) \times 10^2$, M	$[Mg^{2+}] \times 10^2$, M	$[MgHCO_3^+] \times 10^3$, M	$[MgCO_3^0] \times 10^3$, M	$[HCO_3^-] \times 10^2$, M	$[CO_3^{2-}] \times 10^4$, M	$\mu \times 10^2$, M
1.50	6.224	9.236	6.95	1.288	2.10	0.02	2.756	0.04	4.06
1.50	6.912	1.876	6.70	1.236	2.53	0.10	2.725	0.18	3.96
1.50	7.183	0.942	6.60	1.209	2.70	0.21	2.549	0.31	3.83
1.50	7.487	0.470	6.50	1.189	2.49	0.42	2.560	0.62	3.80
1.50	7.880	0.193	6.45	1.180	2.31	0.89	2.600	1.57	3.81
1.98	8.184	0.0886	7.20	1.339	3.62	2.80	2.414	2.98	4.12
1.98	8.384	0.0502	8.05	1.509	2.12	2.59	2.171	4.28	4.30

Intercept = 14.936. Slope = 9.125×10^{-8}.

Table III. Experimental and Computational Results for Estimating Apparent $K_{MgHCO_3^+}$ and $K_{MgCO_3^0}$ at Ionic Strength of Approximately 0.066

$[Mg_T] \times 10^2$, M	pH	$P_{CO_2} \times 10^1$, atm	$(Mg^{2+}) \times 10^2$, M	$[Mg^{2+}] \times 10^2$, M	$[MgHCO_3^+] \times 10^3$, M	$[MgCO_3^0] \times 10^3$, M	$[HCO_3^-] \times 10^2$, M	$[CO_3^{2-}] \times 10^4$, M	$\mu \times 10^2$, M
2.53	6.427	9.202	1.01	2.074	4.48	0.08	4.526	0.11	6.63
2.53	7.113	1.868	0.95	1.934	5.49	0.47	4.447	0.51	6.38
3.43	8.345	0.0890	1.07	2.195	5.04	7.31	3.624	7.18	6.60
3.43	8.595	0.0504	1.03	2.104	3.70	9.56	3.642	12.78	6.47
4.46	8.608	0.0504	1.13	2.360	5.77	15.22	3.778	14.00	7.18

Intercept = 11.925. Slope = 9.792×10^{-8}.

$MgCl_2$–CO_2 solution precludes the presence of CO_3^{2-} and thus K_2; consequently, K_3 cannot be determined by this method. Halla and Van Tassel (*5*) attempted to determine the K_1 at higher pH's using MgO, but were not successful because their pH measurements were not sufficiently sensitive to estimate accurately the Mg complexes (*4*). Furthermore, they did not account for the presence of the ion-pair $MgCO_3^0$ in deriving their relation for K_1.

EXPERIMENTAL

Solutions of $MgCO_3$ and $MgCl_2$, ranging in concentrations from approximately 1 to 6×10^{-2} M, were prepared from reagent-grade salts. Total Mg was checked with the complexometric versenate titration technique. Pure CO_2 and CO_2–N_2 mixtures (99.98 to 0.5% CO_2) were first premoistened and then bubbled through the Mg solutions of different compositions. The partial pressure of CO_2 was estimated from the barometric pressure, the CO_2 composition of the gas mixture, and the vapor pressure of water.

Activities of Mg^{2+} and H^+ at 25° ± 0.5° C were measured simultaneously with the Orion specific-ion liquid membrane and the Corning type 476022 glass electrodes, respectively, using the Orion 801 and Beckman Research pH-millivoltmeters accurate to ±0.1 mV. Sargent-type S30080-15 ceramic plug-type saturated KCl–calomel electrodes were used. The Mg electrode was calibrated in $MgCl_2$ solutions of known Mg^{2+} activities which closely bracketed the Mg activity of the test solution. Hopefully, this would also simulate liquid junction potentials, if they are present, and minimize any error originating from this source. To avoid any stray emf noise affecting the Mg electrode, measurements were made in a Faraday cage. The glass electrode was calibrated against commercial reference solutions which were first checked with NBS standard buffers.

The bicarbonate and carbonate concentrations were estimated from the measured pH and the calculated CO_2 partial pressure using the first [$pK_{1A} = 6.363$(*6*)] and second [$pK_{2A} = 10.327$(*7*)] dissociation constants of carbonic acid, respectively. Henry's law constant ($k = 0.0344 - 0.0084\,\mu$) was recomputed from the data of Harned and Davis (*6*). Activity coefficients for the different ionic species were computed from the extended Debye-Hückel theory $-\log \gamma = Az^2(\mu)^{1/2}/[1 + Ba(\mu)^{1/2}]$ using the appropriate constants tabulated by Kielland (*9*).

The solution of Equation 2 to get K_1 and K_2 required different combinations of $[Mg_T]$ and $[HCO_3^-]$. Experimentally, this can be achieved the easiest by maintaining $[Mg_T]$ constant and by varying the partial pressure of CO_2 which then gives different concentrations of HCO_3^-. However, because the HCO_3^- concentration and the extent of Mg^{2+} complexing are different at the different partial pressures of CO_2, identical ionic strength is not attained for the same $[Mg_T]$ and different CO_2 combinations. Furthermore, since the ionic strengths are not known a priori, the initial ionic strength was assumed to be $3[Mg_T]$ to start the iterative computational procedure. Using this initializing ionic strength, with the measured H^+ and Mg^{2+} activities, CO_2 partial pressure, and $[Mg_T]$, the constituents of Equation 2 were estimated and the apparent K_1' and K_2' calculated from the slope and intercept. Further, refinement in the ionic strength value was made by using the newly established apparent K's to obtain $[MgHCO_3^+]$ and $[MgCO_3^0]$ and using the more appropriate relation $\mu = (4\,[Mg^{2+}] + [HCO_3^-] + 4\,[CO_3^{2-}] + [MgHCO_3^+])/2$. The computational procedure was repeated using improved activity values, and the iteration continued until the slope and intercept became constant. Each set of $MgCO_3$ concentration with its respective CO_2 partial pressure range was treated in this manner.

The preceding computational procedure subsequently permitted the selection of the different $[Mg_T]$–P_{CO_2} combinations with similar ionic strengths which were then recombined to get a new set of K_1' and K_2' by use of Equation 2. The usual practice in following ionic strength dependency of a constant is to vary the ionic strength with an inert electrolyte such as $NaClO_4$ or KCl. Unfortunately, in this case, the Mg electrode was affected by K^+ and Na^+ so that this practice could not be used, and instead ionic strength varied as a function of the $[Mg_T]$ and P_{CO_2} combination.

RESULTS AND DISCUSSION

The experimental and computational results are listed in Tables II–VI for ionic strengths ranging from approximately 0.04 to 0.12M. The $[Mg]_T$, pH, P_{CO_2}, and (Mg^{2+})

Table IV. Experimental and Computational Results for Estimating Apparent $K_{MgHCO_3^-}$ and $K_{MgCO_3^0}$ at Ionic Strength of Approximately 0.085

$[Mg_T] \times 10^2$, M	pH	$P_{CO_2} \times 10^1$, atm	$(Mg^{2+}) \times 10^2$, M	$[Mg^{2+}] \times 10^2$, M	$[MgHCO_3^-] \times 10^3$, M	$[MgCO_3^0] \times 10^2$, M	$[HCO_3^-] \times 10^2$, M	$[CO_3^{2-}] \times 10^3$, M	$\mu \times 10^2$, M
3.43	6.540	9.355	1.22	2.659	7.46	0.02	6.082	0.020	8.74
3.43	7.230	1.841	1.20	2.600	7.13	0.12	5.851	0.094	8.50
3.43	7.500	0.953	1.17	2.518	6.99	0.21	5.631	0.168	8.23
4.46	8.166	0.185	1.32	2.881	6.56	0.92	5.094	0.716	8.78
5.00	8.455	0.0890	1.30	2.822	5.82	1.60	4.753	1.292	8.57
5.59	8.614	0.0504	1.35	2.913	5.39	2.14	3.874	1.509	8.33

Intercept = 9.986. Slope = 1.231×10^{-7}.

Table V. Experimental and Computational Results for Estimating Apparent $K_{MgHCO_3^+}$ and $K_{MgCO_3^0}$ at Ionic Strength of Approximately 0.10

$[Mg_T] \times 10^2$, M	pH	$P_{CO_2} \times 10^1$, atm	$(Mg^{2+}) \times 10^2$, M	$[Mg^{2+}] \times 10^2$, M	$[MgHCO_3^+] \times 10^3$, M	$[MgCO_3^0] \times 10^2$, M	$[HCO_3^-] \times 10^2$, M	$[CO_3^{2-}] \times 10^3$, M	$\mu \times 10^1$, M
4.46	7.311	1.837	1.44	3.279	9.73	2.08	7.143	0.147	1.06
4.46	7.573	0.952	1.38	3.107	9.71	3.82	6.743	0.251	1.01
4.46	7.839	0.485	1.35	3.010	8.38	6.11	6.321	0.429	0.968
5.00	7.898	0.486	1.39	3.161	10.00	8.33	7.301	0.580	1.06
5.00	8.240	0.186	1.37	3.057	6.86	1.26	6.094	1.042	0.971
5.59	8.254	0.186	1.52	3.465	7.38	1.39	6.335	1.146	1.07
6.30	8.459	0.0892	1.50	3.351	7.30	2.22	4.850	1.375	0.977
6.51	8.465	0.0893	1.56	3.515	7.36	2.26	4.936	1.433	1.015

Intercept = 9.305. Slope = 1.272×10^{-7}.

Table VI. Experimental and Computational Results for Estimating Apparent $K_{MgHCO_3^+}$ and $K_{MgCO_3^0}$ at Ionic Strength of Approximately 0.12

$[Mg_T] \times 10^2$, M	pH	$P_{CO_2} \times 10^1$, atm	$(Mg^{2+}) \times 10^2$, M	$[Mg^{2+}] \times 10^2$, M	$[MgHCO_3^+] \times 10^2$, M	$[MgCO_3^0] \times 10^2$, M	$[HCO_3^-] \times 10^2$, M	$[CO_3^{2-}] \times 10^3$, M	μ
4.46	6.630	9.334	1.50	3.454	0.98	0.02	7.592	0.033	0.112
5.00	7.360	1.841	1.51	3.514	1.30	0.18	8.067	0.191	0.118
5.00	7.612	0.953	1.41	3.230	1.42	0.35	7.427	0.308	0.109
5.59	7.907	0.486	1.58	3.687	1.28	0.63	7.511	0.628	0.119
6.31	8.297	0.186	1.57	3.652	1.20	1.45	7.048	1.442	0.117
6.51	8.296	0.186	1.63	3.816	1.22	1.47	7.057	1.451	0.121

Intercept = 10.891. Slope = 8.735×10^{-8}.

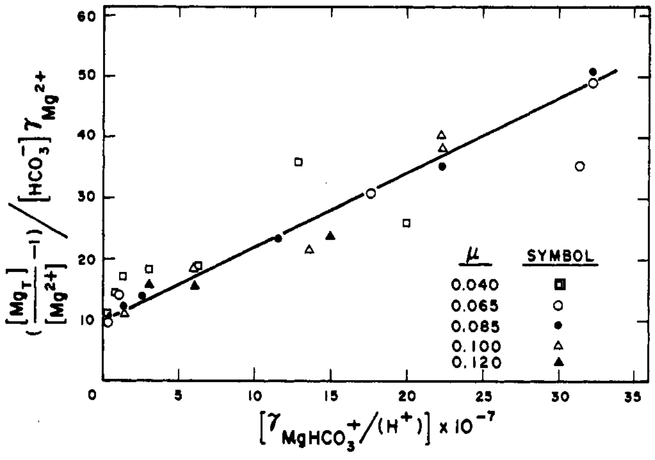

Figure 1. Plots of $\{([Mg_T]/[Mg^{2+}]) - 1\}/[HCO_3^-]\gamma_{Mg^{2+}}$ vs. $\gamma_{MgHCO_3^+}/(H^+)$ for determining dissociation constants of $MgHCO_3^+$ and $MgCO_3^0$

were measured, whereas $[HCO_3^-]$ and $[CO_3^{2-}]$ were calculated from the pH, K_{1A}, and K_{2A} values, and $[MgHCO_3^+]$ and $[MgCO_3^0]$ were estimated from the experimentally determined K_1 and K_2 values. The $[Mg_T]$-CO_2 concentration used provided an adequate range for relating $\{([Mg_T]/[Mg^{2+}]) - 1\}/[HCO_3^-]\gamma_{Mg^{2+}}$ to $\gamma_{MgHCO_3^+}/(H^+)$. Plots of these are shown in Figure 1. The slope and intercepts were statistically computed for each of the ionic strengths.

The pK values for the different Mg carbonates are presented in Table VII, and pK's at $\mu = 0$ were obtained by extrapolation. The pK's for the relation $(Mg^{2+})(HCO_3^-)/(MgHCO_3^+) = 1.23$, $(MgCO_3^0)(H^+)/(MgHCO_3^+) = 8.08$, and $(Mg^{2+})(CO_3^{2-})/(MgCO_3^0) = 3.24$. The standard free energies of formation for $MgHCO_3^+$ and $MgCO_3^0$ at 25° C are −251.10 and −239.63 kcal/mol, respectively, calculated from the extrapolated pK's and the thermodynamic data presented by Latimer (*10*) for Mg^{2+}, H^+, HCO_3^-, and CO_3^{2-}.

The $MgHCO_3^+$ predominates over the $MgCO_3^0$ species at pH 8 and lower, whereas the reverse is true at the higher pH's (Tables II and VI). At the higher pH's the ionic Mg^{2+} form makes up approximately 50% of the total Mg in solution; this behavior can be of significance in defining ionic reactions occurring in this pH range.

The pH measurements and the calculated pK_1' values for the $MgCl_2$-CO_2 system as defined by Equation 3 are presented in Table VIII. In this case, pK_1 at $\mu = 0$ of 1.27 ± 0.01 compares favorably with pK_1 of 1.23 obtained independently through the $MgCO_3$-CO_2 system, using both the Mg- and H-ion activity measurements. The pK_1 in turn is similar to Greenwald's (*3*) value of 1.16, which has been corrected from an ionic strength of 0.15. The difference in pK_1 presented here and that of Hostetler (*8*) can be resolved in part by the choice of the dissociation of carbonic acid, and the assumption that the partial pressure of CO_2 is 1 atm. By use of the pK_{1A} from this paper,

Table VII. Apparent Dissociation Constants for $MgHCO_3^+$ and $MgCO_3^0$

μ	pK_1	$p(1/K_2)$	pK_3
0.00[a]	1.23	8.08	3.24
0.0398	1.17	8.21	3.29
0.0665	1.08	8.08	3.32
0.0852	1.00	7.91	3.42
0.102	0.968	7.86	3.43
0.116	1.04	8.10	3.27

[a] Extrapolated by linear regression statistics.

Table VIII. Apparent pK_1' Values Obtained from the $MgCl_2$–CO_2 System

$MgCl_2$, *M*	pH	μ	pK_1'
0.006	3.907	0.018	1.29
0.0075	3.903	0.022	1.27
0.010	3.899	0.030	1.26
0.0233	3.877	0.070	1.23
0.035	3.860	0.115	1.25
0.050	3.845	0.150	1.22
0.060	3.834	0.180	1.23
0.070	3.824	0.210	1.25

and correcting for the vapor pressure of water and the effect of salt on Henry's law constant, Hostetler's $pK_1 = 0.95$ becomes $pK_1 = 1.21$ at $\mu = 0.07$ and more comparable to the data presented in Table VII. Näsänen's data (*11*), on the other hand, are not reliable. He worked at pH's of about 11, and did not take into account the presence of $MgOH^+$ and $MgCO_3^0$ species. This work (Tables II to VI) and Greenwald's (*3*) show that the $MgCO_3^0$ can become a significant portion of the total Mg as the pH is increased.

The $p(1/K_2)$ at $\mu = 0$ is 8.08 and 8.05 at $\mu = 0.15$ vs. Greenwald's 7.77 at 0.15; at $\mu = 0.07$, $p(1/K_2) = 8.06$ vs. Hostetler's 7.86. In Greenwald's method, he had to assume a value for $1/K_2$ to get his K_1's to compare with each other in the electrotitrimetric method. Hostetler (*8*) used different dissociation constants. His pK_3 of 3.40 was obtained from Garrels et al. (*2*). A pK_3 of 3.24 was derived in this study at $\mu = 0$. By use of extrapolation in Table VII $pK_3 = 3.38$ at $\mu = 0.15$, which is the ionic strength above Garrels et al. (*2*), obtained consistent values for pK_3.

Raaflaub's (*12*) value for $pK_3 = 2.97$ was determined by estimating Mg^{2+} indirectly by measurements of the Mg-eriochrome Black-T complex in solution within a narrow pH range 9.4 to 9.7. At present, a combination of the electrometric determination of (H^+) and (Mg^{2+}) activities and the theoretical approach presented in this paper appears to be the most direct method for estimating the different magnesium carbonate complexes. The *K* values compare favorably with other independent methods, and in addition, apparent dissociation constants can be obtained at a specified ionic strength.

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LITERATURE CITED

(1) Garrels, R. M., Christ, C. L., "Solutions, Minerals and Equilibria," pp 98–99, Harper and Row, New York, N.Y., 1965.
(2) Garrels, R. M., Thompson, M. E., Siever, R., *Amer. J. Sci.*, **259**, 24 (1961).
(3) Greenwald, I., *J. Biol. Chem.*, **141**, 789 (1941).
(4) Greenwald, I., *J. Phys. Chem.*, **63**, 1328 (1959).
(5) Halla, F., Van Tassel, R., *ibid.*, **62**, 1135 (1958).
(6) Harned, H. S., Davis, R., Jr., *J. Amer. Chem. Soc.*, **65**, 2030 (1943).
(7) Harned, H. S., Sholes, S. R., *ibid.*, **63**, 1706 (1941).
(8) Hostetler, P. B., *J. Phys. Chem.*, **67**, 720 (1963).
(9) Kielland, J., *J. Amer. Chem. Soc.*, **59**, 1675 (1937).
(10) Latimer, W. M., "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," pp 30, 128, 316, Prentice-Hall, New York, N. Y., 1952.
(11) Näsänen, R., *Z. Phys. Chem.*, **A190**, 183 (1942).
(12) Raaflaub, J., *Helv. Chim. Acta*, **43**, 629 (1960).

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Solution-Crystal Equilibrium for Pyridine–Water System

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New experimental data on the solid-liquid equilibrium of pyridine–water mixtures are reported. There is a pyridine hydrate which has an incongruent melting point at −28.6° C.

The freezing-point data of Baud (*4*), Ewert (*9*), and Frédéric and Rayet (*9*) for pyridine-water mixtures are shown on Figure 1. If the pyridine-water system is a simple eutectic, then equilibrium is established between pure solid *i* (*i* = 1, 2; pyridine is component 1, water is component 2) and liquid solution. The equilibrium condition for equality of fugacities is (*18*):

$$P_i^s = P_i^l \gamma_i x_i \qquad (1)$$

Equation 1 establishes two equilibrium lines $[x_1(T)$ and $x_2(T)]$ which should intersect at the eutectic composition.

The ratio of the vapor pressure of pure liquid to that of pure solid is given by the Schröder-Van Laar equation (*18*):

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