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

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ABSTRACT. The dissociation constants of the aqueous $MgHCO_3^+$ ion pair were determined experimentally from 10° to 90°C at 15° intervals. The experimental pH change between alternating additions of $MgCl_2$ and $KHCO_3$ to $MgCl_2$–$KHCO_3$ solutions in equilibrium with CO_2 was used to calculate the dissociation constants by a new floating point method which does not require absolute pH and P_{CO_2} values. The approach reduces the sources of error to single-ion activity coefficients and reference electrode liquid-junction potentials. The experimental $pK_{MgHCO_3^+}$ ($-\log K_{dissociation}$) at 25°C is 1.07 ± 0.03, and the pK's increase smoothly to 1.34 ± 0.03 at 90°C. The 25°C result is in general agreement with several previous determinations; the pK variation as a function of temperature is in excellent agreement with that predicted by the Fuoss electrostatic ion pair theory. Derived values of $\Delta G_R°$, $\Delta H_R°$, and $\Delta S_R°$ of dissociation at 25°C are 6087.7 ± 167 J mol^{-1} (1455 ± 40 cal mol^{-1}), −4987.3 J mol^{-1} (−1192 cal mol^{-1}), and −37.15 J deg^{-1} mol^{-1} (−8.88 cal deg^{-1} mol^{-1}), respectively.

INTRODUCTION

The stability of the $MgHCO_3^+$ ion pair has been poorly known at 25°C and not known at other temperatures. This ion pair, present in any solution containing magnesium and bicarbonate ions, is important to the quantitative interpretations of the interaction of natural electrolyte solutions with rock and mineral systems. It is an important species in most groundwaters and in seawater, where it contributes significantly to the control of the carbonate species distribution (Garrels and Thompson, 1962). Knowledge of the $MgHCO_3^+$ stability is important in mineral solubility studies. For instance, solubility work with dolomite (Siebert and Hostetler, 1970) and magnesite (Christ and Hostetler, 1970) at higher temperatures was handicapped by the lack of pertinent $MgHCO_3^+$ data. Finally, accurate $MgHCO_3^+$ dissociation constants are required in the experimental determination of the stability of the $MgCO_3°$ ion pair, which is of paramount importance to the carbonate equilibria in seawater (Garrels and Thompson, 1962).

Previously published values for $pK_{MgHCO_3^+}$ (the $-\log K$ for the dissociation reaction ($MgHCO_3^+ = Mg^{2+} + HCO_3^-$) at 25°C are:

Greenwald (1941) — ionic strength ≈0.15	0.80
Greenwald (1941) — corrected to zero ionic strength by Garrels and Thompson (1962)	1.26
Greenwald (1941) — corrected to zero ionic strength by Nakayama (1971)	1.16
Hostetler (1963)	0.95

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Hostetler (1963) — corrected for first dissociation constant of carbonic acid by Nakayama (1971)	1.21
Nakayama (1971)	1.23
Reardon, Jacobson, and Langmuir (1973) — potentiometric determination	0.96
Reardon, Jacobson, and Langmuir (1973) — conductiometric determination	0.86

Agreement among investigators is poor, the difference between high and low value being approximately 0.4 pK units. All the previous determinations were of the potentiometric (pH measurement) type except for the one conductiometric determination, which may not be reliable because of large uncertainties involved in choosing a limiting equivalent conductance value ($\lambda°$) for the $MgHCO_3^+$ species. Examination of all the potentiometric techniques indicates that experimental uncertainties are on the order of ± 0.1 pK units or more. In addition, the experimental techniques used thus far have the same basic elements in their execution, even though the techniques are superficially different. Because of the poor agreement among previous investigators and because of the lack of data at temperatures other than 25°C, the stability of the $MgHCO_3^+$ ion pair was determined in this study from 10° to 90°C, utilizing a new approach, which eliminated or reduced the experimental uncertainties and errors discussed below.

PRELIMINARY CONSIDERATIONS

The manner in which the dissociation constant is calculated from experimental data has a very strong effect on the reliability and accuracy of the results, since the method of calculation dictates the type of experiment performed and the parameters that must be measured. This relation can be understood by considering the following $MgHCO_3^+$ stability experiment. The experimental technique is the potentiometric titration of a $MgCl_2$ solution with $KHCO_3$ solution (or vice versa). This technique is chosen, because it closely resembles the one used in the present work, but it also includes the same basic elements utilized in the previous investigations. The experimentally determined parameters are:

pH_n = pH of the solution after the addition of $MgCl_2$ or $KHCO_3$ for run point n;
$Mg_{T(n)}$ = molality of total Mg^{2+} added to run point n;
mK_n^+ = molality of potassium which is equal to the total molality of HCO_3^- contributed by the $KHCO_3$ additions for run point n;
mCl_n^- = molality of Cl^- for run point n; it is equal to $2Mg_{T(n)}$.

Two methods can be used to calculate the $MgHCO_3^+$ dissociation constant from the experimental data. These methods are described below and are designated as the pH–P_{CO_2} method and the floating point method. In these methods, it is assumed that there is no ion pairing between K^+ or Mg^{2+} and Cl^- nor between K^+ and HCO_3^-.

pH–P_{CO_2} method.—In order to calculate the $pK_{MgHCO_3^+}$, the activity of HCO_3^- in the solution must be determined. This is conventionally done with the experimentally determined P_{CO_2} and pH and the following equation, where small m and brackets denote molality and activity, respectively.

$$[HCO_3^-] = \frac{K_0 K_1 P_{CO_2} [H_2O]^1}{10^{-pH}} \tag{1}$$

The constants K_0 and K_1 describe the solubility of CO_2 and the first dissociation of carbonic acid, respectively. This result is combined with the two mass balance equations (eqs 3 and 4) and appropriate activity coefficients to calculate the experimental $mMgHCO_3^+$ and, hence, the $pK_{MgHCO_3^+}$. The equations are iterated to a constant ionic strength. For the case where mH^+ is negligible, we have:

$$mHCO_3^- = [HCO_3^-]/\gamma_{HCO_3^-} \tag{2}$$

$$mMgHCO_3^+ = mK^+ - mHCO_3^- \tag{3}$$

$$mMg^{2+} = Mg_T - mMgHCO_3^+ \tag{4}$$

$$[Mg^{2+}] = mMg^{2+} \cdot \gamma_{Mg^{2+}} \tag{5}$$

$$[MgHCO_3^+] = mMgHCO_3^+ \cdot \gamma_{HCO_3^-} \tag{6}$$

The dissociation reaction is:

$$MgHCO_3^+(aq) = Mg^{2+}(aq) + HCO_3^-(aq)$$

and the corresponding equation for the dissociation constant is therefore:

$$K_{MgHCO_3^+} = \frac{[Mg^{2+}]\,[HCO_3^-]}{[MgHCO_3^+]} \tag{7}$$

The experimentally determined parameters (P_{CO_2} and pH) and the equilibrium constants K_0 and K_1 in eq 1 must be known accurately in order to calculate an accurate value of $[HCO_3^-]$. Small errors in $mHCO_3^-$ of eq 3 lead to large errors in the value for $mMgHCO_3^+$ and hence to large errors in $pK_{MgHCO_3^+}$. Unfortunately, the experimental measurements, while adequate for most work, have intrinsic uncertainties that can lead to gross errors in the determination of weak dissociation constants. The practice of equating the experimentally measured pressure of CO_2 (in atm) with the quantity P_{CO_2} in eq 1 and the measured pH with $-\log[H^+]$ is questionable (Christ, Hostetler, and Siebert, 1974). These authors discuss the reasons for this in some detail. In the case of

[1] The activity of water was taken to be unity throughout this work.

CO_2, it is thought that the pressure, measured in the conventional manner, may not represent an equilibrium value. pH measurements suffer in translation to activities chiefly because of liquid-junction potential effects (Ives and Janz, 1961; Bates, 1973). Also, there are the everpresent experimental uncertainties in the values for K_0 and K_1.

These problems apply directly to all the previous investigations, since the $m MgHCO_3^+$ were determined in essentially this manner. Such difficulties are the probable cause for the poor agreement and quality of the $MgHCO_3^+$ stability data.

Floating point method.—In this method, the molality of HCO_3^- for any given experimental point within a run is assumed to be an unknown variable. However, the change in the activity of HCO_3^- between run points, within the same run, may be accurately calculated, if the P_{CO_2} is assumed to be constant during the entire experiment. This relationship is derived as follows. The subscripting numbers designate the respective experimental run points within the same run. The equations:

$$[HCO_3^-]_n = \frac{K_0 K_1 P_{CO_{2(n)}}}{[H^+]_n}, \tag{8}$$

$$P_{CO_{2(1)}} = P_{CO_{2(2)}} = \ldots = P_{CO_{2(n)}}, \tag{9}$$

$$[HCO_3^-]_1 [H^+]_1 + [HCO_3^-]_2 [H^+]_2 = \ldots = [HCO_3^-]_n [H^+]_n \tag{10}$$

lead to

$$[HCO_3^-]_2 = \frac{[HCO_3^-]_1 \, 10^{-pH_1}}{10^{-pH_2}}, \; [HCO_3^-]_n = \frac{[HCO_3^-]_1 \, 10^{-pH_1}}{10^{-pH_n}} \tag{11}$$

or finally

$$[HCO_3^-]_n = [HCO_3^-]_1 \cdot 10^{(pH_n - pH_1)}. \tag{12}$$

This result, in combination with the mass balance equations and activity-molality relations in eqs 2 to 7, allows the calculation of $mMgHCO_3^+$ and, hence, $pK_{MgHCO_3^+}$ for all points in the run if $[HCO_3^-]_1$ is known. Since $[HCO_3^-]_1$ is not known, another independent relation must be introduced in order to reach a unique solution. This relation is provided by the constraint that the dissociation constant for all run points must be the same (at constant temperature), that is

$$K_1 = K_2 = K_3 = \ldots = K_n \tag{13}$$

For practical calculation of experimental results, the value of $[HCO_3^-]_1$ is arbitrarily selected and used, in conjunction with the experimental pH values, to calculate the values of $[HCO_3^-]_n$ for all run points (eq 12). These values of $[HCO_3^-]_n$ are then used in eqs 2 to 7 to calculate the dissociation constants for each run point. Eqs 2 through 7 are solved by choosing a provisional value of the ionic strength and iterating to constant ionic strength. If the resulting K's are not nearly

equal, the value of $[HCO_3^-]_1$ is incremented or decremented ("floated"), and the calculations are repeated. This procedure is interated, until the K's are as nearly equal as is possible.

The significance of this method lies in the greatly reduced number of assumptions and experimental quantities required to calculate the dissociation constant as compared to the P_{CO_2}–pH method. Only the following assumptions and quantities are required to calculate the results, aside from the analytical concentrations of reagents utilized in the experiments.

1. The P_{CO_2} must be assumed constant during the entire run.
2. The change in the experimental pH between run points must be accurately measurable.
3. The single ion activity coefficients used in the calculations must describe adequately the change in ion activities with changes in the ionic strength between run points.

The floating point method is a considerable improvement over the P_{CO_2}–pH method in that no absolute value of either the P_{CO_2} or experimental pH need be determined and that no use is made of other equilibrium constants (K_0 and K_1).

A final consideration is whether it is preferable to titrate a $MgCl_2$ solution with $KHCO_3$ or vice versa. The floating point method was found to give the best results in experiments where both Mg^{2+} and HCO_3^- increase in concentration during the course of the run. Therefore, the experimental approach adopted here was the potentiometric titration of a $MgCl_2$–$KHCO_3$ solution with alternating additions of $MgCl_2$ and $KHCO_3$ solution. Runs were performed at 10°, 25°, 40°, 55°, 70°, and 90°C.

EXPERIMENTAL PROCEDURE

The experimental approach to this investigation was the potentiometric titration of a $KHCO_3$ solution, in equilibrium with pure CO_2 gas, with alternating additions of $MgCl_2$ and $KHCO_3$ solutions. Runs were performed in a 2-l polypropylene reaction vessel, which was sealed gas tight and thermostated in a 40-gallon constant temperature water bath. The lid was fitted with a 300-watt aluminum immersion heater, a heat exchanger coil of stainless steel tubing and holes for reagent additions, stainless steel thermistor probe, and pH electrodes. Approx 1600 g of distilled-deionized water, along with appropriate quantities of $KHCO_3$ and $MgCl_2$ solutions, were weighed into the reaction vessel. The vessel was then sealed, thermostated, and equilibrated with pure CO_2 gas at the temperature of interest. Titration of the solution proceeded by injecting alternating weighed increments of $KHCO_3$ and $MgCl_2$ solutions into the vessel through a soft rubber surgical tubing nipple with two 50-ml syringes and 10-cm hypodermic needles. The pH was monitored after each addition and was recorded along with the weight of solution added. Five additions of $MgCl_2$ alternating with five additions of $KHCO_3$ solution constituted a run.

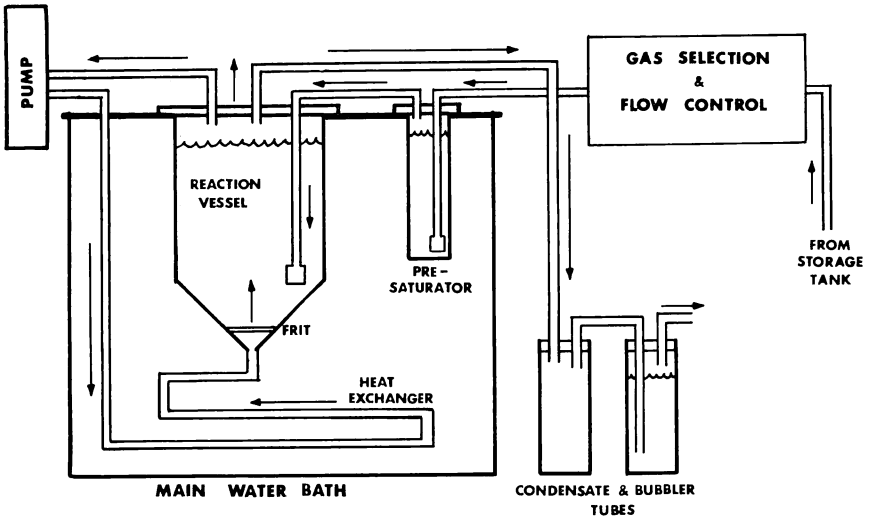

Fig. 1. Schematic diagram of the reaction vessel and gas systems.

Equilibration of the run solutions with CO_2 gas was effected by a unique 2-stage gas system. This system is constructed totally of polyolefin plastic and is presented schematically in figure 1. In the first stage, CO_2 is drawn from a storage tank and bubbled through a water-filled "pre-saturator" vessel in order to equilibrate the gas with respect to water vapor at the temperature of the run. The gas is then bubbled into the reaction vessel through a submerged gas dispersing frit. Excess gas from the space above the run solution is vented to the atmosphere via a condensate catch tube and water valve. Gas flow in this stage is relatively low, being on the order of 100 ml per min. The independent second stage withdraws the gas phase from the top of the run solution with a polyethylene bellows pump and pumps it through 15 m of heat exchange coil to the conically shaped bottom of the reaction vessel. The gas passes into the vessel, through a gas dispersing frit, and bubbles up through the solution. Gas flow is on the order of 2 l per min, and the fountaining of the gas through the solution provides excellent stirring and very intimate contact between the gaseous and aqueous phases. With this two-stage gas system, experimental solutions were found to equilibrate very rapidly (less than 5 min) and demonstrated very stable pH's. For instance, $KHCO_3$ solutions equilibrated with pure CO_2 at 25°C held a constant pH for 6 hrs, indicating that the P_{CO_2} in the apparatus remains accurately constant over long periods of time.

Temperature regulation within the reaction vessel was effected by the immersion heater and an electronic temperature controller utilizing 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 ±

0.05°C. At higher temperatures, only the immersion heater was used and gave regulation to ± 0.04°C. The main water bath was regulated by a separate temperature controller and heater-stirrer unit to ± 0.01°C.

Solutions of $KHCO_3$ were prepared by adding weighed quantities of desiccator dried (over $CaCl_2$), reagent grade $KHCO_3$ to a weighed quantity of distilled-deionized water. Concentrated $MgCl_2$ solutions were prepared by dissolving reagent grade $MgCl_2 \cdot 6H_2O$ in distilled-deionized water and analyzing titrimetrically for Mg^{2+} and Cl^- with EDTA and $AgNO_3$ respectively. The results for cation and anion agreed within 1 part per 500, but the anion analytical value was chosen as being most accurate. All water was weighed to ± 0.1 g accuracy. Additions of $MgCl_2$ and $KHCO_3$ solutions were weighed by difference. A cup containing the solution was weighed, the solution withdrawn with the syringe and immediately injected into the run, and the cup was reweighed. Although the cup weighings were within ± 0.001 g, the precision of any one addition was approx ± 0.05 g because of erratic deliveries by the syringes. Cumulative precision over the course of the run was also ± 0.05 g because no solution was lost from the syringes after injections.

The experimental pH was monitored with an Orion 801 digital pH meter and a Beckman 39000 glass electrode that was paired with an Orion 90-00-03 double junction reference electrode with 10 percent KNO_3 outer filling solution. The pH measuring assembly was calibrated with commercial phthalate (pH = 4.008 at 25°C) and phosphate (pH = 7.000 at 25°C buffers. Both buffers and electrodes were thermostated at the temperature of the run in separate vessels of the water bath. The pH assembly was calibrated to agree within ± 0.005 pH units in both buffers, and then the electrodes were sealed into the reaction vessel along with initial solutions of $MgCl_2$ and $KHCO_3$. The solution was then equilibrated with pure CO_2 gas in the system, and the pH was monitored over the next hour or two. The titration was not begun until the pH had remained constant for half an hour. Approx 5 min equilibration time was allowed after each addition, before the pH was recorded. At the end of each run, the electrodes were checked in both buffers, and agreement with the initial values was usually within ± 0.03 pH units. The slope of the pH measuring assembly (that is, the reading in the 7 buffer minus the reading in the 4 buffer) seldom changed more than 1 part in 300 from the original calibration.

Error contributed to the measured pH by changes in the liquid junction potential of the reference electrode was measured experimentally at 25°C. Distilled-deionized water was titrated with concentrated $MgCl_2$ solution, and the activity of Cl^- was monitored using an Ag–AgCl wire electrode in combination with the Orion double junction electrode. The experimental molalities of Cl^- were converted to activities using appropriate activity coefficients, and these were then converted to relative voltage values using the Nernst equation. Using one experimental point as a reference point, the change in the potential from the reference point was calculated for subsequent points and was compared with the poten-

TABLE 1

Data used in calculating the stability constant

Run Point	pH	Mg_T (m x 10^2)	$mKHCO_3$ (m x 10^3)	I (m)	pK
	Run 7-25, t = 10°C				
1	5.124	2.360	3.656	0.074	1.057
2*	5.248	2.337	4.838	0.074	1.027
3	5.205	3.705	4.781	0.115	1.060
4	5.323	3.660	6.254	0.114	1.051
5	5.286	5.137	6.173	0.158	1.059
6	5.378	5.076	7.593	0.157	1.050
7	5.339	6.845	7.474	0.210	1.058
8	5.416	6.763	8.887	0.208	1.053
9	5.383	8.430	8.754	0.257	1.056
10	5.448	8.330	10.131	0.255	1.053
				Average =	1.055
	Run 7-27, t = 10°C				
1*	5.145	2.303	3.564	0.072	1.022
2*	5.269	2.281	4.747	0.072	1.019
3*	5.229	3.574	4.694	0.111	1.045
4	5.348	3.530	6.204	0.110	1.061
5	5.310	5.010	6.123	0.154	1.068
6	5.397	4.957	7.484	0.154	1.072
7	5.364	6.510	7.381	0.200	1.066
8	5.450	6.422	8.979	0.198	1.066
9	5.415	8.202	8.836	0.251	1.066
10	5.484	8.096	10.335	0.248	1.066
				Average =	1.066
	Run 7-31, t = 10°C				
1	5.209	2.673	4.376	0.084	1.033
2	5.320	2.645	5.653	0.084	1.031
3*	5.280	4.028	5.586	0.125	1.051
4	5.383	3.980	7.036	0.124	1.033
5	5.345	5.702	6.930	0.176	1.028
6	5.436	5.626	8.510	0.174	1.021
7	5.400	7.265	8.386	0.223	1.038
8	5.475	7.171	9.896	0.221	1.026
9	5.440	8.974	9.735	0.274	1.035
10	5.502	8.865	11.126	0.272	1.021
				Average =	1.030
	Run 5-21A, t = 25°C				
1*	5.143	2.765	3.109	0.085	1.071
2	5.326	2.716	4.746	0.085	1.085
3	5.277	4.637	4.681	0.142	1.083
4	5.389	4.567	6.052	0.141	1.090
5	5.345	6.673	5.959	0.204	1.087
6	5.439	6.567	7.358	0.201	1.094
7	5.399	8.849	7.261	0.269	1.086
8	5.477	8.709	8.657	0.266	1.089
9	5.437	11.280	8.490	0.342	1.080
10	5.504	11.107	9.852	0.337	1.081
				Average =	1.086

Run Point	pH	Mg_T (m x 10^2)	$mKHCO_3$ (m x 10^3)	I (m)	pK
	Run 5-30, t = 25°C				
1	5.115	7.279	3.398	0.220	1.040
2	5.256	7.186	4.735	0.218	1.061
3	5.218	9.525	4.653	0.288	1.051
4	5.355	9.362	6.437	0.284	1.077
5	5.316	12.012	6.308	0.363	1.065
6	5.402	11.849	7.702	0.359	1.076
7	5.362	14.904	7.522	0.450	1.059
8	5.436	14.702	8.899	0.444	1.064
9	5.398	17.968	8.671	0.541	1.043
10	5.460	17.731	9.993	0.535	1.050
				Average =	1.059
	Run 6-5, t = 25°C				
1*	5.279	2.450	4.240	0.077	1.076
2	5.388	2.421	5.452	0.077	1.084
3	5.346	3.941	5.393	0.122	1.086
4	5.451	3.886	6.842	0.121	1.085
5	5.403	6.024	6.737	0.185	1.088
6	5.478	5.950	7.984	0.183	1.090
7	5.431	8.504	7.835	0.259	1.086
8	5.497	8.399	9.077	0.257	1.085
9	5.453	11.161	8.890	0.339	1.078
10	5.513	11.017	10.176	0.335	1.082
				Average =	1.085
	Run 6-6A, t = 25°C				
1	5.132	3.020	3.108	0.093	1.050
2	5.280	2.984	4.367	0.093	1.052
3	5.233	4.954	4.305	0.152	1.051
4	5.357	4.888	5.711	0.150	1.052
5	5.315	6.995	5.623	0.213	1.053
6	5.408	6.905	6.953	0.211	1.058
7	5.369	9.258	6.833	0.281	1.049
8	5.444	9.141	8.118	0.278	1.057
9	5.405	11.762	7.958	0.356	1.048
10	5.470	11.615	9.214	0.352	1.051
				Average =	1.052
	Run 6-6B, t = 25°C				
1*	5.121	2.975	2.953	0.092	1.033
2	5.274	2.939	4.236	0.091	1.069
3	5.221	5.095	4.171	0.156	1.073
4	5.335	5.035	5.397	0.155	1.068
5	5.290	7.310	5.307	0.222	1.068
6	5.390	7.212	6.703	0.220	1.083
7	5.350	9.670	6.582	0.293	1.071
8	5.432	9.541	7.950	0.290	1.079
9	5.395	12.154	7.794	0.368	1.063
10	5.463	11.996	9.103	0.364	1.070
				Average =	1.071

Run 5-21B, t = 25°C

1	5.181	2.847	3.402	0.088	1.061
2	5.344	2.799	4.952	0.088	1.069
3	5.290	4.959	4.875	0.152	1.074
4	5.403	4.884	6.263	0.151	1.059
5	5.360	6.970	6.168	0.213	1.065
6	5.465	6.840	7.830	0.210	1.071
7	5.429	8.908	7.710	0.271	1.067
8	5.514	8.750	9.271	0.267	1.058
9*	5.476	11.150	9.105	0.339	1.055
10*	5.526	11.014	10.154	0.345	1.053
				Average =	1.065

Run 5-24A, t = 25°C

1	5.369	2.805	5.608	0.088	1.066
2*	5.464	2.764	6.915	0.088	1.039
3	5.413	4.743	6.817	0.147	1.061
4	5.492	4.672	8.138	0.146	1.057
5	5.455	6.587	8.025	0.202	1.049
6	5.515	6.499	9.186	0.201	1.050
7	5.475	8.653	9.040	0.264	1.058
8	5.533	8.526	10.307	0.261	1.063
9	5.495	10.922	10.123	0.332	1.059
10	5.550	10.750	11.464	0.328	1.065
				Average =	1.059

Run 5-24B, t = 25°C

1*	4.956	2.811	2.371	0.086	1.004
2*	5.147	2.771	3.703	0.086	1.028
3	5.096	4.715	3.651	0.144	1.052
4	5.225	4.651	4.907	0.143	1.058
5	5.186	6.540	4.840	0.199	1.058
6	5.302	6.434	6.306	0.197	1.064
7	5.266	8.537	6.209	0.259	1.054
8	5.354	8.404	7.599	0.256	1.063
9	5.315	10.838	7.461	0.329	1.059
10	5.391	10.676	8.772	0.324	1.048
				Average =	1.057

Run 5-28A, t = 25°C

1*	5.145	4.803	3.512	0.147	1.037
2	5.286	4.741	4.876	0.146	1.052
3	5.249	6.567	4.811	0.200	1.052
4	5.360	6.480	6.198	0.198	1.056
5	5.323	8.577	6.102	0.261	1.053
6	5.416	8.458	7.530	0.258	1.055
7	5.380	10.713	7.403	0.325	1.052
8	5.459	10.560	8.848	0.321	1.055
9	5.424	12.995	8.684	0.393	1.048
10	5.483	12.834	9.930	0.389	1.053
				Average =	1.053

Run 5-28B, t = 25°C

1*	5.257	3.168	3.977	0.098	1.018
2*	5.391	3.124	5.459	0.098	1.055
3	5.345	4.955	5.387	0.152	1.071
4	5.448	4.887	6.803	0.151	1.070
5	5.407	6.894	6.704	0.211	1.072
6	5.498	6.792	8.222	0.209	1.071
7	5.458	9.031	8.087	0.275	1.071
8	5.534	8.895	9.604	0.272	1.076
9	5.495	11.388	9.424	0.346	1.070
10	5.552	11.242	10.694	0.342	1.071
				Average =	1.071

Run 6-11, t = 40°C

1	5.310	3.106	3.648	0.096	1.102
2	5.437	3.070	4.883	0.096	1.106
3	5.397	4.644	4.828	0.142	1.106
4	5.502	4.586	6.130	0.142	1.107
5	5.465	6.312	6.053	0.193	1.106
6	5.556	6.227	7.436	0.191	1.107
7	5.518	8.295	7.324	0.253	1.103
8	5.590	8.187	8.639	0.250	1.110
9	5.550	10.756	8.474	0.326	1.097
10	5.611	10.620	9.748	0.323	1.104
				Average =	1.105

Run 6-12A, t = 40°C

1	5.294	3.116	3.453	0.096	1.101
2	5.426	3.079	4.681	0.096	1.109
3	5.384	4.752	4.625	0.146	1.107
4	5.481	4.699	5.785	0.145	1.116
5	5.441	6.688	5.701	0.204	1.105
6	5.536	6.599	7.084	0.202	1.110
7	5.498	8.700	6.974	0.264	1.106
8	5.570	8.592	8.239	0.262	1.116
9	5.532	10.977	8.092	0.333	1.107
10	5.597	10.838	9.367	0.329	1.110
				Average =	1.109

Run 6-12B, t = 40°C

1*	5.211	2.801	2.680	0.086	1.064
2	5.370	2.769	3.900	0.086	1.100
3	5.327	4.465	3.853	0.137	1.092
4	5.439	4.417	4.995	0.136	1.104
5	5.395	6.502	4.919	0.198	1.100
6	5.493	6.425	6.152	0.196	1.103
7	5.454	8.605	6.054	0.261	1.097
8	5.539	8.497	7.346	0.259	1.101
9	5.500	10.973	7.210	0.332	1.092
10	5.573	10.830	8.533	0.329	1.101
				Average =	1.099

Run 6-18, t = 40°C

1	5.281	2.678	3.192	0.083	1.120
2	5.422	2.647	4.403	0.083	1.114
3	5.376	4.349	4.350	0.133	1.115
4	5.490	4.295	5.634	0.133	1.114
5	5.448	6.202	5.560	0.189	1.114
6	5.543	6.122	6.900	0.188	1.117
7	5.500	8.461	6.781	0.257	1.110
8	5.580	8.348	8.150	0.254	1.118
9*	5.543	10.800	8.000	0.327	1.101
10*	5.612	10.657	9.336	0.324	1.103
				Average =	1.115

Run 6-19A, t = 40°C

1*	5.194	3.048	2.769	0.095	1.095
2	5.362	3.010	4.087	0.093	1.108
3	5.322	4.587	4.041	0.140	1.105
4	5.455	4.523	5.495	0.139	1.117
5	5.413	6.588	5.413	0.201	1.105
6	5.504	6.508	6.679	0.199	1.115
7	5.468	8.602	6.577	0.261	1.101
8	5.553	8.482	8.002	0.258	1.111
9	5.517	10.760	7.866	0.326	1.102
10	5.593	10.600	9.346	0.322	1.107
				Average =	1.108

TABLE 1 (continued)

Run Point	pH	Mg_T ($\underline{m} \times 10^2$)	$\underline{m}KHCO_3$ ($\underline{m} \times 10^3$)	I ($\underline{m}$)	pK
	Run 6-19B, t = 40°C				
1	5.283	2.902	3.319	0.090	1.111
2	5.422	2.868	4.567	0.089	1.114
3	5.383	4.373	4.517	0.134	1.110
4	5.505	4.311	5.985	0.133	1.120
5	5.465	6.198	5.904	0.189	1.111
6	5.559	6.113	7.315	0.188	1.116
7	5.522	8.136	7.207	0.248	1.108
8	5.593	8.033	8.493	0.245	1.118
9	5.556	10.351	8.347	0.314	1.106
10	5.619	10.217	9.650	0.311	1.114
				Average =	1.113
	Run 6-20, t = 55°C				
1*	5.301	2.992	2.580	0.092	1.154
2	5.471	2.957	3.824	0.091	1.166
3	5.430	4.477	3.782	0.137	1.162
4	5.561	4.420	5.123	0.136	1.175
5	5.521	6.265	5.054	0.191	1.163
6	5.622	6.185	6.387	0.189	1.175
7	5.585	8.184	6.293	0.248	1.162
8	5.663	8.086	7.521	0.246	1.168
9*	5.625	10.404	7.391	0.315	1.155
10	5.689	10.287	8.537	0.312	1.158
				Average =	1.166
	Run 6-21, t = 55°C				
1	5.250	2.827	2.300	0.086	1.152
2*	5.463	2.795	3.764	0.086	1.164
3	5.422	4.313	3.723	0.132	1.156
4	5.585	4.257	5.414	0.131	1.163
5	5.544	6.110	5.341	0.186	1.154
6	5.661	6.032	6.985	0.185	1.161
7	5.623	8.023	6.883	0.244	1.153
8	5.704	7.934	8.284	0.242	1.159
9	5.669	9.966	8.159	0.302	1.153
10	5.735	9.862	9.466	0.300	1.155
				Average =	1.156
	Run 6-25A, t = 55°C				
1	5.334	2.997	2.727	0.092	1.160
2	5.492	2.970	3.930	0.092	1.169
3	5.453	4.467	3.888	0.136	1.158
4	5.591	4.417	5.331	0.137	1.161
5	5.548	6.325	5.257	0.193	1.159
6	5.659	6.250	6.776	0.191	1.164
7	5.620	8.350	6.671	0.254	1.154
8	5.705	8.255	8.113	0.251	1.162
9*	5.666	10.737	7.963	0.325	1.146
10*	5.736	10.619	9.345	0.322	1.151
				Average =	1.161

Run Point	pH	Mg_T ($\underline{m} \times 10^2$)	$\underline{m}KHCO_3$ ($\underline{m}$) $\times 10^3$	I ($\underline{m}$)	pK
	Run 7-13A, t = 70°C				
1	5.652	2.702	3.659	0.084	1.209
2	5.775	2.678	4.853	0.084	1.212
3	5.732	4.187	4.800	0.129	1.204
4	5.854	4.136	6.348	0.128	1.210
5	5.812	5.906	6.267	0.181	1.205
6	5.906	5.837	7.762	0.179	1.209
7	5.866	7.723	7.654	0.235	1.210
8	5.946	7.629	9.190	0.233	1.216
9	5.909	9.698	9.049	0.294	1.208
10	5.976	9.581	10.552	0.292	1.215
				Average =	1.210
	Run 7-13B, t = 70°C				
1*	5.692	2.726	3.945	0.085	1.216
2	5.806	2.700	5.164	0.085	1.242
3	5.757	4.263	5.106	0.131	1.251
4	5.873	4.211	6.680	0.130	1.263
5	5.831	5.982	6.595	0.183	1.251
6	5.923	5.910	8.137	0.181	1.251
7	5.883	7.866	8.021	0.239	1.247
8	5.961	7.767	9.611	0.237	1.257
9	5.923	9.929	9.456	0.301	1.243
10	5.988	9.808	10.968	0.298	1.249
				Average =	1.250
	Run 7-14A, t = 70°C				
1*	5.674	2.817	3.837	0.087	1.224
2	5.798	2.790	5.079	0.087	1.215
3	5.753	4.364	5.022	0.134	1.212
4	5.870	4.311	6.565	0.133	1.218
5	5.829	6.043	6.483	0.185	1.215
6	5.929	5.964	8.144	0.183	1.220
7	5.889	7.959	8.025	0.242	1.213
8	5.962	7.865	9.503	0.240	1.223
9	5.925	10.051	9.349	0.305	1.209
10	5.989	9.932	10.821	0.302	1.215
				Average =	1.216
	Run 7-14B, t = 70°C				
1*	5.614	2.988	3.460	0.092	1.164
2	5.739	2.959	4.717	0.092	1.234
3	5.695	4.509	4.664	0.138	1.230
4	5.822	4.454	6.250	0.137	1.240
5	5.783	6.146	6.174	0.188	1.230
6	5.880	6.072	7.706	0.186	1.236
7	5.841	7.990	7.598	0.243	1.230
8	5.919	7.895	9.095	0.241	1.238
9	5.882	9.962	8.955	0.302	1.229
10	5.948	9.845	10.414	0.299	1.236
				Average =	1.234

	Run 6-25B, t = 55°C				
1*	5.507	2.972	4.044	0.092	1.142
2	5.619	2.943	5.273	0.092	1.171
3	5.577	4.502	5.214	0.138	1.168
4	5.690	4.447	6.777	0.138	1.181
5	5.648	6.419	6.680	0.196	1.167
6	5.738	6.342	8.191	0.195	1.169
7	5.693	8.682	8.050	0.264	1.166
8	5.765	8.581	9.511	0.262	1.175
9*	5.726	11.070	9.334	0.335	1.159
10*	5.793	10.933	10.828	0.332	1.159
				Average =	1.171
	Run 6-26A, t = 55°C				
1*	5.615	2.226	5.002	0.071	1.155
2	5.709	2.206	6.176	0.071	1.139
3	5.670	3.477	6.120	0.109	1.144
4	5.753	3.443	7.379	0.108	1.139
5	5.717	4.871	7.303	0.151	1.142
6	5.796	4.816	8.736	0.150	1.143
7	5.757	6.648	8.619	0.204	1.142
8	5.818	6.580	9.909	0.203	1.147
9	5.780	8.682	9.755	0.265	1.139
10	5.833	8.595	10.995	0.263	1.142
				Average =	1.142
	Run 6-26B, t = 55°C				
1	5.278	2.314	2.266	0.071	1.165
2*	5.471	2.291	3.551	0.071	1.185
3	5.430	3.710	3.515	0.114	1.166
4	5.581	3.669	4.975	0.113	1.173
5	5.538	5.476	4.911	0.167	1.163
6	5.646	5.417	6.302	0.166	1.173
7	5.608	7.318	6.214	0.223	1.163
8	5.703	7.230	7.729	0.221	1.171
9	5.665	9.347	7.608	0.284	1.164
10	5.738	9.246	8.968	0.281	1.166
				Average =	1.167
	Run 7-12A, t = 70°C				
1	5.675	2.562	3.816	0.080	1.220
2	5.788	2.539	4.949	0.080	1.225
3	5.744	4.046	4.896	0.124	1.214
4	5.857	4.001	6.339	0.124	1.218
5	5.816	5.636	6.264	0.172	1.219
6	5.907	5.572	7.712	0.171	1.224
7	5.864	7.655	7.595	0.233	1.216
8	5.945	7.561	9.139	0.231	1.223
9	5.906	9.691	8.994	0.294	1.216
10	5.978	9.568	10.577	0.291	1.219
				Average =	1.219
	Run 7-12B, t = 70°C				
1	5.642	2.676	3.561	0.083	1.248
2*	5.762	2.652	4.711	0.083	1.265
3	5.719	4.151	4.661	0.127	1.246
4	5.839	4.103	6.149	0.127	1.256
5	5.797	5.874	6.071	0.179	1.243
6	5.893	5.805	7.573	0.178	1.251
7	5.852	7.771	7.464	0.236	1.244
8	5.935	7.674	9.023	0.234	1.250
9	5.896	9.800	8.881	0.297	1.241
10	5.966	9.678	10.432	0.294	1.250
				Average =	1.248
	Run 7-16, t = 90°C				
1	6.108	2.450	3.352	0.076	1.313
2	6.238	2.428	4.565	0.076	1.346
3	6.187	4.030	4.513	0.123	1.325
4	6.311	3.982	6.050	0.123	1.350
5	6.266	5.709	5.975	0.174	1.337
6	6.361	5.642	7.468	0.173	1.352
7	6.319	7.519	7.366	0.228	1.342
8	6.397	7.431	8.840	0.226	1.354
9	6.354	9.653	8.694	0.292	1.341
10	6.420	9.540	10.165	0.289	1.354
				Average =	1.347
	Run 7-17, t = 90°C				
1	6.141	2.722	3.699	0.084	1.339
2	6.270	2.695	4.971	0.084	1.343
3	6.225	4.184	4.918	0.128	1.323
4	6.338	4.135	6.418	0.128	1.344
5	6.295	5.794	6.341	0.176	1.334
6	6.389	5.725	7.862	0.175	1.340
7	6.342	7.721	7.747	0.234	1.340
8	6.418	7.631	9.199	0.232	1.343
9	6.381	9.618	9.063	0.291	1.329
10	6.444	9.506	10.510	0.288	1.340
				Average =	1.339
	Run 7-20A, t = 90°C				
1	6.047	2.696	2.832	0.083	1.331
2	6.211	2.669	4.118	0.083	1.331
3*	6.163	4.199	4.073	0.128	1.320
4	6.301	4.149	5.599	0.128	1.330
5	6.257	5.844	5.531	0.178	1.323
6	6.367	5.770	7.141	0.176	1.336
7	6.323	7.742	7.038	0.235	1.328
8	6.410	7.645	8.625	0.232	1.341
9	6.371	9.687	8.494	0.293	1.330
10	6.442	9.569	10.015	0.290	1.340
				Average =	1.331
	Run 7-20B, t = 90°C				
1	6.203	3.177	4.115	0.098	1.332
2	6.319	3.146	5.375	0.098	1.339
3*	6.276	4.686	5.316	0.143	1.320
4	6.385	4.630	6.838	0.142	1.330
5	6.341	6.328	6.754	0.193	1.331
6	6.436	6.246	8.392	0.191	1.338
7	6.395	8.195	8.272	0.249	1.327
8	6.467	8.096	9.782	0.246	1.338
9	6.430	10.145	9.633	0.307	1.324
10	6.494	10.020	11.163	0.304	1.332
				Average =	1.332

*Deleted from run average

tial change observed by direct measurement. The difference between the two sets of values represents the contribution from changes in the liquid junction potential of the reference electrode. This difference totaled only 0.5 mv over the concentration range which corresponds with the concentration ranges of the $MgHCO_3^+$ experiments. Therefore, errors due to liquid junction potential changes (with changes in concentration of reactants) are considered to be minimal.

RESULTS

The thermodynamic dissociation constants were calculated from the experimental data presented in table 1 by the floating point method. The only important aqueous species assumed present in these solutions are Mg^{2+}, $MgHCO_3^+$, K^+, HCO_3^-, and Cl^-. The ratio of the activity of CO_3^{2-} to the activity of HCO_3^- was usually much less than 10^{-4} at the pH values (usually less than 6) generated in the experimental solutions, and, thus, the $MgCO_3^\circ$ ion pair and CO_3^{2-} can be safely neglected.

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

$$\log \gamma_i = -(Az_i^2 I^{1/2})/(1 + \mathring{a}_i BI^{1/2}) \qquad (14)$$

Values of A and B were taken from Helgeson (1967); I is the ionic strength in molal units:

$$I = 0.5(4m\mathrm{Mg}^{2+} + m\mathrm{MgHCO_3}^+ + m\mathrm{K}^+ + m\mathrm{HCO_3}^- + m\mathrm{Cl}^-) \qquad (15)$$

The value used for the HCO_3^- ion size parameter (å) was 5.5×10^{-8} cm (Christ and Hostetler, 1970) for 25°C. Values of $\gamma_{Mg^{2+}}$ were derived from an extended form of eq 14 obtained by adding a $bI^{3/2}$ term to the right side. The resulting equation was fitted to $\gamma_{Mg^{2+}}$ values calculated by the mean salt method (Garrels and Christ, 1965) from data for $\gamma_\pm$ $MgCl_2$ (Harned and Owen, 1958) and $\gamma_\pm$ KCl (Hostetler, Truesdell and Christ, 1967). The resulting $\mathring{a}_{Mg^{2+}}$ was 6.5×10^{-8} cm, and b was 0.12 at 25°C. This equation fits the data well even for ionic strengths far in excess of those reached in this work. It was assumed that the γ-values for $MgHCO_3^+$ are the same as those for HCO_3^-. In all cases, the temperature dependence of the Debye-Huckel equation was assumed to predict adequately γ_i values at temperatures other than 25°C.

An example of the results from the calculation process and the convergence to the final result is given in table 2. The value of $p[HCO_3^-]$ (—log of the HCO_3^- activity) was arbitrarily selected or "floated" and the values of the $pK_{MgHCO_3^+(n)}$ were calculated. The resulting pK's were examined for equivalence, that is, convergence. If this requirement was not met, the $p[HCO_3^-]$ was incremented or decremented repeatedly (as in the first column of table 2), and the value of the pK calculated until convergence was attained. The non-convergence was readily recognized with large "errors" in $p[HCO_3^-]$ (as with the first and last pairs of $p[HCO_3^-]$ in table 2), but with small "errors," the choice of the final

result was difficult. Therefore, the average of the pK values and the average internal deviation, the mean of the deviation from the mean of the pK values for each run point, were calculated as an aid in determining the result where the computed pK values have the greatest statistical consistency. The final result taken to be correct was the one that had minimum internal deviation. Finally, the example in table 2 also illustrates the extreme sensitivity of the calculated $pK_{MgHCO_3^+}$ to errors in the activity of HCO_3^-. For instance, a 0.014 error in the $p[HCO_3^-]_1$ ($p[HCO_3^-]_1 = 2.650$ as compared to the final value of $p[HCO_3^-]_1 = 2.644$) yields a difference in the calculated $pK_{MgHCO_3^+}$ values of 0.13 for the first run point and 0.05 for the last run point.

Thirty-five experimental runs (totaling 350 run points) were performed from 10° to 90°C. The results are summarized in table 3. The raw experimental data used in the calculations and the resulting dissociation constants are tabulated in table 1. A more complete result for one representative run at 25°C is presented in table 4.

DISCUSSION

Two major sources of error in this work are the errors in the single ion activity coefficients and errors in the measured pH change between run points. As an aid to the visualization of the possible magnitude of

TABLE 2

Example of convergence with the "floating point" for run 6-6A (25°C)

	$p[HCO_3^-]$ values of pK for the ten run points calculated from the value of $p[HCO_3^-]$ in the first column.						
	1	2	3	4	5	9	10
2.640	0.8010	0.7979	0.8848	0.8825	0.9242	0.9560	0.9583
2.650	0.9207	0.9203	0.9608	0.9600	0.9818	0.9961	0.9988
2.661	1.0254	1.0270	1.0332	1.0338	1.0388	1.0373	1.0403
2.663	1.0423	1.0441	1.0453	1.0461	1.0486	1.0445	1.0475
2.664*	1.0505	1.0525	1.0513	1.0522	1.0534	1.0481	1.0512
2.665	1.0586	1.0607	1.0572	1.0582	1.0582	1.0516	1.0547
2.667	1.0744	1.0768	1.0688	1.0700	1.0676	1.0587	1.0618
2.680	1.1668	1.1706	1.1388	1.1412	1.1254	1.1026	1.1061
2.690	1.2281	1.2328	1.1873	1.1903	1.1662	1.1345	1.1381

* Taken as final result based on a minimum average internal deviation.

TABLE 3

Experimental results for $K_{MgHCO_3^+}$ determinations

T°C	$-\log K$	Average internal deviation	# of runs	Standard deviation
10	1.051	0.003095	3	0.01840
25	1.066	0.003945	10	0.01231
40	1.108	0.003329	6	0.00586
55	1.160	0.003417	6	0.01054
70	1.230	0.003546	6	0.01726
90	1.337	0.004140	4	0.00730

these errors, an "error analysis" table was calculated. The calculation was made by giving a plus and a minus error to the parameter of interest, while holding all others at the "correct" value, and calculating the $pK_{MgHCO_3^+}$. The results are presented in table 5.

The error analysis indicates that the value of $pK_{MgHCO_3^+}$ is relatively sensitive to errors in the activity coefficients for Mg^{2+} and HCO_3^-. Unfortunately, the accuracy of a single ion activity coefficient value at a given ionic strength is impossible to evaluate satisfactorily. The activity coefficients used in this study are calculated by the Debye-Huckel equation, based on experimentally determined mean salt values ($\gamma_\pm$) for $MgCl_2$, KCl, and $KHCO_3$ solutions. In order to maintain high concentrations of $MgCl_2$ (to insure substantial $MgHCO_3^+$ formation) but avoid the high ionic strengths where the $\gamma_{Mg^{2+}}$ values become less certain, the experiments were performed over a relatively narrow range of ionic strengths (approx 0.07-0.53).

The second potential source of error is a nearly linear drift (a constant rate of error operating during the run) in the measured pH change between run points. This type of pH drift is particularly serious in that it cannot be detected in the results for a given run, whereas a non-linear drift or a drift that started in the middle of a run is readily detected, because some or all of the calculated pK's will fail to reach consistency. The magnitude of the error in the resulting $pK_{MgHCO_3^+}$ can be seen in table 5. For instance, a ± 0.01 drift in pH over the run resulted in a

TABLE 4

Complete results of calculations for run 6-6A (25°C)

	pH	Mg_T	$m KHCO_3$	$m Mg^{2+}$	$m MgHCO_3^+$	$m HCO_3^-$
1	5.132	0.0302	0.00311	0.0298	0.00039	0.00273
2	5.280	0.0298	0.00437	0.0293	0.00054	0.00384
3	5.233	0.0495	0.00431	0.0488	0.00074	0.00358
4	5.357	0.0489	0.00571	0.0479	0.00097	0.00476
5	5.315	0.0699	0.00562	0.0688	0.00119	0.00444
6	5.408	0.0691	0.00695	0.0676	0.00147	0.00549
7	5.369	0.0926	0.00683	0.0909	0.00170	0.00514
8	5.444	0.0914	0.00812	0.0894	0.00202	0.00610
9	5.405	0.1176	0.00796	0.1154	0.00227	0.00569
10	5.470	0.1162	0.00921	0.1135	0.00262	0.00661

	$\frac{m MgHCO_3^+}{Mg_T}$ %	$\frac{m MgHCO_3^+}{m KHCO_3}$ %	$[HCO_3^-] \cdot [H^+] \times 10^8$	γMg^{2+}	γHCO_3^-	I	$-\log K_{MgHCO_3^+}$
1	1.2	12.5	1.5996	0.424	0.794	0.093	1.050
2	1.8	12.3	1.5992	0.424	0.794	0.093	1.052
3	1.5	17.1	1.5999	0.375	0.765	0.152	1.051
4	1.9	16.9	1.5988	0.375	0.765	0.150	1.052
5	1.7	21.2	1.5992	0.345	0.744	0.213	1.053
6	2.1	21.1	1.5999	0.346	0.745	0.211	1.058
7	1.8	24.9	1.5992	0.324	0.728	0.281	1.049
8	2.2	24.9	1.5988	0.325	0.728	0.278	1.057
9	1.9	28.5	1.5996	0.309	0.714	0.356	1.048
10	2.3	28.4	1.5981	0.310	0.714	0.352	1.051

± 0.05 pK unit error in the result. This error calculation is performed by assuming that the first experimental pH has a 0.001 error, the second pH has a 0.002 error, and so forth, until the tenth pH has the full 0.01 error.

Possible sources for this pH error are variations in pressure of CO_2 during the run, thermal or electronic drift of the electrodes and pH meter, inaccurate pH slope calibration, and changing liquid junction potential in the reference electrode. As stated previously, the experimental apparatus and pH monitoring equipment were capable of maintaining accurately constant pH values in test solutions for many hours. Great care was taken to insure initial P_{CO_2} and electrode equilibration in the experimental solutions, and the titration was not begun until the pH was constant to ± 0.001 for approximately 30 min. An example of the combined stability of the pH measuring assembly and the constancy of the experimental P_{CO_2} for the ten points constituting an experiment is given in table 3 by the tabulation of the ion activity product, $[HCO_3^-][H^+]$, which is proportional to P_{CO_2} by eq 1. Consequently, errors from the first two sources above are considered negligible in this study.

The electrode pair, which was found to exhibit a theoretical response to H^+ activity changes, was accurately calibrated with pH = 4 and pH = 7 buffer solutions. If an error of ± 0.03 pH units was assumed in the slope calibration, that is, $\Delta EMF/\Delta pH$, then the drift error in the experimental pH's would amount to 1 part in 100. Since the pH range covered in an experiment was only 0.3 to 0.4 pH units, the total error in the experimental pH over the course of the run would be 0.003 to 0.004 pH units. Since the slope calibration is believed to be more accurate than ± 0.03 pH units, errors in the results due to inaccurate pH slopes are considered minimal.

The last source of pH error is change in the liquid junction potential during a run. Unfortunately, liquid junction potentials in reference electrodes cannot be avoided, and their changing contributions to the experimental pH cannot be dealt with adequately. The Orion double junction electrode with 10 percent KNO_3 filling solution was found to

TABLE 5

Error analysis for run 5-28A (25°C)

Source of error	Error	Error in $pK_{MgHCO_3^+}$	% Change in γ's
Linear drift in pH	+0.01	−0.062	—
	−0.01	+0.052	—
	+0.02	−0.127	—
	−0.02	+0.100	—
$å_{HCO_3^-}$	+0.5	+0.023	0.9 to 1.7%
	−0.5	−0.022	0.9 to 1.6%
$å_{Mg^{2+}}$	+0.5	−0.033	3.4 to 5.4%
	−0.5	+0.038	3.5 to 5.6%

be the best of all the reference electrodes tested with regard to changes in the junction potential with changes in $MgCl_2$ concentrations. Still, the double junction electrode exhibited 0.5 mv junction potential (approx 0.01 pH units) change with $MgCl_2$ concentration changes comparable to those of the $MgHCO_3^+$ runs. This error in the pH would generate an error of 0.05 pK units in the dissociation constant. However, the calculated magnitude of this effect appears to be much larger than that actually present. The $MgCl_2$ in the experimental solutions is the dominant factor controlling the liquid junction potential because of its greater concentration, the charge of the cation, and the concentration of the anion and its large mobility. (A detailed discussion of liquid junction potential may be found in Bates, 1973, chap. 3.) Consequently, the error in the pH change will be reflected almost exclusively in the calculated $pK_{MgHCO_3^+}$ of the $MgCl_2$ addition step. Examination of the raw results for 25°C indicates that the pK of the $MgCl_2$ addition steps (the odd numbered run points) averaged approx 0.005 units lower (for 29 out of a possible 37 cases) than the pK for the preceding $KHCO_3$ additions (even numbered points). If this difference is representative of the junction potential error per $MgCl_2$ addition, then the cumulative error over four $MgCl_2$ additions (the first addition is the reference pH in the calculations) would yield an average error in the final $pK_{MgHCO_3^+}$ of 0.02 units. Since this error is systematic, the results reported are probably all approx 0.02 pK units too low. Overall experimental uncertainty at all temperatures for $pK_{MgHCO_3^+}$ is believed to be ± 0.03 pK units, because this value is believed to encompass all reasonable errors.

ELECTROSTATIC ION PAIR THEORY

The experimental 25°C value ($pK_{MgHCO_3^+} = 1.067$) is in general agreement with the value obtained by Reardon, Jacobson, and Langmuir (1973) and by Nakayama's (1971) correction of Greenwald's (1941) data but is significantly lower than the value of Nakayama (1971) and his corrected value from Hostetler's (1963) data. There are no data at temperatures other than at 25°C, except for those herein reported, which extend from 10° to 90°C at 15° intervals. The present experimental data provide an excellent opportunity to check the usefulness of the temperature variation of $pK_{MgHCO_3^+}$ predicted by the ion pair theory of Fuoss (1958).

The Fuoss theory of ion pair formation 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 by the following equations (Robinson and Stokes, 1970, p. 552).

$$\ln K_F = A - B/(\varepsilon T) \tag{16}$$

$$A = \ln \frac{3000}{4\pi N a^3} \qquad B = \frac{z_1 z_2 e^2}{ka}$$

Where:

ε = dielectric constant of the bulk solvent
T = temperature (K)

a = ion size parameter
z = ion charges
e = charge of the electron
N = Avogadro's number
k = Boltzmann's constant
K_F = Fuoss dissociation constant

Comparison between the experimental $MgHCO_3^+$ results and those predicted by the Fuoss equation was obtained in the following way. Since there is no way of knowing the $MgHCO_3^+$ ion size parameter ($a_{MgHCO_3^+}$) *a priori,* the Fuoss equation was solved, by trial and error, for that parameter using the experimental value of $\ln K_{MgHCO_3^+}$ at 25°C. The result, 2.53×10^{-8} cm, was then used along with appropriate dielectric constants and temperatures to calculate the constants at other temperatures. The values of the dielectric constant were those of Malmberg and Maryott (1956) as tabulated by Robinson and Stokes (1970, p. 457). Thus the theoretical variation of the constant with temperature is generated but is "hinged" on an experimental value at one temperature. The results are plotted in figure 2. Agreement between the theoretical and experimental temperature dependence is excellent. The uncomplexed Mg^{2+} ion, with crystal radius of 0.65 Å, in aqueous solution is coordinated to water molecules with diameters of 2.8 Å. In the Fuoss theory, the size parameter

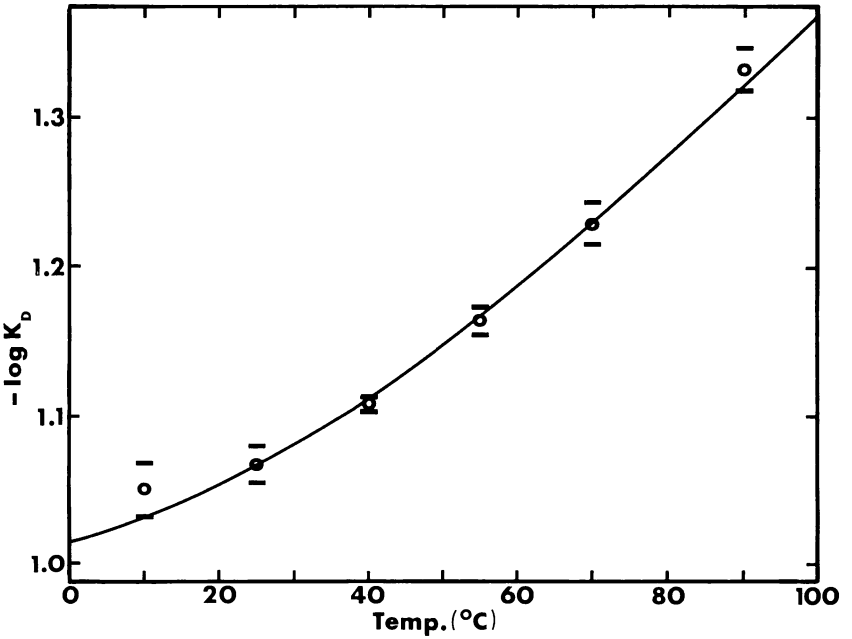

Fig. 2. Graph of the experimental results. The circles and bounding bars represent the experimental values and the experimental standard deviation. The solid line is calculated from the Fuoss equation.

a is the radius of the cation; a value for it of 2.53Å, as found here, means that there is penetration of the water sheath surrounding the Mg^{2+} ion by the HCO_3^- to form the $MgHCO_3^+$ ion pair. Thus, the ion pair can be represented by the formula $Mg^{2+}(H_2O)_{x-1}(HCO_3^-)$.

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.

$$MgHCO_3^+(aq) = Mg^{2+}(aq) + HCO_3^-(aq)$$

The thermodynamic quantities were calculated by the following equations.

$$\Delta G°_R = RT\ln K \tag{17}$$

$$\ln K = A - B/(\epsilon T) \tag{18}$$

$$\frac{d(\Delta G°_R)}{dT} = -S°_R = -RA - \frac{RB\frac{d\varepsilon}{dT}}{\varepsilon^2} \tag{19}$$

$$\frac{d\ln K}{dT} = \frac{\Delta H°_R}{RT^2} \tag{20}$$

$$\Delta H°_R = RB\left(\frac{1}{\varepsilon} + \frac{T\frac{d\varepsilon}{dT}}{\varepsilon^2}\right) \tag{21}$$

The quantity $d\varepsilon/dT$ was calculated from the temperature dependence of the dielectric constant data and was found to be −0.356 per degree at 25°C. Using $a_{MgHCO_3^+} = 2.53 \times 10^{-8}$ cm, the results gave $\Delta G°_R = 6087.7 \pm 167$ J mol^{-1} (1455 ± 40 cal mol^{-1}); $\Delta H°_R = -4987.3$ J mol^{-1} (−1192 cal mol^{-1}); and $\Delta S°_R = -37.15$ − deg^{-1} mol^{-1} (−8.88 cal deg^{-1} mol^{-1}) at 25°C. For comparison, these quantities were calculated directly from the experimental results. A lnK versus $1/T$(K) plot of the experimental data was made. A straight line, drawn between the 25° and 40°C points, was considered to be representative of the slope at 25°C. Such an approach is preferable to the differentiation of at least squares fit of the data because of distortion from such a fit that would result from the error in the 10° point (fig. 2). This is representative of the errors that can arise in such an approach to the calculation of thermodynamic quantities. Using the slope given by the eq, $d\ln K/d(1/T) = -\Delta H°/R = 607.14$ deg, $\Delta H°_R$ and $\Delta S°_R$ were calculated and were found to be −5045.9 J mol^{-1} (−1206 cal mol^{-1}) and −37.36 J deg^{-1} mol^{-1} (−8.93 cal deg^{-1} mol^{-1}) respectively. The agreement between the two is reasonably good, but the results derived from the Fuoss equation are considered more accurate and therefore preferred.

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