

$T_r$	reduced temperature ( $=T/T_c$ )
$V$	volume, cm <sup>3</sup> /mol
$V_c$	critical volume, cm <sup>3</sup> /mol
$V_r$	reduced volume ( $=V/V_c$ )
$z$	compressibility factor ( $=PV/RT$ )
$\epsilon/k$	intermolecular force parameter in Lennard-Jones 12-6 model, K
$\eta$	viscosity, $\mu\text{Pa}\cdot\text{s}$
$\eta_1$	atmospheric viscosity, $\mu\text{Pa}\cdot\text{s}$
$\rho$	density, kg/m <sup>3</sup>
$\sigma$	intermolecular force parameter in Lennard-Jones 12-6 model, nm

Registry No. Chlorotrifluoromethane, 75-72-9.

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## Thermodynamics of Aqueous Magnesium and Calcium Bicarbonates and Mixtures with Chloride

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#### The potential for the cell

$\text{Pt}, \text{H}_2, \text{CO}_2 | \text{M}(\text{HCO}_3)_2, \text{MCl}_2, \text{CO}_2(\text{aq}) | \text{AgCl}, \text{Ag}$  with  $\text{M} = \text{Mg}$  and  $\text{Ca}$  was measured over a wide range of molalities at 298.15 K. The data were interpreted by the mixed-electrolyte equations of Pitzer and Kim to yield the ion-interaction parameters for  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ , and for  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ . The trace activity coefficients of  $\text{M}(\text{HCO}_3)_2$  in  $\text{MCl}_2$  and in  $\text{NaCl}$  are calculated.

#### Introduction

In many natural waters, including seawater, there are significant molalities of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{HCO}_3^-$ , and these ions enter into various reactions of importance. Hence, the thermodynamic properties of  $\text{Mg}(\text{HCO}_3)_2$  and  $\text{Ca}(\text{HCO}_3)_2$  in mixed electrolytes are a matter of considerable interest. The mixed-electrolyte equations of Pitzer and Kim (1) have been used with great success for complex natural brines, especially by Harvie and Weare (2) and Millero (3). Thus, it is desirable to determine the pertinent parameters for  $\text{Mg}(\text{HCO}_3)_2$  and  $\text{Ca}(\text{HCO}_3)_2$  in these equations which are based on a Debye-Hückel term and a virial expansion including second and third virial coefficients representing short-range interactions between pairs and triplets of ions.

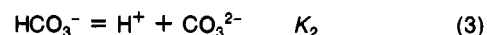
Values for the second virial parameters  $\beta^{(0)}$  and  $\beta^{(1)}$  for  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$  at 25 °C have been determined by Millero and Thurmond (4) from potentiometric titrations in solution with  $\text{MgCl}_2$  and  $\text{NaCl}$ . Harvie et al. (5) have given values for these parameters for both  $\text{Mg}(\text{HCO}_3)_2$  and  $\text{Ca}(\text{HCO}_3)_2$  on the basis of calculations of solid solubilities in brines. The present investigation was designed specifically to yield these parameters as accurately

as possible in simple mixtures with minimum uncertainty related to the other parameters required. The method is that used for the alkali bicarbonates  $\text{NaHCO}_3$  (6, 7) and  $\text{KHCO}_3$  (8, 9) which were successfully investigated by measurements of mixed solutions with chlorides in electrochemical cells with hydrogen and silver-silver chloride electrodes. We extend this method to magnesium and calcium bicarbonate with the cell

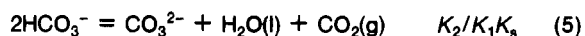
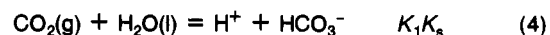


where M is either Mg or Ca.

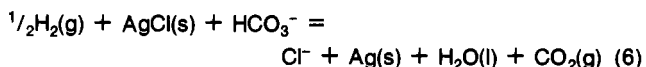
Various aqueous carbonate species are at equilibrium in the following reactions



with the indicated equilibrium constants. Two combinations of these reactions are particularly useful.



The reaction for the electrochemical cell is



with the potential given by

$$E = E_A^\circ - \frac{RT}{F} \left[ \ln \left( \frac{m_{\text{Cl}^-} a_{\text{H}_2\text{O}}^f a_{\text{CO}_2}}{m_{\text{HCO}_3^-}^f a_{\text{H}_2}^{1/2}} \right) + \ln \left( \frac{\gamma_{\text{Cl}^-}}{\gamma_{\text{HCO}_3^-}} \right) \right] \quad (7)$$

Table I. Experimental Cell Potentials at 25 °C and Solution Molalities  $m_1$  ( $\text{Mg}(\text{HCO}_3)_2$ ) and  $m_2$  ( $\text{MgCl}_2$ )

$m_1$	$m_2$	$E/V$	$m_1$	$m_2$	$E/V$	$m_1$	$m_2$	$E/V$
Run 1 (Mole Fraction of $\text{CO}_2 = 0.74402$ )			Run 4 (Mole Fraction of $\text{CO}_2 = 0.25628$ )			Run 7 (Mole Fraction of $\text{CO}_2 = 0.74402$ )		
0.003 1180	0.049 93	0.602 32	0.006 2409	0.099 06	0.641 42	0.043 962	0.034 270	0.680 11
0.003 1045	0.099 61	0.583 34	0.006 246 7	0.296 20	0.610 35	0.049 877	0.039 722	0.679 34
0.003 119 2	0.199 85	0.563 50	0.006 241 7	0.494 61	0.594 42	0.055 957	0.044 995	0.678 56
0.003 119 9	0.299 43	0.551 04	0.006 234 9	0.702 19	0.580 98	0.068 680	0.054 960	0.677 75
0.003 119 4	0.399 59	0.542 15	0.006 256 0	0.800 95	0.577 80	0.074 885	0.059 482	0.677 55
0.003 109 2	0.896 31	0.513 86	0.006 238 1	0.990 61	0.569 48	0.080 957	0.064 369	0.677 40
0.003 119 1	0.999 17	0.509 00	0.006 242 1	1.291 38	0.559 04	0.088 172	0.070 700	0.676 83
			0.006 243 6	1.497 92	0.551 53			
Run 2 (Mole Fraction of $\text{CO}_2 = 0.74420$ )			Run 5 (Mole Fraction of $\text{CO}_2 = 0.74402$ )			Run 8 (Mole Fraction of $\text{CO}_2 = 0.25628$ )		
0.006 134 0	0.049 92	0.620 64	0.014 198	0.098 56	0.623 37	0.043 810	0.034 918	0.718 86
0.006 153 8	0.100 23	0.601 42	0.013 887	0.299 02	0.590 74	0.063 296	0.049 625	0.718 08
0.006 330 9	0.205 54	0.581 19	0.013 887	0.499 84	0.572 59	0.069 18	0.055 062	0.717 89
0.006 377 4	0.311 05	0.568 98	0.013 576	0.700 26	0.561 74	0.075 76	0.059 992	0.717 64
0.006 148 4	0.400 42	0.560 46	0.013 265	0.803 03	0.556 66	0.080 86	0.064 546	0.717 00
0.006 174 9	0.708 68	0.541 69	0.013 105	0.998 50	0.548 24	0.881 74	0.070 640	0.716 21
0.006 118 6	0.886 88	0.532 62	0.012 802	1.299 51	0.536 75			
			0.012 335	1.511 06	0.526 90			
Run 3 (Mole Fraction of $\text{CO}_2 = 0.25628$ )			Run 6 (Mole Fraction of $\text{CO}_2 = 0.25628$ )			Run 9 (Mole Fraction of $\text{CO}_2 = 0.74402$ )		
0.006 239 9	0.049 82	0.660 62	0.014 196	0.100 11	0.663 24	0.006 079 9	0.242 40	0.575 59
0.006 116 9	0.097 23	0.642 30	0.013 884	0.300 97	0.630 32	0.005 893 2	0.472 19	0.554 08
0.006 276 9	0.198 81	0.623 08	0.013 884	0.499 84	0.613 76	0.005 718 2	0.695 59	0.540 14
0.006 199 4	0.298 18	0.610 76	0.013 572	0.502 50	0.601 81	0.005 731 6	0.901 81	0.531 32
0.006 291 9	0.397 40	0.601 04	0.013 267	0.698 64	0.601 81	0.005 511 2	1.102 59	0.522 57
0.006 078 7	0.672 94	0.583 46	0.013 109	0.801 04	0.596 52	0.005 363 4	1.292 88	0.515 54
0.006 260 5	0.897 99	0.573 09	0.012 816	0.989 95	0.587 99	0.005 270 9	1.468 16	0.509 90
0.006 227 1	0.987 92	0.569 76	0.012 340	1.296 71	0.575 05	0.005 106 4	1.635 81	0.504 22
			0.012 036	1.492 30	0.567 32			

The standard potential for this cell is related to other quantities as follows:

$$E_A^\circ = E^\circ(\text{Ag}, \text{AgCl}) - (RG/F) \ln(K_1 K_2) \quad (8)$$

where  $E^\circ(\text{Ag}, \text{AgCl})$  is the standard potential of the silver-silver chloride electrode and  $K_1 K_2$  is the equilibrium constant (7) for reaction 4.

Since all quantities in the first set of parentheses in eq 7 can be measured or calculated in good approximation, the cell potential yields the ratio of activity coefficients  $\gamma_{\text{Cl}^-}/\gamma_{\text{HCO}_3^-}$ . For this quantity eq 17 of Pitzer and Kim (7) yields

$$\ln(\gamma_{\text{Cl}^-}/\gamma_{\text{HCO}_3^-}) = 2m_{\text{M}}[B_{\text{M}, \text{Cl}} - B_{\text{M}, \text{HCO}_3} + 2m_{\text{M}}(C_{\text{M}, \text{Cl}} - C_{\text{M}, \text{HCO}_3})] + (m_{\text{HCO}_3} - m_{\text{Cl}})(2\beta_{\text{Cl}, \text{HCO}_3} + m_{\text{M}}\psi_{\text{M}, \text{Cl}, \text{HCO}_3}) \quad (9)$$

The coefficients  $B_{\text{MX}}$  have an ionic strength dependence given by

$$B_{\text{MX}} = \beta_{\text{MX}}^{(0)} + \beta_{\text{MX}}^{(1)}g(I) \quad (10)$$

$$g(I) = (2/\alpha^2 I)[1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] \quad (11)$$

with  $I$  the ionic strength and  $\alpha = 2 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  for 1-1 or 2-1 electrolytes. The parameters for  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ , and for  $\text{HCO}_3^-$ - $\text{Cl}^-$  mixing are known (7, 10).

Of the molalities in eq 9,  $m_{\text{Mg}} = m_1 + m_2$  and  $m_{\text{Cl}} = 2m_2$  but  $m_{\text{HCO}_3} = 2m_1 - 2m_{\text{CO}_2}$  where the last term is a correction for disproportionation following eq 5. All of the solutions measured have relatively low molality of bicarbonate and high carbon dioxide fugacity. Consequently, the correction for carbonate ion is small. As discussed below, corrections for carbonate proved to be insignificant. A wide range of chloride molality was considered which in turn gives a range of ionic strength.

## Experimental Section

Solutions were prepared by dissolving ACS reagent-grade calcium chloride (anhydrous) or magnesium chloride (hexahydrate) in previously prepared calcium or magnesium bicarbonate solutions. These stock solutions had been made by bubbling carbon dioxide gas through a suspension of calcium or magnesium carbonate (ACS reagent grade) for from 3 days to 3 weeks, depending upon the desired bicarbonate concentration. The bicarbonate solution was verified by titration with standardized HCl, using bromocresol green indicator. The HCl concentration had been gravimetrically determined as AgCl, with both the titrations and the gravimetric determinations agreeing to well within  $\pm 0.05\%$ .

Cells were filled with the respective solutions on the same day as the run and were bubbled with a primary grade mixture of  $\text{H}_2$  and  $\text{CO}_2$  gases for at least 1 h (and in some cases, 3 h) before the initial readings were taken. Measurements were actually made in sequence at 25, 5, 25, 45, and finally again at 25 °C, but on analysis of the data it was found that the results at 5 and 45 °C were somewhat erratic. Hence, only the measurements at 25 °C are reported. Normally each value is the average of the three measurements at that temperature. The difficulty at the other temperatures may have been insufficient time for equilibration. The bath temperature was regulated to 0.05 °C. Initial intercomparison of electrodes gave agreement within 0.1 mV; the emf readings were taken on digital voltmeters (Keithley Model 191).

Electrode preparation, application of vacuum corrections to the weighings, collection of emf data, and other experimental details followed the usual procedure established in previous research work (8, 9, 11).

## Results

The experimental results are reported in Tables I and II, where the mole fraction of  $\text{CO}_2$  in the  $\text{CO}_2$ - $\text{H}_2$  gas mixture was the same for all cells in a given run. These results were first treated by eq 9 and 10 without correction for carbonate for-

**Table II. Experimental Cell Potentials at 25 °C and Solution Molalities  $m_1$  (Ca(HCO<sub>3</sub>)<sub>2</sub>) and  $m_2$  (CaCl<sub>2</sub>)**

$m_1$	$m_2$	$E/V$
Run 1 (Mole Fraction of CO <sub>2</sub> = 0.74402)		
0.000 620 24	0.100 65	0.543 68
0.000 620 24	0.150 62	0.532 56
0.000 624 82	0.199 21	0.525 23
0.000 620 99	0.300 98	0.513 90
0.000 616 02	0.404 24	0.503 38
0.000 619 37	0.702 78	0.488 38
0.000 616 73	0.801 90	0.486 73
0.000 641 20	0.959 87	0.481 66
Run 2 (Mole Fraction of CO <sub>2</sub> = 0.74402)		
0.001 243 30	0.049 788	0.579 31
0.001 239 80	0.069 403	0.569 70
0.001 247 8	0.099 893	0.560 29
0.001 241 40	0.148 66	0.548 96
0.001 249 3	0.200 33	0.540 63
0.001 242 90	0.249 24	0.534 38
0.001 241 0	0.298 58	0.528 08
0.001 244 4	0.397 64	0.521 22

**Table III. Ion-Interaction Parameters at 298.15 K**

	$\beta^{(0)}/$ (kg·mol <sup>-1</sup> )	$\beta^{(1)}/$ (kg·mol <sup>-1</sup> )	$C^\phi /$ (kg <sup>2</sup> ·mol <sup>-2</sup> )
Mg(HCO <sub>3</sub> ) <sub>2</sub>	0.03 <sub>3</sub>	0.8 <sub>5</sub>	
Ca(HCO <sub>3</sub> ) <sub>2</sub>	0.2 <sub>8</sub>	0.3	
MgCl <sub>2</sub> <sup>a</sup>	0.352 <sub>4</sub>	1.681 <sub>5</sub>	0.0051 <sub>9</sub>
CaCl <sub>2</sub> <sup>a</sup>	0.315 <sub>9</sub>	1.614	-0.0003 <sub>4</sub>

$\theta_{\text{Cl,HCO}_3} = 0.0359 \text{ kg}\cdot\text{mol}^{-1} \text{ b}$

<sup>a</sup> From ref 10. <sup>b</sup> From ref 7.

mation. The vapor pressure of water was recognized in calculating the fugacity of CO<sub>2</sub> and H<sub>2</sub>. The activity of water was given with sufficient accuracy by the simple equation

$$-55.5 \ln a_{\text{H}_2\text{O}} = 3(m_1 + m_2) + m_3 + 2A_\phi I^{3/2} / (1 + bI^{1/2}) + 2m_{\text{Mg}}m_{\text{Cl}}B^\phi_{\text{Mg,Cl}} \quad (12)$$

$$B^\phi = \beta^{(0)} + \beta^{(1)} \exp(-\alpha I^{1/2}) \quad (13)$$

where  $A_\phi$  is the Debye-Hückel parameter (0.391 kg<sup>1/2</sup>·mol<sup>-1/2</sup>),  $b = 1.2 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$ , and the molality of pure water (55.5 mol·kg<sup>-1</sup>) is shown. The molality of dissolved CO<sub>2</sub>,  $m_3$ , is taken as the solubility in pure water at the partial pressure of the experiment. The complete equation for the activity of water contains many other terms which are negligible for the solutions in Tables I and II.

The virial parameters for MgCl<sub>2</sub> and CaCl<sub>2</sub> and the mixing parameter  $\theta_{\text{Cl,HCO}_3}$  are well-known from earlier investigations (7, 11) and are shown in Table III together with the new results for the second virial parameters for Mg(HCO<sub>3</sub>)<sub>2</sub> and Ca(HCO<sub>3</sub>)<sub>2</sub>. It was found that there was no need for the third virial coefficient for either the magnesium or calcium bicarbonate or for the triple ion mixing parameters  $\psi_{\text{M,Cl,HCO}_3}$ . The parameters for Mg(HCO<sub>3</sub>)<sub>2</sub> are  $\beta^{(0)} = 0.03_3 \pm 0.01$  and  $\beta^{(1)} = 0.8_5 \pm 0.1$ , and those for Ca(HCO<sub>3</sub>)<sub>2</sub> are  $\beta^{(0)} = 0.28 \pm 0.04$  and  $\beta^{(1)} = 0.3 \pm 0.2$ . In each case the two parameters are strongly coupled. Thus, one parameter can be changed by several times the indicated error provided the other is appropriately changed in the opposite direction without serious degradation in the fit to observed cell potentials. The standard deviations of fit are 0.9 mV for Mg(HCO<sub>3</sub>)<sub>2</sub> and 1.1 mV for Ca(HCO<sub>3</sub>)<sub>2</sub>. These are somewhat larger than were obtained for the sodium and potassium bicarbonate systems (6-9). However, the need to keep the bicarbonate molality very small increased the uncertainties for these systems.

### Effect of Carbonate Formation

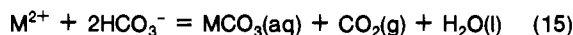
The disproportionation of HCO<sub>3</sub><sup>-</sup> with formation of CO<sub>3</sub><sup>2-</sup> was mentioned above and is now considered further. For most of

the experiments listed in Tables I and II the effect is clearly negligible. It will be largest for run 8 on Table I. There it is found that correction for formation of CO<sub>3</sub><sup>2-</sup> will increase slightly the deviation between calculated and experimental cell potentials. Thus, we conclude that the effect may be neglected for the interpretation of the present measurements.

Millero and Thurmond (4) gave alternate treatments for aqueous MgCO<sub>3</sub>. One was based on an ion pairing equilibrium as follows:



$K_A = 1000$  and  $\log \gamma(\text{MgCO}_3) = 0.056I$  at 298.15 K. Harvie et al. (5) likewise assume ion pairing with  $\gamma = 1$  and  $K_A = 850$  for MgCO<sub>3</sub> and 1400 for CaCO<sub>3</sub> at 298.15 K. Then



$$K = K_A K_2 / K_1 K_3 \quad (16)$$

On this basis one can readily calculate the molality of MgCO<sub>3</sub>(aq) or CaCO<sub>3</sub>(aq). The correction to the bicarbonate molality is found to be small for all of our experiments. This is consistent with our observations.

The alternate treatment of Millero and Thurmond follows a pattern successful for 2-2 metal sulfates in which one assumes no explicit ion pairs but rather a special, negative term in the second virial coefficient. In all there are four parameters (some very large and negative) in their expression for the activity coefficient. The ion pairing is much stronger for Mg<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup> than for the sulfates. Use of their four-term virial coefficient expression for our solutions yields extremely small activity coefficients for MgCO<sub>3</sub>, significant molalities of CO<sub>3</sub><sup>2-</sup> and discrepancies between calculated and experimental cell potentials. The introduction of the unlike-ion mixing parameter  $\psi_{\text{Na,Mg,CO}_3}$  would probably allow both the present measurements and those of Millero and Thurmond to be fitted quite accurately. Indeed, it would probably suffice to replace the coefficient  $C^\phi_{\text{Mg,CO}_3}$  by  $\psi_{\text{Na,Mg,CO}_3}$  leaving a four-parameter expression. However, this complexity and possible ambiguity is undesirable when the simple ion pairing equilibrium constant suffices.

This result suggests that the ion-pairing method is preferable for 2-2 electrolytes when  $K_A$  approaches 1000. For the sulfates where  $K_A$  is in the range 200-300, however, the virial expansion including the special term has found to be very satisfactory and better than the ion-pairing method in many applications (2, 5).

### Discussion

The principal use of these results will be in calculations for mixed electrolytes containing many other ions. For seawater and other natural waters as well as for many other systems the dominant negative ion will be chloride. Thus, there will be minimum uncertainty in using parameters determined from solutions such as were used here which were dominated by chloride. The interactions of bicarbonate with sodium and potassium ions are now well-known. Thus, all of the major terms are well established for most practically important systems. It is impractical to tabulate properties for a wide variety of examples, but it is of interest to give the trace activity coefficient of Mg(HCO<sub>3</sub>)<sub>2</sub> and Ca(HCO<sub>3</sub>)<sub>2</sub> in MgCl<sub>2</sub> and CaCl<sub>2</sub>, respectively, and in NaCl. The equation for the MgCl<sub>2</sub> solutions of molality  $m_2$  is

$$\ln \gamma_{\pm}^{\text{tr}} = 2f^\gamma + (4/3)m_2(B_{\text{M,HCO}_3} + 2\theta_{\text{Cl,HCO}_3} + B^\phi_{\text{M,Cl}} + m_2 C^\phi_{\text{M,Cl}}/2^{1/2}) \quad (17)$$

while for the NaCl solutions of molality  $m_2$  it is

$$\ln \gamma_{\pm}^{\text{tr}} = 2f^\gamma + (2/3)m_2(B_{\text{M,Cl}} + 2B_{\text{Na,HCO}_3} + 2\theta_{\text{Cl,HCO}_3}) + m_2^2(2B'_{\text{Na,Cl}} + 2C^\phi_{\text{Na,Cl}}/3 + C^\phi_{\text{M,Cl}}/3(2^{1/2})) \quad (18)$$

**Table IV. Trace Activity Coefficients of  $\text{Mg}(\text{HCO}_3)_2$  and  $\text{Ca}(\text{HCO}_3)_2$  in  $\text{MgCl}_2$  and  $\text{CaCl}_2$ , Respectively, and in  $\text{NaCl}$  at 298.15 K**

$m_{\text{MCl}_2}$	$\gamma_{\pm}^{\text{tr}}$	
	$\text{Mg}(\text{HCO}_3)_2$	$\text{Ca}(\text{HCO}_3)_2$
0.001	0.8874	0.8870
0.01	0.7209	0.7182
0.02	0.6520	0.6480
0.05	0.5556	0.5499
0.10	0.4846	0.4790
0.20	0.4203	0.4187
0.50	0.3567	0.3747
1.00	0.3470	0.4102

$m_{\text{NaCl}}$	$\gamma_{\pm}^{\text{tr}}$	
	$\text{Mg}(\text{HCO}_3)_2$	$\text{Ca}(\text{HCO}_3)_2$
0.001	0.9315	0.9315
0.01	0.8151	0.8146
0.02	0.7604	0.7595
0.05	0.6764	0.6744
0.10	0.6088	0.6055
0.20	0.5441	0.5387
0.50	0.4751	0.4648
1.00	0.4488	0.4312

Certain quantities in these equations were defined above in eq 10 and 13. In addition

$$f^{\gamma} = -A_{\phi} [I^{1/2} / (1 + bI^{1/2}) + (2/b) \ln(1 + bI^{1/2})] \quad (19)$$

$$B^{\gamma} = (2\beta^{(1)} / \alpha^2 I^2) [-1 + (1 + \alpha I^{1/2} + \alpha^2 I/2) \exp(-\alpha I^{1/2})] \quad (20)$$

where  $b$ ,  $A_{\phi}$ , and  $\alpha$  were given above. Several terms were omitted from eq 17 and 18 because the coefficients are zero or so small as to have negligible effect. The values in Table IV indicate the activity coefficients of the  $\text{M}(\text{HCO}_3)_2$  in solutions dominated by  $\text{MCl}_2$  or  $\text{NaCl}$  provided the carbon dioxide pressure is sufficient to suppress formation of carbonate.

Our results for the parameters are compared with those from several other investigations in Table V. At substantial ionic strength the effect on experimental properties of  $\beta^{(1)}$  is much less than that of  $\beta^{(0)}$ . Thus, our parameters will yield essentially the same results as those of Millero and Thurmond (4) for the range of their measurements at ionic strength above 0.5  $\text{mol}\cdot\text{kg}^{-1}$ .

The values of Harvie et al. (5) and of Weare (12) arise from calculations of solid solubility in various mixed electrolytes and depend on a variety of parameters for the other ions present. Thus, it is difficult to judge whether there are serious disagreements with respect to experimental quantities. Since these various parameters are somewhat coupled in their evaluation, one should not change one or two parameters without investigating their effect on the known experimental properties. One does note that Weare's latest value for  $\beta^{(0)}$  for  $\text{Mg}(\text{HCO}_3)_2$  is closer to our and Millero's values than the earlier value from Weare's laboratory (5).

**Table V. Comparison with Other Investigations**

	$\beta^{(0)}$	$\beta^{(1)}$
	$\text{Mg}(\text{HCO}_3)_2$	
this research	0.03 <sub>3</sub>	0.8 <sub>5</sub>
ref 4	0.01 <sub>9</sub>	0.5 <sub>8</sub>
ref 5	0.32 <sub>9</sub>	0.6 <sub>1</sub>
ref 12	0.18	0.4 <sub>9</sub>
	$\text{Ca}(\text{HCO}_3)_2$	
this research	0.28	0.3
ref 5	0.4	3.0

In comparison with other simple 2-1 electrolytes such as the chlorides, the bicarbonate parameters are smaller but still positive. This can be interpreted as a smaller effective repulsive radius for  $\text{M}-\text{HCO}_3$  as compared to  $\text{M}-\text{Cl}$ . Alternatively one may assume a weak short-range attraction for the  $\text{M}-\text{HCO}_3$  interaction. The latter view is consistent with the weak  $\text{MgHCO}_3^+$  and  $\text{CaHCO}_3^+$  ion pairing tendencies assumed by some investigators who assume standard activity coefficient expressions. But, if there were significant ion pairing, the second virial coefficients would be negative and that is not the case for these examples. Thus, there is no need to complicate treatments of mixed electrolytes by assuming these ion-pair species; the virial expansion is adequate and more appropriate for the bicarbonates. The contrary situation for the carbonates is discussed above.

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**Registry No.**  $\text{MgCl}_2$ , 7786-30-3;  $\text{Mg}(\text{HCO}_3)_2$ , 2090-64-4;  $\text{Ca}(\text{HCO}_3)_2$ , 3983-19-5;  $\text{CaCl}_2$ , 10043-52-4;  $\text{NaCl}$ , 7647-14-5.

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