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THE STABILITY OF THE MAGNESIUM CARBONATE ION PAIR FROM 10° TO 90°C

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ABSTRACT. The dissociation constants of the aqueous $MgCO_3°$ ion pair were determined experimentally from 10° to 90°C at 15° intervals. Absolute pH measurements in $MgCl_2$–$KHCO_3$ solutions being titrated with K_2CO_3 were used to calculate the results. The experimental $pK_{MgCO_3°}$ ($-\log K_{dissociation}$) at 25°C is 2.98 ± 0.03, and the pK values rise smoothly, as a function of temperature, to a value of 3.41 ± 0.067 at 90°C. The temperature variation is in excellent agreement with that predicted by electrostatic ion pair theory. The derived values of $\Delta G_R°$, $\Delta H_R°$, and $\Delta S_R°$ of dissociation at 25°C are 17050 ± 125 J mol^{-1} (4075 ± 30 cal mol^{-1}, −8439 J mol^{-1} (−2017 cal mol^{-1}), and −85.48 J deg^{-1} mol^{-1} (−20.43 cal deg^{-1} mol^{-1}), respectively.

INTRODUCTION

The $MgCO_3°$ ion pair is a geochemically very important aqueous species. This ion pair is present in significant concentrations in alkaline solutions containing magnesium ions and carbonate species and thus is important to the quantitative interpretation of mineral and electrolyte solution interactions. For instance, Garrels and Thompson (1962) showed that the $MgCO_3°$ ion pair is the dominant factor determining the activity of CO_3^{2-} (aq) in seawater and is thus a determining factor in the interaction of seawater with carbonate minerals. Knowledge of the stability of $MgCO_3°$ can also be important in experimental mineral solubility studies. Solubility studies at 90°C on dolomite by Siebert and Hostetler (1970) and on magnesite by Christ and Hostetler (1970) were limited to high experimental values of P_{CO_2} and hence low values of pH because of lack of $MgCO_3°$ data at higher temperatures. Thus, reliable data for the $MgCO_3°$ stability over a wide range of temperatures is desirable.

Previous published values of $-\log K_{dissoc}$ for $MgCO_3°$ at 25°C are:

Greenwald (1941)	3.26
Raaflaub (1960)	2.97
Garrels, Thompson, and Siever (1961)	3.40
Nakayama (1971)	3.24
Larson, Sollo, and McGurk (1973)	2.90
Reardon and Langmuir (1974)	2.88

Reardon and Langmuir also reported values at 10°, 40°, and 50°C. The agreement between investigators is poor. Examination of the procedures used in some of the above determinations reveals problems that

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**School of Earth Sciences, Macquarie University, North Ryde, New South Wales 2113, Australia cast doubt on the validity of the results. For example, Garrels, Thompson, and Siever (1961) failed to take into account the $MgHCO_3^+$, $NaHCO_3^\circ$, and $NaCO_3^-$ ion pairs in their calculations. Similarly, Larson, Sollo, and McGurk (1973) failed to take into account the $MgHCO_3^+$ ion pair in the calculation of his result. Nakayama (1971) used a slope-intercept method, where the slope is a function of $K_{MgCO_3^\circ}$ in his equation. This slope is dependent on $[H^+]^{-2}$, and the quantity dK_2/dH^+ is proportional to $[H^+]^{-3}$, greatly magnifying pH errors in the results. The recent work of Reardon and Langmuir (1974) appears to be the best to date, and their values from 10° to 50°C will be used for comparison with the results reported here.

EXPERIMENTAL PROCEDURE

Because of the scarcity of quality data and the scarcity of data at temperatures other than 25°C, the stability of $MgCO_3^\circ$ ion pair was determined from 10° to 90°C, the goal being to maximize the accuracy of the determination. This was allowed, in part, by the availability of data for the $MgHCO_3^+$ ion pair from 10° to 90°C (Siebert and Hostetler, 1977). The experiments were performed at relatively high concentrations of reactants and at high activities of CO_3^{2-} (high pH values) in order to generate large concentrations of $MgCO_3^\circ$; high concentrations were achieved by virtue of the large degree of supersaturation with respect to magnesite (3 to 4 orders of magnitude) tolerated by most of these solutions. The experimental approach utilized in this study was that of the potentiometric titration of a $MgCl_2$ and $KHCO_3$ solution with K_2CO_3 solution. The approach did not follow the customary equilibration of a gas phase of known CO_2 content with the experimental solutions and the subsequent calculation of the HCO_3^- and CO_3^{2-} activities from the P_{CO_2} and pH. The method used here removes the uncertainties implicit in an experimental P_{CO_2} value (Christ, Hostetler, and Siebert, 1974), and the equilibrium constants describing the solubility of CO_2 and the dissociation of carbonic acid. Experimental runs were performed at 10°, 25°, 40°, 55°, 70°, and 90°C.

Experimental runs were performed in a one liter Pyrex beaker that was fitted with a tight-sealing polyvinyl plastic lid. This lid was fitted with a 300-watt stainless steel immersion heater, a heat exchanger coil of stainless steel tubing and holes for a buret, thermometer, stainless steel thermistor probe, and pH electrodes. Appropriate quantities of distilled-deionized water, solid $KHCO_3$, and $MgCl_2$ solution were weighed into the beaker, and the solution was thermostated at the temperature of the run. The solution was then titrated with K_2CO_3 solution. The pH and volume of titrant were recorded at intervals of 0.1 and 0.2 pH units, until the run was terminated by precipitation. No gas was bubbled through the run solution. Stirring was provided by a magnetic stirrer and a Teflon-coated stirring bar.

Temperature regulation was achieved with the immersion heater and an electronic temperature controller using a thermistor temperature sensor. At 10° and 25°C, the immersion heater was balanced against the heat exchange coil, through which coolant flowed from a refrigeration-circulator unit, to produce regulation of ±0.04°C. At higher temperatures, only the immersion heater was used to give ±0.03°C regulation. Solid $KHCO_3$ was prepared for weighing by drying reagent grade $KHCO_3$ over $CaCl_2$ in a desiccator for several days, whereas the K_2CO_3 was prepared by heating reagent grade K_2CO_3 at 275°C for 2 hrs. Concentrated $MgCl_2$ solution was prepared by dissolving $MgCl_2 \cdot 6H_2O$ in distilled-deionized water and analyzing titrimetrically for Mg^{2+} and Cl^- with EDTA and $AgNO_3$, respectively. Results for both the cation and anion agreed to within 1 part per 500. The solid $KHCO_3$ and the $MgCl_2$ solutions were weighed to ±1 mg, while water was weighed to ±0.1 g precision. Solutions of K_2CO_3 were prepared fresh for each day's work and were added to the run from a 100-ml burette with ±0.02 ml readability. The distilled-deionized water used throughout this work is presumed to contain little dissolved CO_2. Efforts to obtain a stable and meaningful pH on this water failed, and specific conductance measurements yielded values of less than 1.0 micromhos. Both suggest that the water is far from equilibrium with atmospheric CO_2. If equilibrium with atmospheric CO_2 ($P_{CO_2} \approx 10^{-3.5}$) is assumed, the total dissolved inorganic carbon would not exceed approx 2×10^{-5} molal, and this value is small relative to the 0.01 to 0.08 molal solutions of total carbon in these runs. No attempt was made to seal completely the run vessel from contact with atmospheric CO_2, because it was believed that no significant quantity of CO_2 could be absorbed into the solution during the course of runs that lasted less than 1 hr. If the rate of exchange for CO_2 from gas to solution is a function of the P_{CO_2}, then the rate of absorption across the relatively small gas-liquid interface would be approx 3000 times slower for a P_{CO_2} of $10^{-3.5}$ than for a P_{CO_2} of 1. By experiment, approx 3 min were required for pure water in the run vessel to absorb approx 10^{-4} mols of CO_2 at $P_{CO_2} = 1$.

The experimental pH was monitored with an Orion 801 digital pH meter and a Sargent-Welch S-30072 combination electrode with thallium amalgam internal electrodes and a platinum fiber junction. This electrode, with its low temperature hysteresis internal electrodes, proved to equilibrate rapidly and to be stable, particularly at higher temperatures. The combination of the Beckman 39099 Glass and Orion double junction reference electrode with 10 percent KNO_3 filling solution was also used to a limited extent in the low temperature work but was discarded when their potential became erratic during handling between buffer readings at higher temperatures. This behavior apparently resulted from changes in liquid junction potential due to mechanical changes in the junction of the reference electrode. Where satisfactory data were collected, both electrodes gave results that were in agreement. The pH measuring assembly was calibrated with commercial phosphate and borax buffers which were constantly checked for agreement with a $NaHCO_3$–Na_2CO_3 buffer made from the NBS formula given by Bates (1973, p. 73). The electrodes and buffers were all thermostated to the temperature of the run in a separate water bath. Agreement between buffers was seldom worse than ±0.01 pH units, and buffer checks after the run termination were within ±0.02 pH units of the assigned buffer values.

CALCULATION OF THE STABILITY CONSTANT

The experimental molality and the thermodynamic dissociation constant were calculated for $MgCO_3^\circ$ from the experimentally determined parameters and the equations that describe the distribution of the various aqueous species. The experimentally determined quantities are:

pH — solution pH after K_2CO_3 increment is added;
Mg_T — molality of total Mg^{2+} added;
C_T — molality of total inorganic carbon defined as the sum of molalities contributed by the $KHCO_3$ and K_2CO_3 respectively;
mK^+ — molality of K^+ from $KHCO_3$ and K_2CO_3; and
mCl^- — molality of Cl^- equal to $2Mg_T$.

The only aqueous species assumed present in these solutions are Mg^{2+}, $MgHCO_3^+$, $MgCO_3^\circ$, $MgOH^+$, K^+, $H_2CO_3^\circ$, HCO_3^-, CO_3^{2-}, OH^-, and Cl^-. No association is assumed between K^+ and HCO_3^- or CO_3^{2-}, and between Mg^{2+} and Cl^-. The distribution of these various species is described by the total Mg^{2+} and total carbon mass balance equations, the charge balance equations, and the mass action equations for the stability of the various species. This leads to the following set of independent equations. The small *m* and brackets denote molality and activity, respectively. A form of equations that describes the dissociation equilibria of HCO_3^- is

$$mCO_3^{2-} = K_2[HCO_3^-]/(10^{-pH}\,\gamma_{CO_3^{2-}}) \tag{1}$$

The expression for the charge balance can be written as

$$\begin{aligned} mHCO_3^- = {} & 2mMg^{2+} + mMgHCO_3^+ + mMgOH^+ \\ & + mK^+ - 2mCO_3^{2-} - mHCO_3^- \\ & - mOH^-\ mCl^- \end{aligned} \tag{2}$$

The mass action equations describing the distribution of appropriate species are

$$mMgHCO_3^+ = [Mg^{2+}] \cdot mHCO_3^-/K_{MgHCO_3^+} \tag{3}$$

where $\gamma_{MgHCO_3^+}$ is assumed to be equal to $\gamma_{HCO_3^-}$

$$mOH^- = K_w/(10^{-pH} \cdot \gamma_{OH^-}), \tag{4}$$

$$mMgOH^+ = [Mg^{2+}] \cdot mOH^-/K_{MgOH^+} \tag{5}$$

where γ_{MgOH^-} is assumed equal to γ_{OH^-}, and

$$mH_2CO_3^\circ = [HCO_3^-] \cdot 10^{-pH}/K_1 \tag{6}$$

where $\gamma_{H_2CO_3^\circ}$ is assumed to be equal to 1.

The mass balance equations for total carbon and total Mg^{2+} can be written as

$$mMgCO_3{}^\circ = C_T - mMgHCO_3{}^+ - mHCO_3{}^- - mCO_3{}^{2-} - mH_2CO_3{}^\circ \tag{7}$$

$$mMg^{2+} = Mg_T - mMgHCO_3{}^+ - mMgCO_3{}^\circ - mMgOH^+ \tag{8}$$

where:

K_1 — first dissociation constant of carbonic acid;
K_2 — second dissociation constant of carbonic acid;
K_w — dissociation constant of water;
$K_{MgHCO_3{}^+}$ — dissociation constant of $MgHCO_3{}^+$ ion pair;
K_{MgOH^+} — dissociation constant of $MgOH^+$ ion pair.

These eight equations with their eight unknowns would normally be solved by an iteration technique in which provisional values of the unknowns are cycled through the equations to generate better approximations, which are, in their turn, recycled through the equations. The equations are iterated to a constant ionic strength. However, in practice, this approach led to convergence in only rare cases. An alternative approach was used in which the charge balance equation (eq 2) was removed from the iteration cycle, and, in its place, the activity of $CO_3{}^{2-}$ was arbitrarily specified. The $mHCO_3{}^-$ was then calculated by rearrangement of eq 1. The set of equations (excluding eq 2) was then iterated to constant ionic strength. These results were used to calculate the charge balance. If the charge balance equation was not satisfied, the activity of $CO_3{}^{2-}$ was incremented or decremented repeatedly, and the results recalculated until the charge balance was satisfied. Finally, for the dissociation reaction of $MgCO_3{}^\circ$, the thermodynamic dissociation constant was calculated by:

$$MgCO_3{}^\circ(aq) = Mg^{2+}(aq) + CO_3{}^{2-}(aq)$$

$$K_{MgCO_3{}^\circ} = \frac{[Mg^{2+}]\,[CO_3{}^{2-}]}{mMgCO_3{}^\circ} \tag{9}$$

By decreasing the size of the increments and decrements, the results were calculated with a precision of ±0.0001 $pK_{MgCO_3{}^\circ}$ units.

Single ion activity coefficients, γ_i, were calculated from the Debye-Huckel equation (Garrels and Christ, 1965, p. 61):

$$\log \gamma_i = -(Az_i{}^2I^{1/2})/(1 + \text{å}\,BI^{1/2}) \tag{10}$$

Values of A and B were taken from Helgeson (1967); I is the ionic strength in molal units. Values of the ion size parameter (å) used were 5.5×10^{-8} cm (Christ and Hostetler, 1970) for $HCO_3{}^-$ and 4.5×10^{-8} cm (Klotz, 1964, p. 417) for $CO_3{}^{2-}$. Values of $\gamma_{Mg^{2+}}$ were derived from eq 10, to which a $+bI^{3/2}$ term was added on the right side. The resulting equation was fitted to $\gamma_{Mg^{2+}}$ values calculated by the mean salt method (Garrels and Christ, 1965, p. 58), based on the MacInnes convention, from $MgCl_2$ (Harned and Owen, 1958) and $\gamma \pm$ KCl (Hostetler, Truesdell, and Christ, 1967) data. The resulting å was 5.5×10^{-8} cm, and b was 0.12 for 25°C. This equation fits the data well to ionic strengths far above those reached in this work. The å value for OH^- ion was taken to be 9×10^{-8} cm; the same value as for H^+ ion (Klotz, 1964). It was assumed that the å values for $MgHCO_3^+$ and $MgOH^-$ were the same as those for HCO_3^- and Mg^{2+}, respectively. Errors resulting from this assumption are negligible (Christ, Hostetler, and Siebert, 1974). Also, it is assumed that $[MgCO_3^\circ] = mMgCO_3^\circ$. For all single ions, the temperature dependence of the Debye-Huckel equation was assumed to predict adequately values of γ_i at temperatures other than 25°C.

The first and second dissociation constants of carbonic acid (K_1 and K_2) used at 10°, 25°, and 40°C are from Harned and Davis (1943) and Harned and Scholes (1941), respectively. Higher temperature values for K_2 were derived from Cuta and Strafelda (1954) by lowering the log K_2's by approx 0.03 units to bring their data into better agreement with those of Harned and Scholes (1941). Higher temperature values for K_1 were interpolated from the data of Ellis (1959) Values for $K_{MgHCO_3^+}$ have been taken from the work of Siebert and Hostetler (1977), K_{MgOH^+} is from McGee and Hostetler (1973), and K_w is from Ackerman (1958). For convenience, a compilation of the data used in these calculations is presented in table 1.

RESULTS AND DISCUSSION

Thirty-eight experimental runs (totalling 260 run points) were performed from 10° to 90°C. The results are summarized in table 2. The raw experimental data used in the calculations, along with the calculated ionic strength and dissociation constants, are tabulated in table 3. A more complete result for one representative run at 25°C is presented in table 4. The calculated molalities of the various species and their percentage of the total Mg^{2+} and carbon that are tabulated in table 4 are representative of the distribution of the aqueous species in the experiment. At 25°C, over the pH range of 8.9 to 9.8 $mMgCO_3^\circ$ rose from 16 to 60 percent of Mg_T and from 25 to 44 percent of C_T. Similarly, mMg^{2+}

TABLE 1

Constants used in calculating $pK_{MgCO_3^\circ}$

Temperature	A	B	$\log K_1$	$\log K_2$	$\log K_{MgHCO_3^+}$	$\log K_{MgOH^+}$	$\log K_w$
10°C	0.4960	0.3258	−6.464	−10.490	−1.051	−2.18	−14.534
25°C	0.5095	0.3284	−6.352	−10.329	−1.067	−2.20	−13.999
40°C	0.5244	0.3310	−6.298	−10.22	−1.108	−2.29	−13.533
55°C	0.5413	0.3338	−6.28	−10.15	−1.160	−2.37	−13.137
70°C	0.5596	0.3366	−6.27	−10.125	−1.230	−2.44	−12.800
90°C	0.5871	0.3406	−6.25	−10.12	−1.337	−2.54	−12.422

and $m\mathrm{HCO_3}^-$ never fell below 35 percent of $\mathrm{Mg_T}^{2+}$ and 30 percent of $\mathrm{C_T}$, respectively. The $m\mathrm{CO_3}^{2-}$ rose from 6 to 24 percent of $\mathrm{C_T}$.

The upper concentrations of $\mathrm{Mg_T}$ in these experiments were limited by the nucleation and precipitation of an amorphous magnesium carbonate of unknown composition. The degree of supersaturation with respect to magnesite tolerated by these experiments was found to decrease rapidly with rising temperature. Thus the range of concentrations and pH's and the number of experimental points per run rapidly decreased with increasing temperature. This trend is readily seen in the data of table 3. Consequently, the precision of the determinations became worse with increasing temperature, although the trend was offset to some extent by increasing stability of $\mathrm{MgCO_3}^\circ$.

Frequently, the calculated results of run points near the precipitation barrier were found to differ substantially from the main values of the run. These points always gave larger pK values and probably represented incipient nucleation and precipitation. Such points were deleted from the data. Also, some points at very low concentrations and pH's (pH $\approx$ 8.5) differed grossly from the bulk of the data, and these were also deleted.

As a consequence of the experimental approach, runs were performed over a relatively narrow ionic strength range. For instance, at 25°C, the ionic strength varied only from 0.1 to 0.2. A plot of $\mathrm{p}K_{\mathrm{MgCO_3}^\circ}$ (25°C) versus I is presented in figure 1. No gross trend is evident in the figure, and minor trends are probably not statistically significant because the data points belonging to the same run are strongly related to each other. Ionic strength trends within a run are indeterminate, because I remains virtually constant throughout the bulk of the run (see data in table 3). However, a glance at table 3 shows that there is a distinct trend of $\mathrm{p}K_{\mathrm{MgCO_3}^\circ}$ with the experimental pH in a majority of the runs. This trend is usually toward more negative values, whereas a few runs show little trend or a reversal of trend. The trend is slight at lower temperatures (0.02-0.05 log units over a run) but increases with increasing temperature. As an aid to the interpretation of this trend, an "error analysis" table was calculated. The calculation is performed by giving a plus and a minus error to one of the parameters, while holding all others at the "correct" value and calculating the $\mathrm{p}K_{\mathrm{MgCO_3}^\circ}$. All the major parameters used in the calculations were given this treatment in turn. The results for a low,

TABLE 2

Experimental dissociation constants for the $\mathrm{MgCO_3}^\circ$ ion pair

Temperature	pK	Standard deviation	Number of points	Number of runs
10°C	2.89	±0.019	42	5
25°C	2.984	±0.0279	81	10
40°C	3.07	±0.021	39	6
55°C	3.18	±0.026	43	7
70°C	3.28	±0.042	26	4
90°C	3.41	±0.067	25	6

medium, and high pH experimental point of a representative run at 25°C are given in table 4. Two observations may be made from the table. The first is the relatively low magnitude of error in the results with relatively gross errors in the input parameters. Thus a ± 0.5 error in the Debye-Huckel å and a ± 5 percent error in the analytical data produce an error of less than 0.03 log units. The error produced per ± 0.01 unit error in pH and $-\log K_2$ is much less than ± 0.03 in most cases. The second observation is the increasing rate of error with increasing pH. In most cases, the error at high pH's is 2 to 3 times greater than at low pH's. The exception to this is the case of $\mathring{a}_{CO_3^{2-}}$ where the error is 4 times as great at high pH. This was the justification for using $\mathring{a}_{CO_3^{2-}} = 4.5 \times 10^{-8}$ cm rather than the more commonly used value of 5.5×10^{-8} cm derived from the $\gamma_{CO_3^{2-}}$ data of Walker, Bray, and Johnston (1927). The value of 4.5×10^{-8} cm greatly reduced the trend with pH while affecting the average $pK_{MgCO_3^\circ}$ by less than 0.02 log units. This probably should be considered an artificial appliance in that the observed trend with pH still exists and represents a systematic error. Errors in the equilibrium constants for $H_2CO_3^\circ$, $MgOH^+$, and H_2O are of no consequence to the error in $pK_{MgCO_3^\circ}$ because they may be completely ignored without adversely affecting the results. Errors in the values of γ_i (other than $\gamma_{CO_3^{2-}}$) do not account for the trend. Errors in measured pH's might be the answer. Another possible source for this trend with pH might be the existence of unrecognized ion pairing, such as the $Mg(CO_3)_2^{2-}$ ion pair. Although there is systematic error within a run, the error appears to be random between runs. The standard deviation of the results at each temperature is taken as a measure of the accuracy of the determination.

The experimental 25°C value ($pK_{MgCO_3^\circ} = 2.98$) is in general agreement with the values of Reardon and Langmuir (1974), Larson, Sollo, and McGurk (1973), and Raaflaub (1960). The values of the experimental p*K* rise smoothly as a function of temperature, to a value of 3.41 at 90°C. This result can be compared with the temperature variation of $pK_{MgCO_3^\circ}$ obtained by Reardon and Langmuir (1974). When both sets of p*K* values are plotted as a function of temperature (fig. 2), the shapes of the two curves may be seen to differ substantially. It was expected that the shape of the two curves would be very similar even though the p*K*'s at 25°C differ by 0.1 units. Since this is not the case, one of the experimental data sets is in error.

The present experimental data were compared to the temperature variation of $pK_{MgCO_3^\circ}$ predicted by the ion pair theory of Fuoss (1958). The details of the equations and the procedure used in the comparison are identical to that used for $MgHCO_3^+$ ion pair by Siebert and Hostetler (1977) and will not be repeated here. In general, the Fuoss theory presents the ion pair dissociation constant in terms of the energy of electrostatic interaction and is calculated using properties of both the ions involved and of the solvent. The experimental value of $\ln K_{MgCO_3^\circ}$ at 25°C is used to calculate the value of the ion size parameter (the only unknown in the

TABLE 3

Raw experimental data and results for individual run points

pH	Mg_T (m)	C_T (m)	mK^+	I (m)	pK
Run 18-1, t = 10°C					
8.970	0.0503	0.0432	0.0524	0.175	2.86
9.139	0.0496	0.0467	0.0598	0.173	2.88
9.303	0.0488	0.0508	0.0686	0.172	2.88
9.442	0.0479	0.0551	0.0777	0.172	2.89
9.633	0.0466	0.0618	0.0921	0.175	2.89
9.760	0.0454	0.0674	0.1040	0.179	2.90
9.957	0.0435	0.0771	0.1248	0.192	2.90
10.047	0.0424	0.0823	0.1359	0.202	2.90
Run 18-2, t = 10°C					
8.612	0.0614	0.0333	0.0373	0.202	2.87
8.907	0.0605	0.0370	0.0452	0.199	2.90
9.085	0.0597	0.0403	0.0521	0.196	2.90
9.218	0.0589	0.0436	0.0592	0.194	2.91
9.379	0.0579	0.0481	0.0686	0.192	2.91
9.535	0.0566	0.0536	0.0802	0.190	2.91
9.697	0.0553	0.0589	0.0914	0.193	2.87
9.843	0.0538	0.0655	0.1054	0.196	2.86
9.966	0.0522	0.0720	0.1192	0.202	2.87
Run 18-3, t = 10°C					
8.720	0.0554	0.0283	0.0325	0.181	2.87
8.980	0.0547	0.0314	0.0390	0.179	2.89
9.147	0.0541	0.0344	0.0451	0.177	2.89
9.345	0.0532	0.0389	0.0546	0.175	2.90
9.520	0.0521	0.0441	0.0654	0.173	2.90
9.676	0.0509	0.0496	0.0770	0.173	2.90
9.888	0.0493	0.0576	0.0937	0.178	2.86
10.038	0.0477	0.0650	0.1093	0.186	2.86
Run 19-2, t = 10°C					
9.171	0.0474	0.0338	0.0440	0.158	2.87
9.315	0.0469	0.0368	0.0503	0.157	2.88
9.458	0.0462	0.0405	0.0580	0.157	2.88
9.616	0.0453	0.0454	0.0682	0.157	2.88
9.772	0.0443	0.0512	0.0804	0.159	2.89
9.929	0.0431	0.0581	0.0946	0.165	2.90
10.076	0.0417	0.0657	0.1107	0.174	2.92
10.179	0.0406	0.0719	0.1235	0.185	2.93
Run 5-4, t = 25°C					
8.569	0.0588	0.0424	0.0502	0.197	3.03
8.825	0.0571	0.0470	0.0603	0.191	3.05
9.017	0.0554	0.0513	0.0700	0.186	3.05
9.231	0.0532	0.0573	0.0832	0.181	3.05
9.471	0.0506	0.0643	0.0988	0.180	3.02
9.620	0.0486	0.0696	0.1106	0.183	3.01
9.816	0.0455	0.0776	0.1284	0.192	3.02
Run 24-1, t = 25°C					
8.985	0.0383	0.0299	0.0387	0.130	2.96
9.150	0.0378	0.0330	0.0451	0.129	2.97
9.311	0.0373	0.0366	0.0526	0.129	2.96
9.420	0.0369	0.0395	0.0587	0.130	2.97
9.528	0.0364	0.0428	0.0655	0.131	2.97
9.614	0.0360	0.0457	0.0715	0.133	2.97
9.716	0.0354	0.0495	0.0795	0.136	2.98
9.829	0.0347	0.0542	0.0892	0.142	2.99
9.918	0.0341	0.0584	0.0981	0.148	3.00
10.013	0.0333	0.0634	0.1084	0.158	3.01
Run 24-2, t = 25°C					
9.102	0.0350	0.0297	0.0396	0.120	2.95
9.270	0.0346	0.0330	0.0465	0.120	2.95
9.413	0.0341	0.0365	0.0538	0.121	2.96
9.512	0.0338	0.0392	0.0594	0.122	2.96
9.610	0.0334	0.0422	0.0655	0.124	2.95
9.717	0.0328	0.0460	0.0735	0.127	2.97
9.830	0.0322	0.0504	0.0825	0.133	2.97
9.918	0.0317	0.0544	0.0909	0.139	2.98
10.039	0.0309	0.0605	0.1037	0.151	2.99
10.125	0.0302	0.0657	0.1144	0.167	3.00
Run 24-3, t = 25°C					
8.927	0.0518	0.0330	0.0432	0.169	2.99
9.057	0.0513	0.0356	0.0487	0.167	2.98
9.211	0.0505	0.0395	0.0569	0.165	2.99
9.310	0.0499	0.0424	0.0629	0.164	2.99
9.414	0.0492	0.0457	0.0699	0.164	2.98
9.512	0.0485	0.0493	0.0772	0.164	2.98
9.681	0.0476	0.0535	0.0862	0.165	2.99
9.742	0.0465	0.0590	0.0976	0.168	3.00
9.824	0.0457	0.0630	0.1060	0.172	3.01

Run 19-3, t = 10°C					
8.926	0.0460	0.0320	0.0384	0.155	2.88
9.122	0.0455	0.0346	0.0440	0.155	2.86
9.268	0.0450	0.0376	0.0501	0.154	2.87
9.453	0.0442	0.0422	0.0598	0.153	2.87
9.626	0.0433	0.0476	0.0710	0.154	2.87
9.793	0.0423	0.0538	0.0840	0.158	2.87
9.919	0.0413	0.0597	0.0964	0.163	2.90
10.078	0.0399	0.0678	0.1135	0.175	2.91
10.212	0.0384	0.0761	0.1309	0.191	2.92
Run 4-1, t = 25°C					
8.850	0.0327	0.0387	0.0468	0.123	2.96
9.033	0.0323	0.0418	0.0535	0.123	2.97
9.296	0.0316	0.0479	0.0663	0.125	2.97
9.486	0.0309	0.0538	0.0786	0.130	2.98
9.667	0.0301	0.0606	0.0929	0.140	2.99
9.823	0.0293	0.0679	0.1083	0.154	3.01
Run 4-3, t = 25°C					
8.634	0.0476	0.0320	0.0376	0.160	2.96
8.884	0.0470	0.0357	0.0455	0.158	2.98
9.063	0.0463	0.0395	0.0533	0.156	2.98
9.229	0.0456	0.0437	0.0621	0.155	2.98
9.430	0.0446	0.0499	0.0752	0.156	2.97
9.636	0.0433	0.0578	0.0916	0.161	2.97
9.745	0.0425	0.0626	0.1017	0.167	2.97
9.892	0.0412	0.0701	0.1175	0.179	2.96
Run 5-1, t = 25°C					
8.631	0.0286	0.0255	0.0291	0.102	2.97
8.857	0.0282	0.0276	0.0335	0.101	2.99
9.045	0.0278	0.0299	0.0386	0.101	3.00
9.246	0.0273	0.0333	0.0457	0.101	3.00
9.429	0.0266	0.0370	0.0537	0.102	3.01
9.626	0.0258	0.0420	0.0643	0.106	3.02
9.832	0.0247	0.0485	0.0781	0.115	3.04
Run 5-3, t = 25°C					
8.649	0.0399	0.0278	0.0329	0.135	3.02
8.858	0.0393	0.0303	0.0384	0.133	3.04
9.035	0.0386	0.0332	0.0445	0.131	3.04
9.232	0.0377	0.0371	0.0529	0.129	3.04
9.491	0.0363	0.0431	0.0657	0.129	3.01
9.649	0.0352	0.0477	0.0755	0.132	3.00
9.824	0.0338	0.0537	0.0883	0.139	3.00
9.978	0.0323	0.0599	0.1015	0.150	3.00
Run 24-4, t = 25°C					
9.075	0.0361	0.0363	0.0478	0.128	2.95
9.220	0.0357	0.0393	0.0541	0.128	2.95
9.320	0.0353	0.0419	0.0594	0.129	2.95
9.416	0.0349	0.0446	0.0651	0.130	2.96
9.519	0.0345	0.0478	0.0718	0.132	2.96
9.615	0.0340	0.0512	0.0789	0.135	2.97
9.731	0.0334	0.0553	0.0876	0.141	2.95
Run 24-5, t = 25°C					
9.068	0.0366	0.0275	0.0364	0.123	2.95
9.214	0.0362	0.0302	0.0421	0.123	2.95
9.332	0.0359	0.0326	0.0470	0.123	2.96
9.424	0.0356	0.0351	0.0522	0.123	2.96
9.513	0.0352	0.0376	0.0574	0.124	2.96
9.619	0.0348	0.0409	0.0641	0.125	2.96
9.720	0.0342	0.0444	0.0716	0.128	2.97
9.830	0.0337	0.0486	0.0801	0.133	2.97
10.027	0.0324	0.0577	0.0990	0.149	2.98
10.123	0.0316	0.0634	0.1109	0.160	3.00
Run 6-1, t = 40°C					
8.617	0.0328	0.0348	0.0417	0.119	3.08
8.832	0.0324	0.0381	0.0487	0.118	3.09
9.218	0.0312	0.0468	0.0672	0.119	3.11
9.404	0.0304	0.0526	0.0793	0.123	3.14
Run 6-2, t = 40°C					
8.950	0.0190	0.0381	0.0474	0.085	3.05
9.130	0.0187	0.0412	0.0540	0.088	3.06
9.313	0.0184	0.0452	0.0624	0.093	3.07
9.510	0.0180	0.0564	0.0739	0.103	3.08
9.626	0.0176	0.0547	0.0826	0.112	3.10
9.742	0.0172	0.0596	0.0930	0.126	3.08
Run 9-1, t = 40°C					
8.459	0.0325	0.0266	0.0304	0.114	3.04
8.647	0.0321	0.0283	0.0342	0.112	3.06
8.905	0.0314	0.0317	0.0413	0.111	3.06
9.012	0.0311	0.0334	0.0451	0.110	3.06
9.213	0.0303	0.0373	0.0535	0.110	3.06
9.352	0.0296	0.0405	0.0604	0.111	3.06
9.500	0.0288	0.0444	0.0687	0.114	3.06

TABLE 3 (continued)

pH	Mg_T (m)	C_T (m)	mK^+	I (m)	pK
Run 20-2,	t = 40°C				
8.835	0.0269	0.0279	0.0350	0.097	3.03
9.013	0.0265	0.0305	0.0405	0.097	3.04
9.158	0.0261	0.0331	0.0460	0.097	3.05
9.317	0.0257	0.0365	0.0531	0.098	3.05
9.458	0.0252	0.0400	0.0605	0.101	3.06
9.618	0.0245	0.0447	0.0704	0.107	3.08
Run 20-3,	t = 40°C				
8.613	0.0302	0.0268	0.0318	0.106	3.04
8.816	0.0298	0.0292	0.0369	0.105	3.05
9.007	0.0293	0.0322	0.0432	0.105	3.06
9.112	0.0290	0.0342	0.0474	0.105	3.06
9.208	0.0287	0.0362	0.0516	0.105	3.07
9.319	0.0283	0.0387	0.0569	0.106	3.07
9.407	0.0279	0.0410	0.0617	0.107	3.07
9.515	0.0274	0.0441	0.0683	0.110	3.08
Run 20-5,	t = 40°C				
8.615	0.0276	0.0236	0.0279	0.097	3.05
8.815	0.0273	0.0257	0.0323	0.096	3.06
9.023	0.0269	0.0286	0.0385	0.096	3.07
9.119	0.0266	0.0303	0.0421	0.096	3.07
9.221	0.0264	0.0323	0.0463	0.096	3.08
9.321	0.0261	0.0344	0.0506	0.097	3.08
9.419	0.0257	0.0368	0.0556	0.098	3.09
9.518	0.0253	0.0394	0.0612	0.100	3.09
Run 11-1,	t = 55°C				
8.469	0.0225	0.0265	0.0307	0.085	3.15
8.652	0.0222	0.0282	0.0344	0.084	3.16
8.822	0.0219	0.0302	0.0387	0.083	3.16
9.020	0.0214	0.0330	0.0448	0.084	3.17
Run 11-3,	t = 55°C				
8.338	0.0244	0.0317	0.0358	0.094	3.16
8.519	0.0241	0.0332	0.0390	0.094	3.16
8.662	0.0239	0.0346	0.0421	0.093	3.14
Run 12-1,	t = 55°C				
8.017	0.0318	0.0271	0.0290	0.112	3.15
8.222	0.0314	0.0284	0.0319	0.111	3.19
8.433	0.0310	0.0304	0.0362	0.109	3.22
8.570	0.0306	0.0320	0.0396	0.108	3.23
8.661	0.0303	0.0332	0.0424	0.107	3.23
8.764	0.0300	0.0348	0.0459	0.106	3.24
Run 13-2,	t = 70°C				
8.015	0.0231	0.0149	0.0161	0.078	3.23
8.131	0.0230	0.0154	0.0171	0.078	3.26
8.212	0.0229	0.0158	0.0180	0.078	3.28
8.323	0.0228	0.0165	0.0193	0.077	3.30
8.417	0.0227	0.0172	0.0208	0.077	3.32
8.513	0.0226	0.0180	0.0224	0.076	3.32
8.606	0.0224	0.0189	0.0243	0.075	3.33
Run 13-3,	t = 70°C				
8.710	0.0277	0.0011	0.0022	0.082	3.28
Run 13-4,	t = 70°C				
8.025	0.0301	0.0200	0.0220	0.102	3.27
8.115	0.0300	0.0206	0.0231	0.101	3.29
8.225	0.0298	0.0214	0.0248	0.100	3.31
8.311	0.0297	0.0220	0.0263	0.100	3.33
8.417	0.0295	0.0231	0.0285	0.099	3.34
8.507	0.0292	0.0242	0.0308	0.097	3.35
Run 13-5,	t = 70°C				
8.013	0.0193	0.0154	0.0164	0.068	3.22
8.122	0.0193	0.0157	0.0171	0.068	3.21
8.213	0.0192	0.0161	0.0180	0.068	3.23
8.316	0.0192	0.0167	0.0191	0.067	3.26
8.415	0.0191	0.0173	0.0203	0.067	3.27
8.513	0.0190	0.0180	0.0218	0.067	3.28
8.613	0.0189	0.0188	0.0236	0.066	3.29
8.714	0.0187	0.0199	0.0259	0.066	3.32
Run 16-1,	t = 90°C				
7.926	0.0216	0.0192	0.0207	0.076	3.37
8.012	0.0214	0.0197	0.0217	0.075	3.42
8.107	0.0212	0.0202	0.0229	0.075	3.46
8.146	0.0211	0.0207	0.0240	0.074	3.52
Run 16-2,	t = 90°C				
8.011	0.0160	0.0185	0.0198	0.060	3.31
8.064	0.0160	0.0187	0.0202	0.060	3.33
8.110	0.0160	0.0189	0.0207	0.060	3.35
8.162	0.0159	0.0191	0.0213	0.060	3.37
8.205	0.0158	0.0194	0.0218	0.059	3.40

Run 12-2,	t = 55°C				
8.465	0.0204	0.0180	0.0209	0.072	3.15
8.635	0.0202	0.0192	0.0234	0.072	3.16
8.743	0.0201	0.0202	0.0255	0.071	3.17
8.835	0.0200	0.0211	0.0274	0.071	3.17
8.930	0.0198	0.0222	0.0298	0.071	3.18
9.040	0.0196	0.0236	0.0328	0.071	3.18
9.140	0.0194	0.0254	0.0365	0.071	3.22
Run 12-3,	t = 55°C				
8.392	0.0232	0.0256	0.0292	0.086	3.15
8.515	0.0231	0.0266	0.0314	0.086	3.16
8.624	0.0229	0.0277	0.0336	0.085	3.17
8.726	0.0227	0.0288	0.0361	0.085	3.18
8.837	0.0225	0.0302	0.0392	0.084	3.18
8.924	0.0223	0.0315	0.0418	0.084	3.18
9.018	0.0220	0.0330	0.0452	0.084	3.20
Run 12-4,	t = 55°C				
8.226	0.0233	0.0224	0.0247	0.085	3.15
8.352	0.0232	0.0231	0.0263	0.084	3.17
8.509	0.0230	0.0243	0.0288	0.083	3.18
8.621	0.0228	0.0254	0.0310	0.083	3.18
8.720	0.0226	0.0264	0.0333	0.083	3.19
8.830	0.0224	0.0278	0.0362	0.082	3.19
8.919	0.0222	0.0290	0.0388	0.082	3.20
9.023	0.0219	0.0307	0.0424	0.082	3.21
Run 12-5,	t = 55°C				
8.014	0.0351	0.0251	0.0270	0.120	3.15
8.151	0.0349	0.0260	0.0288	0.119	3.18
8.314	0.0346	0.0272	0.0316	0.118	3.20
8.412	0.0343	0.0282	0.0336	0.117	3.20
8.510	0.0340	0.0293	0.0359	0.116	3.21
8.613	0.0337	0.0306	0.0388	0.115	3.21
8.713	0.0333	0.0320	0.0419	0.114	3.22
8.813	0.0329	0.0337	0.0455	0.112	3.22
Run 13-1,	t = 70°C				
8.115	0.0226	0.0231	0.0250	0.083	3.18
8.313	0.0224	0.0244	0.0279	0.082	3.25
8.419	0.0223	0.0253	0.0299	0.081	3.27
8.511	0.0221	0.0262	0.0318	0.081	3.29
Run 26-1,	t = 90°C				
7.975	0.0144	0.0123	0.0132	0.051	3.37
8.062	0.0143	0.0125	0.0138	0.051	3.42
8.163	0.0143	0.0130	0.0147	0.050	3.46
8.258	0.0142	0.0134	0.0157	0.050	3.49
Run 26-2,	t = 90°C				
8.162	0.0125	0.0109	0.0121	0.044	3.32
8.260	0.0124	0.0113	0.0128	0.044	3.37
8.354	0.0124	0.0117	0.0137	0.044	3.41
Run 26-3,	t = 90°C				
7.965	0.0142	0.0088	0.0095	0.048	3.31
8.052	0.0141	0.0091	0.0100	0.048	3.36
8.154	0.0141	0.0094	0.0107	0.047	3.42
8.240	0.0140	0.0097	0.0114	0.047	3.46
8.332	0.0139	0.0102	0.0123	0.047	3.49
Run 26-4,	t = 90°C				
7.970	0.0150	0.0141	0.0152	0.054	3.40
8.053	0.0149	0.0144	0.0159	0.054	3.44
8.140	0.0148	0.0148	0.0167	0.053	3.47
8.233	0.0146	0.0154	0.0181	0.052	3.56

TABLE 4

Calculated results for run 24-3 (25°C)

pH	Mg_T	$m\mathrm{Mg}^{2+}$	$m\mathrm{MgHCO_3}^+$	$m\mathrm{MgCO_3}^\circ$	$\% \frac{m\mathrm{Mg}^{2+}}{\mathrm{Mg_T}}$	$\% \frac{m\mathrm{MgHCO_3}^+}{\mathrm{Mg_T}}$	$\% \frac{m\mathrm{MgCO_3}^\circ}{\mathrm{Mg_T}}$	p*K*
8.927	0.05184	0.04018	0.00332	0.00828	77.51	6.40	15.97	2.99
9.057	0.05131	0.03765	0.00312	0.01046	73.38	6.08	20.39	2.98
9.211	0.05052	0.03403	0.00283	0.01357	67.36	5.60	26.86	2.99
9.310	0.04993	0.03145	0.00262	0.01576	62.99	5.25	31.56	2.99
9.414	0.04926	0.02863	0.00238	0.01812	58.12	4.83	36.78	2.98
9.512	0.04853	0.02580	0.00214	0.02046	53.16	4.41	42.16	2.98
9.618	0.04767	0.02258	0.00186	0.02308	47.37	3.90	48.42	2.99
9.742	0.04656	0.01893	0.00154	0.02592	40.66	3.31	55.67	3.00
9.824	0.04574	0.01652	0.00133	0.02771	36.12	2.91	60.58	3.01

pH	C_T	$m\mathrm{CO_3}^{2-}$	$m\mathrm{HCO_3}^-$	$\% \frac{m\mathrm{MgCO_3}^\circ}{\mathrm{C_T}}$	$\% \frac{m\mathrm{HCO_3}^-}{\mathrm{C_T}}$	*I*	$\gamma\mathrm{Mg}^{2+}$	$\gamma\mathrm{HCO_3}^-$	$\gamma\mathrm{CO_3}^{2-}$
8.927	0.03302	0.00194	0.01943	25.0	58.8	0.1691	0.365	0.758	0.301
9.057	0.03566	0.00261	0.01944	29.3	54.5	0.1675	0.366	0.759	0.302
9.211	0.03955	0.00370	0.01943	34.3	49.1	0.1656	0.367	0.759	0.303
9.310	0.04244	0.00464	0.01941	37.1	45.7	0.1646	0.367	0.760	0.304
9.414	0.04578	0.00588	0.01938	39.5	42.3	0.1641	0.367	0.760	0.304
9.512	0.04930	0.00736	0.01933	41.5	39.2	0.1642	0.367	0.760	0.304
9.618	0.05358	0.00937	0.01926	43.0	35.9	0.1652	0.367	0.760	0.304
9.742	0.05905	0.01245	0.01912	43.9	32.3	0.1685	0.365	0.758	0.302
9.824	0.06309	0.01503	0.01900	43.9	30.1	0.1721	0.363	0.757	0.299

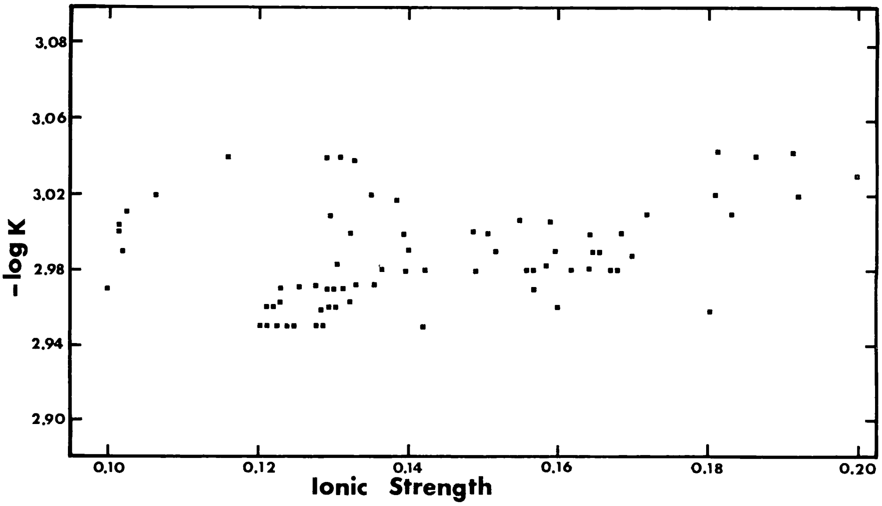

Fig. 1. Graph of $-\log K_{MgCO_3°}$ versus ionic strength for all 25°C data points.

Fuoss eq), and this value, 2.99×10^{-8} cm, was used to calculate the constants at other temperatures. The results are plotted in figure 2; the agreement between the theoretical and the experimental temperature dependence is excellent. Also plotted in figure 2 are the experimental data of Reardon and Langmuir (1974) and the Fuoss curve which was calculated on the basis of their 25°C point. The agreement between the two is poor, suggesting that the experimental temperature dependence reported here is correct and that of Reardon and Langmuir (1974) is not.

Since the Fuoss equation fits the experimental data so well, it may also be used to calculate the thermodynamic quantities, $\Delta H°_R$ and $\Delta S°_R$, for the reaction:

$$MgCO_3°(aq) = Mg^{2+}(aq) + CO_3^{2-}(aq).$$

Such a calculation may be more accurate in defining the above quantities than their calculation from a van't Hoff plot or least squares curve fit, because, assuming pure electrostatic bonding, the theoretical equation can predict the slope, $d\ln K/dT$, more accurately than may be done with a few experimental points which usually have relatively large uncertainties. The thermodynamic quantities were calculated by the equations derived from the Fuoss equation, given by Siebert and Hostetler (1977).

Using $a_{MgCO_3°} = 2.99 \times 10^{-8}$ cm, the results gave $\Delta G°_R = 17050 \pm 125$ J mol^{-1} (4075 ± 30 cal mol^{-1}; $\Delta H°_R = -8439$ J mol^{-1} (−2017 cal mol^{-1}); and $\Delta S°_R = -85.48$ J deg^{-1} mol^{-1} (−20.43 cal deg^{-1} mol^{-1}) at 25°C. For comparison, these quantities were calculated directly from the experimental results. From figure 2, it may be seen that a straight line would fit the experimental points quite well. Using the slope of this line ($d\ln K/dT = -0.01468$ per deg), $\Delta H°_R$ and $\Delta S°_R$ were calculated

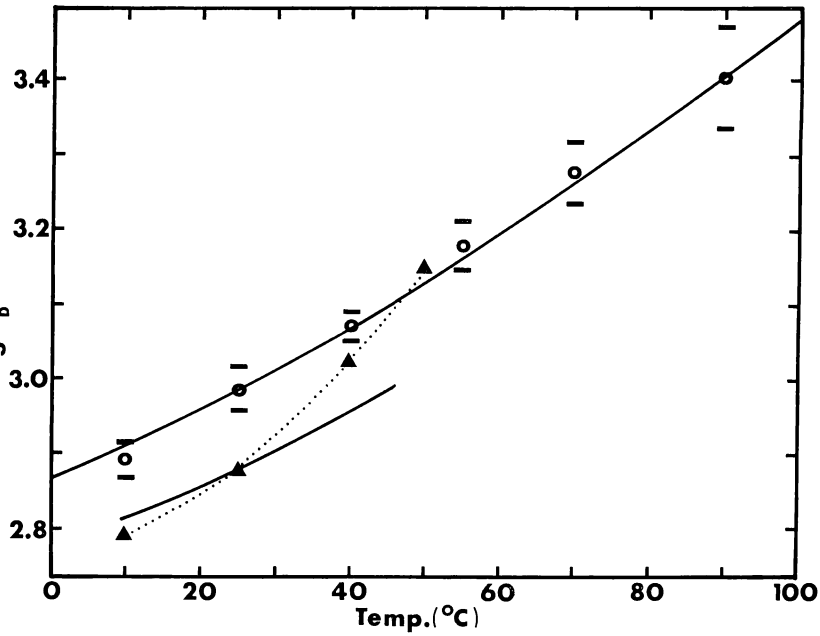

Fig. 2. Graph of $MgCO_3^\circ$ experimental results. Circles and bounding bars represent experimental values and the standard deviation. Solid triangles represent the experimental values from Reardon and Langmuir (1974). Solid lines calculated from the Fuoss equation.

and found to be —10841 J mol^{-1} (—2591 cal mol^{-1}), respectively. The agreement between the two is not particularly good and illustrates the errors that may arise in such calculations. The results derived from the Fuoss equation are considered more accurate and therefore preferred.

GEOLOGIC DISCUSSION

Significant concentrations of $MgCO_3^\circ$ and $MgHCO_3^+$ ion pairs will be formed in any alkaline solution containing appreciable magnesium ion and carbonate species. Since these ion pairs, in effect, remove free HCO_3^- and CO_3^{2-} from solution, they help to control and buffer the thermodynamic activities of HCO_3^- and CO_3^{2-} in electrolyte solutions. Likewise, $MgHCO_3^+$ and $MgCO_3^\circ$ ion pairs also influence the thermodynamic activities of other cations and anions insofar as the HCO_3^- and CO_3^{2-} ions associate with other cations in solution, as for example, Ca^{2+} and Na^+. Consequently, the choice of dissociation constants for $MgHCO_3^+$ and $MgCO_3^\circ$ will have a marked effect on the thermodynamic calculation of ion activity products (I.A.P.'s) and will have a marked effect on the interpretations of the interaction of natural electrolyte solutions with mineral systems.

A very important example illustrating the above discussion is the case of seawater and related solutions. The $MgCO_3^\circ$ and $MgHCO_3^+$ ion pairs are important in this case because of the high concentration of total Mg^{2+} relative to total Ca^{2+} (total Mg^{2+}/total CA^{2+} = 5.4) in seawater.

Garrels and Thompson (1962) were the first to calculate a detailed chemical model for seawater. They calculated the distribution, at 25°C and 1 atm, of the dissolved ions as free ions and complexed ions using those equilibrium constants and single-ion activity coefficients available at that time. Since the appearance of the Garrels and Thompson model, a number of investigators have attacked the same problem from various points of view. Some recent publications bearing on the subject include Pytkowicz and Hawley (1974), Whitfield (1974), and Dryssen and Wedborg (1974). These may be consulted for details and for additional references to the general field.

It is not our purpose here to consider the problem in detail or to evaluate the literature in any way. Rather, we have simply recalculated the Garrels-Thompson model using our new values for the dissociation constants of $MgHCO_3^+$ and $MgCO_3^\circ$ but keeping all other constants the same as the Garrels and Thompson original ones and also using their

TABLE 5

Error analysis table for run 24-3 (25°C)

Source of error	Error	At pH=8.927 (pK error)	At pH=9.414 (pK error)	At pH=9.742 (pK error)	Normal values
$\mathring{a}_{HCO_3^-}$	−0.5A° +0.5A°	+0.0061 −0.0055	+0.0069 −0.0065	+0.0096 −0.0091	5.5
$\mathring{a}_{Mg^{2+}}$	−0.5A° +0.5A°	+0.0128 −0.0118	+0.0128 −0.0119	+0.0130 −0.0122	6.5
$\mathring{a}_{CO_3^{2-}}$	−0.5A° +0.5A°	−0.0062 +0.0052	−0.0111 +0.0092	−0.0244 +0.0206	4.5
pK_2	−0.1 +0.1	−0.1303 +0.1233	−0.1545 +0.1411	−0.2154 +0.1913	10.329
pH	−0.1 +0.1	+0.1233 −0.1303	+0.1411 −0.1545	+0.1913 −0.2154	
p$K_{MgHCO_3^+}$	−0.1 +0.1	−0.0212 +0.0253	−0.0200 +0.0233	−0.0194 +0.0231	1.067
Wt of H_2O added	−5% +5%	−0.0115 +0.0115	−0.0125 +0.0118	−0.0149 +0.0139	688.8g
Wt of K_2CO_3	−5% +5%	−0.0317 +0.0301	−0.0438 +0.0426	−0.0679 +0.0689	39.62
Wt of $KHCO_3$ added	−5% +5%	+0.0260 −0.0250	+0.0301 −0.0295	+0.0423 −0.0415	1.708
Wt of $MgCl_2$ soln. added	−5% +5%	+0.0182 −0.0168	+0.0278 −0.0254	+0.0458 −0.0404	37.652
Original Ionic Strength		0.1691	0.1641	0.1685	
Original p$K_{MgCO_3^\circ}$		2.986	2.983	3.000	

activity coefficients, in order to illustrate the effect of equilibrium constant accuracy in such calculations. The results obtained here are compared with the original results in tables 6 and 7. From table 6, it may be seen that there is considerable change in the relative concentrations of most of the ion pair species, whereas most of the free ion activities (table 7) have remained essentially unchanged. The exception is the increase of the CO_3^{2-} activity by a factor of almost two, as would be expected, because the $pK_{MgCO_3°}$ used in the recalculation is considerably smaller (less stable) than the constant used by Garrels and Thompson ($pK_{MgCO_3°} = 2.98$ versus 3.40), and consequently, less CO_3^{2-} is associated with Mg^{2+}. This increase in CO_3^{2-} activity raises the calculated ion activity product for calcite ($K = [Ca^{2+}]\ [Co_3^{2-}]$) from 1.24×10^{-8} to 2.18×10^{-8}. This result indicates that the calcite ion activity product in seawater is 7.2 times larger than the equilibrium value, $10^{-8.52}$ (Christ, Hostetler, and Siebert, 1974). The new calculation does not explain the apparent supersaturation of seawater with respect to aragonite and calcite, but it does illustrate the importance of having precise values of the $MgHCO_3^+$ and $MgCO_3°$ ion pair dissociation constants.

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TABLE 6

Original and recalculated results from the Garrels and Thompson (1962) model for seawater

A. Results from original model for seawater

Ion	Molality (total)	% Free ion	% Me-SO_4 pair	% Me-HCO_3 pair	% Me-CO_3 pair
Ca^{2+}	0.0104	91	8	1	0.2
Mg^{2+}	0.0540	87	11	1	0.3
Na^+	0.4752	99	1.2	0.01	—
K^+	0.0100	99	1	—	—

Ion	Molality (total)	% Free ion	% Ca-anion pair	% Mg-anion pair	% Na-anion pair	% K-anion pair
SO_4^{2-}	0.0284	54	3	21.5	21	0.5
HCO_3^-	0.00238	69	4	19	8	—
CO_3^{2-}	0.000269	9	7	67	17	—

B. Recalculated model using new values of $pK_{MgHCO_3^+}$ and $pK_{MgCO_3°}$

Ion	Molality (total)	% Free ion	% Me-SO_4 pair	% Me-HCO_3 pair	% Me-CO_3 pair
Ca^{2+}	0.0104	90.3	8.7	1	0.3
Mg^{2+}	0.0540	87.1	12.1	1	0.2
Na^+	0.4752	98.4	1.0	0.01	—
K^+	0.0100	98.9	1.0	—	—

Ion	Molality (total)	% Free ion	% Ca-anion pair	% Mg-anion pair	% Na-anion pair	% K-anion pair
SO_4^{2-}	0.0284	55.7	3.1	23.0	17.6	0.5
HCO_3^-	0.00238	69.0	3.3	12.9	14.8	—
CO_3^{2-}	0.000269	15.4	11.4	44.1	29.1	—

TABLE 7

Original and recalculated ion activities from the Garrels and Thompson (1962) model for seawater

	Original	Recalculated
Ca^{2+}	0.00264	0.00263
Mg^{2+}	0.0169	0.01694
Na^{+}	0.356	0.357
K^{+}	0.0063	0.0063
SO_4^{2-}	0.00179	0.00190
HCO_3^{-}	0.000975	0.00112
CO_3^{2-}	4.7×10^{-6}	8.3×10^{-6}

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