T_r	reduced temperature ($=T/T_c$)
V	volume, cm^3/mol
V_c	critical volume, cm^3/mol
V_r	reduced volume ($=V/V_c$)
z	compressibility factor ($=PV/RT$)
ϵ/k	intermolecular force parameter in Lennard-Jones 12-6 model, K
η	viscosity, μPa·s
η_1	atmospheric viscosity, μPa·s
ρ	density, kg/m^3
σ	intermolecular force parameter in Lennard-Jones 12-6 model, nm

Registry No. Chlorotrifluoromethane, 75-72-9.

Literature Cited

(1) Takahashi, M.; Takahashi, S.; Iwasaki, H. *Kagaku Kogaku Ronbunshu* **1984**, *10*, 7.
(2) Takahashi, M.; Takahashi, S.; Iwasaki, H. *Kagaku Kogaku Ronbunshu* **1983**, *9*, 482.
(3) Tsui, C. Y. M.S. Thesis, Purdue University, West Lafayette, IN, 1959.
(4) Wellman, E. J. M.S. Thesis, Purdue University, West Lafayette, IN, 1953.
(5) Reed, J. F.; Rabinovitch, B. S. *Chem. Eng. Data Ser.* **1957**, *2*, 75.
(6) Kamien, C. Z.; Witzell, O. W. *ASHRAE J.* **1959**, *65*, 663.
(7) Wilbers, O. J. M.S. Thesis, Purdue University, West Lafayette, IN, 1961.
(8) Latto, B.; Hesoun, P.; Asrani, S. C. *Proc. Symp. Thermophys. Prop.* **1970**, 177.
(9) Michels, A.; Wassenaar, T.; Wolkers, G. J.; Prins, Chr.; Klundert, L. v. d. *J. Chem. Eng. Data* **1966**, *11*, 449.
(10) Iwasaki, H.; Takahashi, H. *Bull. Chem. Res. Inst. Non-Aqueous Solutions, Tohoku Univ.* **1956**, *6*, 61.
(11) Iwasaki, H.; Takahashi, M. *Rev. Phys. Chem. Jpn.* **1968**, *38*, 18.
(12) Iwasaki, H.; Kestin, J. *Physica* **1963**, *29*, 1345.
(13) Kestin, J.; Whitelaw, J. H. *Physica* **1963**, *29*, 335.
(14) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. "Molecular Theory of Gases and Liquids"; Wiley: New York, 1954; p 528.
(15) "Thermophysical Properties of Refrigerants"; American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Inc.: New York, 1976; p 13.
(16) Albright, L. F.; Martin, J. J. *Ind. Eng. Chem.* **1952**, *44*, 188.
(17) Kondo, K.; Watanabe, K.; Tanishita, I. *Trans. Jpn. Soc. Mech. Eng. Ser. B* **1973**, *39*, 3124; and private communication.
(18) Morsy, T. E. *J. Chem. Eng. Data* **1970**, *15*, 256.

Received for review February 28, 1984. Accepted July 12, 1984.

Thermodynamics of Aqueous Magnesium and Calcium Bicarbonates and Mixtures with Chloride

Kenneth S. Pitzer,* Joyce Olsen, and John M. Simonson

Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Rabindra N. Roy, James J. Gibbons, and LeAnn Rowe

Department of Chemistry, Drury College, Springfield, Missouri 65802

The potential for the cell $Pt,H_2,CO_2|M(HCO_3)_2,MCl_2,CO_2(aq)|AgCl,Ag$ with M = Mg and 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 Mg^{2+}, HCO_3^-, and for Ca^{2+}, HCO_3^-. The trace activity coefficients of $M(HCO_3)_2$ in MCl_2 and in NaCl are calculated.

Introduction

In many natural waters, including seawater, there are significant molalities of Mg^{2+}, Ca^{2+}, and HCO_3^-, and these ions enter into various reactions of importance. Hence, the thermodynamic properties of $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ 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 $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ 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 Mg^{2+}, HCO_3^- at 25 °C have been determined by Millero and Thurmond (*4*) from potentiometric titrations in solution with $MgCl_2$ and NaCl. Harvie et al. (*5*) have given values for these parameters for both $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ 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 $NaHCO_3$ (*6*, *7*) and $KHCO_3$ (*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

$$Pt,H_2,CO_2|M(HCO_3)_2(m_1),MCl_2(m_2),CO_2(m_3)|AgCl,Ag \quad \text{(A)}$$

where M is either Mg or Ca.

Various aqueous carbonate species are at equilibrium in the following reactions

$$CO_2(g) = CO_2(aq) \qquad K_s \tag{1}$$

$$CO_2(aq) + H_2O(l) = H^+ + HCO_3^- \qquad K_1 \tag{2}$$

$$HCO_3^- = H^+ + CO_3^{2-} \qquad K_2 \tag{3}$$

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

$$CO_2(g) + H_2O(l) = H^+ + HCO_3^- \qquad K_1K_s \tag{4}$$

$$2HCO_3^- = CO_3^{2-} + H_2O(l) + CO_2(g) \qquad K_2/K_1K_s \tag{5}$$

The reaction for the electrochemical cell is

$$^1/_2H_2(g) + AgCl(s) + HCO_3^- = Cl^- + Ag(s) + H_2O(l) + CO_2(g) \tag{6}$$

with the potential given by

$$E = E_A{}^\circ - \frac{RT}{F}\left[\ln\left(\frac{m_{Cl}a_{H_2O}f_{CO_2}}{m_{HCO_3}f_{H_2}{}^{1/2}}\right) + \ln\left(\frac{\gamma_{Cl^-}}{\gamma_{HCO_3^-}}\right)\right] \tag{7}$$

Table I. Experimental Cell Potentials at 25 °C and Solution Molalities m_1 ($Mg(HCO_3)_2$) and m_2 ($MgCl_2$)

m_1	m_2	E/V
Run 1 (Mole Fraction of CO_2 = 0.74402)		
0.0031180	0.04993	0.60232
0.0031045	0.09961	0.58334
0.0031192	0.19985	0.56350
0.0031199	0.29943	0.55104
0.0031194	0.39959	0.54215
0.0031092	0.89631	0.51386
0.0031191	0.99917	0.50900
Run 2 (Mole Fraction of CO_2 = 0.74420)		
0.0061340	0.04992	0.62064
0.0061538	0.10023	0.60142
0.0063309	0.20554	0.58119
0.0063774	0.31105	0.56898
0.0061484	0.40042	0.56046
0.0061749	0.70868	0.54169
0.0061186	0.88688	0.53262
Run 3 (Mole Fraction of CO_2 = 0.25628)		
0.0062399	0.04982	0.66062
0.0061169	0.09723	0.64230
0.0062769	0.19881	0.62308
0.0061994	0.29818	0.61076
0.0062919	0.39740	0.60104
0.0060787	0.67294	0.58346
0.0062605	0.89799	0.57309
0.0062271	0.98792	0.56976
Run 4 (Mole Fraction of CO_2 = 0.25628)		
0.0062409	0.09906	0.64142
0.0062467	0.29620	0.61035
0.0062417	0.49461	0.59442
0.0062349	0.70219	0.58098
0.0062560	0.80095	0.57780
0.0062381	0.99061	0.56948
0.0062421	1.29138	0.55904
0.0062436	1.49792	0.55153
Run 5 (Mole Fraction of CO_2 = 0.74402)		
0.014198	0.09856	0.62337
0.013887	0.29902	0.59074
0.013576	0.49984	0.57259
0.013265	0.70026	0.56174
0.013105	0.80303	0.55666
0.012802	0.99850	0.54824
0.012335	1.29951	0.53675
0.012007	1.51106	0.52690
Run 6 (Mole Fraction of CO_2 = 0.25628)		
0.014196	0.10011	0.66324
0.013884	0.30097	0.63032
0.013572	0.50250	0.61376
0.013267	0.69864	0.60181
0.013109	0.80104	0.59652
0.012816	0.98995	0.58799
0.012340	1.29671	0.57505
0.012036	1.49230	0.56732
Run 7 (Mole Fraction of CO_2 = 0.74402)		
0.043962	0.034270	0.68011
0.049877	0.039722	0.67934
0.055957	0.044995	0.67856
0.068680	0.054960	0.67775
0.074885	0.059482	0.67755
0.080957	0.064369	0.67740
0.088172	0.070700	0.67683
Run 8 (Mole Fraction of CO_2 = 0.25628)		
0.043810	0.034918	0.71886
0.63296	0.049625	0.71808
0.06918	0.055062	0.71789
0.07576	0.059992	0.71764
0.08086	0.064546	0.71700
0.88174	0.070640	0.71621
Run 9 (Mole Fraction of CO_2 = 0.74402)		
0.0060799	0.24240	0.57559
0.0058932	0.47219	0.55408
0.0057182	0.69559	0.54014
0.0057316	0.90181	0.53132
0.0055112	1.10259	0.52257
0.0053634	1.29288	0.51554
0.0052709	1.46816	0.50990
0.0051064	1.63581	0.50422

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

$$E_A^\circ = E^\circ(\mathrm{Ag,AgCl}) - (RG/F)\ln(K_1K_s) \qquad (8)$$

where E°(Ag,AgCl) is the standard potential of the silver–silver chloride electrode and K_1K_s 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 $\gamma_{Cl^-}/\gamma_{HCO_3^-}$. For this quantity eq 17 of Pitzer and Kim (*1*) yields

$$\ln(\gamma_{Cl^-}/\gamma_{HCO_3^-}) = 2m_M[B_{M,Cl} - B_{M,HCO_3} + 2m_M(C_{M,Cl} - C_{M,HCO_3})] + (m_{HCO_3} - m_{Cl})(2\theta_{Cl,HCO_3} + m_M\psi_{M,Cl,HCO_3}) \qquad (9)$$

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

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

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

with I the ionic strength and $\alpha = 2$ kg$^{1/2}\cdot$mol$^{-1/2}$ for 1–1 or 2–1 electrolytes. The parameters for $MgCl_2$, $CaCl_2$, and for HCO_3^-–Cl^- mixing are known (*7*, *10*).

Of the molalities in eq 9, $m_{Mg} = m_1 + m_2$ and $m_{Cl} = 2m_2$ but $m_{HCO_3} = 2m_1 - 2m_{CO_3}$ 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 ±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 H_2 and 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. Intitial 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 CO_2 in the CO_2–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 ($Ca(HCO_3)_2$) and m_2 ($CaCl_2$)

m_1	m_2	E/V
Run 1 (Mole Fraction of CO_2 = 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_2 = 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^{-1})	$\beta^{(1)}$/ (kg·mol^{-1})	C^{ϕ}/ (kg^2·mol^{-2})
$Mg(HCO_3)_2$	0.03_3	0.8_5	
$Ca(HCO_3)_2$	0.2_8	0.3	
$MgCl_2$[a]	0.352_4	1.681_5	0.0051_9
$CaCl_2$[a]	0.315_9	1.614	-0.0003_4
θ_{Cl,HCO_3} = 0.0359 kg·mol^{-1} [b]			

[a] From ref *10*. [b] From ref *7*.

mation. The vapor pressure of water was recognized in calculating the fugacity of CO_2 and H_2. The activity of water was given with sufficient accuracy by the simple equation

$$-55.5 \ln a_{H_2O} = 3(m_1 + m_2) + m_3 + 2A_{\phi}I^{3/2}/(1 + bI^{1/2}) + 2m_{Mg}m_{Cl}B^{\phi}_{Mg,Cl} \qquad (12)$$

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

where A_{ϕ} is the Debye–Hückel parameter (0.391 kg$^{1/2}$·mol$^{-1/2}$), b = 1.2 kg$^{1/2}$·mol$^{-1/2}$, and the molality of pure water (55.5 mol·kg^{-1}) is shown. The molality of dissolved CO_2, 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 $MgCl_2$ and $CaCl_2$ and the mixing parameter θ_{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 $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$. 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 ψ_{M,Cl,HCO_3}. The parameters for $Mg(HCO_3)_2$ are $\beta^{(0)} = 0.03_3 \pm 0.01$ and $\beta^{(1)} = 0.8_5 \pm 0.1$, and those for $Ca(HCO_3)_2$ 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 $Mg(HCO_3)_2$ and 1.1 mV for $Ca(HCO_3)_2$. 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_3^- with formation of CO_3^{2-} 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_3^{2-} 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 $MgCO_3$. One was based on an ion pairing equilibrium as follows:

$$Mg^{2+} + CO_3^{2-} = MgCO_3(aq) \qquad (14)$$

K_A = 1000 and log $\gamma(MgCO_3) = 0.056I$ at 298.15 K. Harvie et al. (*5*) likewise assume ion pairing with $\gamma = 1$ and K_A = 850 for $MgCO_3$ and 1400 for $CaCO_3$ at 298.15 K. Then

$$M^{2+} + 2HCO_3^- = MCO_3(aq) + CO_2(g) + H_2O(l) \qquad (15)$$

$$K = K_AK_2/K_1K_s \qquad (16)$$

On this basis one can readily calculate the molality of $MgCO_3$(aq) or $CaCO_3$(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^{2+}, CO_3^{2-} than for the sulfates. Use of their four-term virial coefficient expression for our solutions yields extremely small activity coefficients for $MgCO_3$, significant molalities of CO_3^{2-} and discrepancies between calculated and experimental cell potentials. The introduction of the unlike-ion mixing parameter ψ_{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^{ϕ}_{Mg,CO_3} by ψ_{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 $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ in $MgCl_2$ and $CaCl_2$, respectively, and in NaCl. The equation for the MCl_2 solutions of molality m_2 is

$$\ln \gamma_{\pm}^{tr} = 2f^{\gamma} + (4/3)m_2(B_{M,HCO_3} + 2\theta_{Cl,HCO_3} + B^{\phi}_{M,Cl} + m_2C^{\phi}_{M,Cl}/2^{1/2}) \qquad (17)$$

while for the NaCl solutions of molality m_2 it is

$$\ln \gamma_{\pm}^{tr} = 2f^{\gamma} + (2/3)m_2(B_{M,Cl} + 2B_{Na,HCO_3} + 2\theta_{Cl,HCO_3}) + m_2^2(2B'_{Na,Cl} + 2C^{\phi}_{Na,Cl}/3 + C^{\phi}_{M,Cl}/3(2^{1/2})) \qquad (18)$$

Table IV. Trace Activity Coefficients of $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ in $MgCl_2$ and $CaCl_2$, Respectively, and in NaCl at 298.15 K

	$\gamma_{\pm}^{tr}$	
m_{MCl_2}	$Mg(HCO_3)_2$	$Ca(HCO_3)_2$
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

	$\gamma_{\pm}^{tr}$	
m_{NaCl}	$Mg(HCO_3)_2$	$Ca(HCO_3)_2$
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

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

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

where b, A_{ϕ}, and α 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 $M(HCO_3)_2$ in solutions dominated by MCl_2 or 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 mol·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 $Mg(HCO_3)_2$ is closer to our and Millero's values than the earlier value from Weare's laboratory (*5*).

Table V. Comparison with Other Investigations

	$\beta^{(0)}$	$\beta^{(1)}$
	$Mg(HCO_3)_2$	
this research	0.03_3	0.8_5
ref *4*	0.01_9	0.5_8
ref *5*	0.32_9	0.6_1
ref *12*	0.18	0.4_9
	$Ca(HCO_3)_2$	
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 M–HCO_3 as compared to M–Cl. Alternatively one may assume a weak short-range attraction for the M–HCO_3 interaction. The latter view is consistent with the weak $MgHCO_3^+$ and $CaHCO_3^+$ 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.

Acknowledgment

We thank Gigi Baker, Randy Pogue, and Tim McGinnis for assistance with the experiments.

Registry No. $MgCl_2$, 7786-30-3; $Mg(HCO_3)_2$, 2090-64-4; $Ca(HCO_3)_2$, 3983-19-5; $CaCl_2$, 10043-52-4; NaCl, 7647-14-5.

Literature Cited

(1) Pitzer, K. S.; Kim, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 9701.
(2) Harvie, C. E.; Weare, J. H. *Geochim. Cosmochim. Acta* **1980**, *44*, 981.
(3) Millero, F. J. *Geochim. Cosmochim. Acta* **1983**, *47*, 2121.
(4) Millero, F. J.; Thurmond, V. *J. Solution Chem.* **1983**, *12*, 401.
(5) Harvie, C. E.; Moller, N.; Weare, J. H. *Geochim. Cosmochim. Acta*, in press.
(6) Pitzer, K. S.; Peiper, J. C. *J. Phys. Chem.* **1980**, *84*, 2396.
(7) Peiper, J. C.; Pitzer, K. S. *J. Chem. Thermodn.* **1982**, *14*, 613.
(8) Roy, R. N.; Gibbons, J. J.; Wood, M. D.; Williams, R. W.; Peiper, J. C.; Pitzer, K. S. *J. Chem. Thermodn.* **1983**, *15*, 37.
(9) Roy, R. N.; Gibbons, J. J.; Williams, R.; Godwin, L.; Baker, G.; Simonson, J. M.; Pitzer, K. S. *J. Chem. Thermodn.*, in press.
(10) Pitzer, K. S.; Mayorga, G. *J. Phys. Chem.* **1973**, *77*, 2300.
(11) Roy, R. N.; Gibbons, J. J.; Trower, J. K.; Lee, G. K.; Hartley, J. J.; Mack, J. G. *J. Chem. Thermodn.* **1982**, *14*, 473.
(12) Weare, J. H., private communication.

Received for review March 26, 1984. Accepted July 16, 1984. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Engineering, Mathematics, and Geosciences of the U.S. Department of Energy under contract No. DE-AC03-76SF00098. Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society, for partial support of this work (through ACS-PRF grant no. 13988-B5-C).