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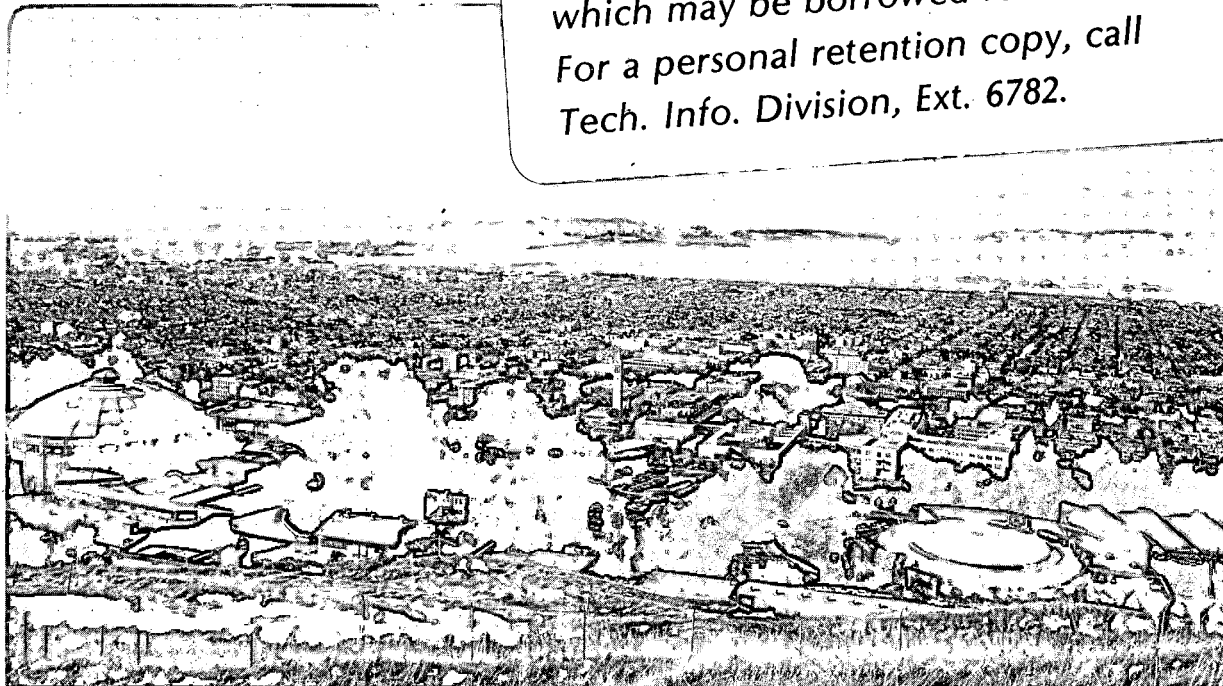
THE THERMODYNAMICS OF AQUEOUS CARBONATE SOLUTIONS  
INCLUDING MIXTURES OF POTASSIUM CARBONATE,  
BICARBONATE, AND CHLORIDE

R.N. Roy, J.J. Gibbons, R. Williams, L. Godwin,  
G. Baker, J.M. Simonson and K.S. Pitzer

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The Thermodynamics of Aqueous Carbonate Solutions Including Mixtures of Potassium Carbonate, Bicarbonate, and Chloride

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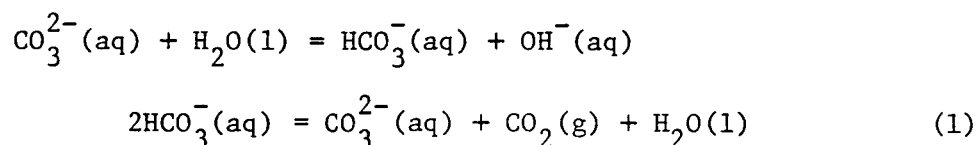
Abstract

Electromotive force data for the cell without liquid junction  $\text{Pt, H}_2/\text{K}_2\text{CO}_3(m_1), \text{KHCO}_3(m_2), \text{KCl}(m_3)/\text{AgCl, Ag}$  have been obtained over a broad range of solute concentration at 278.15, 298.15, 310.15 and 318.15 K. These data have been used in conjunction with previously available electrochemical cell data and isopiestic data to calculate activity and osmotic coefficients of aqueous  $\text{K}_2\text{CO}_3$  and  $\text{KHCO}_3$  using the ion-interaction equations of Pitzer for mixed electrolyte systems.

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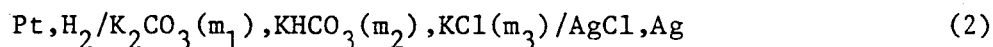
## 1. Introduction

Recent studies<sup>(1-3)</sup> have demonstrated the applicability of the ion-interaction theory of Pitzer<sup>(4)</sup> and its extension to systems of mixed strong electrolytes by Pitzer and Kim,<sup>(5)</sup> to systems including mixtures of carbonate, bicarbonate and chloride ions. Explicit consideration of the hydrolysis and disproportionation equilibria:

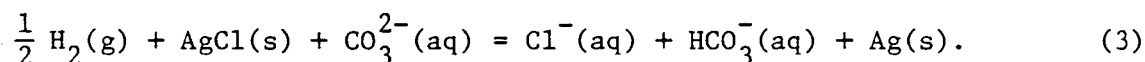


necessitates the use of mixed-electrolyte theory for even stoichiometrically single-solute systems which contain carbonate or bicarbonate.

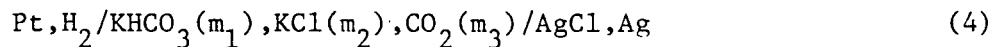
The experimental data presented here were obtained using the electrochemical cell without liquid junction



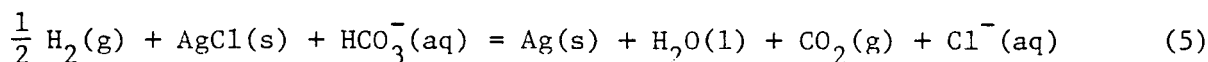
with reaction



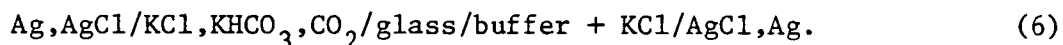
Additional data considered in the determination of thermodynamic properties of this mixed electrolyte system include the measurements of Roy et al.<sup>(3)</sup> for the cell



with reaction



and of MacInnes and Belcher<sup>(6)</sup> for the related cell with glass electrode



The data of MacInnes and Belcher<sup>(6,7)</sup> for cell (2) at 25 and 38°C were checked for consistency against the data of the present study and against the precise modern value of  $\text{pK}_2$  as calculated by Peiper and Pitzer.<sup>(2)</sup> In both of these data sets, although the internal precision of the data is quite good, significant differences from the values of Peiper and Pitzer were noted in the extrapolated values of  $\text{pK}_2$ . In addition, systematic deviations on the order of 1 mV between the data of MacInnes and Belcher and those of the present study were noted. In light of these inconsistencies, the MacInnes and Belcher data were not included in the combined data set used to calculate the various thermodynamic properties.

Sarbar, Covington, Nuttall and Goldberg<sup>(8)</sup> have determined osmotic and activity coefficients for  $\text{K}_2\text{CO}_3$  solutions at 298.15 K over a broad range of molalities by the isopiestic method using sodium chloride and calcium chloride reference solutions. As their treatment of these data does not take the hydrolysis and disproportionation equilibria (1) into account, we do not use their calculated osmotic and activity coefficients, but include their experimental values in our combined data set.

## 2. Experimental Technique

### Chemicals

Potassium chloride, potassium hydrogen carbonate, and potassium carbonate were all A.C.S. certified-grade, obtained from Fisher Scientific. These salts were used as purchased after drying the KCl and without further purification of  $\text{KHCO}_3$  and  $\text{K}_2\text{CO}_3$ . Each solution was prepared by

weighing solid KCl,  $\text{KHCO}_3$ ,  $\text{K}_2\text{CO}_3$ , and carbon dioxide-free doubly-distilled water. Vacuum corrections were applied to all the weighings. The molalities of KCl,  $\text{KHCO}_3$ , and  $\text{K}_2\text{CO}_3$  were calculated from the masses of the salts and water added.

#### Apparatus and Method

Dissolved air was removed from the solutions by purging hydrogen gas (purified through two De-Oxo catalysts) through the cells for about 30 min before they were filled. The temperature of the bath in which the cells were immersed was controlled to better than  $\pm 0.03$  K. These e.m.f. cells displayed excellent stability for all the molality ranges studied. The e.m.f. readings were made first at 298.15 K. After reaching this initial equilibrium, the temperature was changed to 278.15 K, then to 310.15 K, and finally to 318.15 K. Sometimes as a check, the e.m.f. readings were taken at 298.15 K again in the middle and at the end of the run. The average deviation of these readings at 298.15 K were well within  $\pm 0.12$  mV.

Measurements of the e.m.f. were taken by means of a Leeds and Northrup type K-3 potentiometer, in conjunction with a Leeds and Northrup d.c. null detector (model 9828), with a range of sensitivities from 250 to 25  $\mu\text{V}$ .

Preparation of the silver-silver chloride electrodes were of the thermal electrolytic type.<sup>(9)</sup> The bias potential of the silver-silver chloride electrodes was always better than  $\pm 0.06$  mV. The detailed experimental procedures for the preparation of the hydrogen electrodes, silver-silver chloride electrodes, filling of the cells, controlling the temperature, etc., are given elsewhere.<sup>(10,11)</sup>

A standardization of the silver-silver chloride electrodes was performed in a routine manner, as recommended by Bates et al.,<sup>(12)</sup> since the

values of  $E_m^0$  (the standard potential of the silver-silver chloride electrodes on the molal scale) vary by as much as 0.3 mV from various laboratories. In our present work, we have used the values of  $E_m^0$  given in ref (11) for all temperatures except at 310.15 K, where  $E_m^0 = 0.21444$  V.

### 3. Experimental Results

Table 1 presents experimental molalities and observed cell potentials corrected to unit fugacity of  $H_2$ , determined using cell (2). Solution ionic strengths range from 0.03 to  $7.0 \text{ mol} \cdot \text{kg}^{-1}$  at 278.15, 298.15, 310.15, and 318.15 K.

A preliminary check of the accuracy of these data was carried out by graphical analysis. Apparent values of  $pK_2$  at solution ionic strength I are given by

$$-2.303 pK_2' = \left(\frac{F}{RT}\right) [E^0(\text{Ag,Cl,Ag}) - E] + \ln(m_{\text{CO}_3}^0 / m_{\text{HCO}_3} m_{\text{Cl}}). \quad (7)$$

In the limit of zero ionic strength, all activity coefficients approach unity and  $pK_2'$  extrapolates to the negative logarithm of the thermodynamic second ionization constant  $pK_2$ . The measurements of this investigation do not extend to sufficiently low ionic strength to contribute to our knowledge of  $pK_2$ , but they are fully consistent with the values of  $pK_2$  from studies of the sodium carbonate, bicarbonate, chloride system. Hence we adopt the values of  $pK_2$  from Peiper and Pitzer. (2)

### 4. Calculation of Osmotic and Activity Coefficients

The mixed electrolyte ion interaction model introduced by Pitzer and Kim (5) provides the basis for our calculation of activity and osmotic coefficients for  $K_2CO_3$  AND  $KHCO_3$ . The combined data set used to determine



the parameters of this model consists of three distinct types of data. Measurements involving cell (4) yield potentials according to

$$E = E^{\circ}(\text{AgCl}, \text{Ag}) - \frac{RT}{F} \left[ \ln(K_1 K_s) + \ln(a_w f_{\text{CO}_2} / (p^{\circ} f_{\text{H}_2})^{\frac{1}{2}}) \right. \\ \left. + \ln(m_{\text{Cl}} \gamma_{\text{Cl}} / m_{\text{HCO}_3} \gamma_{\text{HCO}_3}) \right] \quad (8)$$

The potentials for the related cell (6) as obtained in the work of MacInnes and Belcher differ from those given by equation (7) only in the substitution of the value  $E^{\circ} = E^{\circ}(\text{Ag}, \text{AgCl}) - E^{\circ}(\text{glass})$  for the quantity  $E^{\circ}(\text{Ag}, \text{AgCl})$ . The potentials observed in measurements using cell (2) are given by

$$E = E^{\circ}(\text{AgCl}, \text{Ag}) - \frac{RT}{F} \left[ \ln(K_2 (p^{\circ} / f_{\text{H}_2})^{\frac{1}{2}}) + \ln(m_{\text{Cl}} \gamma_{\text{Cl}} m_{\text{HCO}_3} \gamma_{\text{HCO}_3} / m_{\text{CO}_3} \gamma_{\text{CO}_3} m^{\circ}) \right] \quad (9)$$

In these equations,  $E^{\circ}(\text{Ag}, \text{AgCl})$  is the standard half-cell potential of the (silver + silver chloride) electrode;  $K_1, K_2$ , and  $K_s$  are the first and second ionization constants of carbonic acid and the Henry's law constant for the solution of  $\text{CO}_2$ , respectively;  $a_w$  and  $f_i$  are the activity of water and the fugacity of gaseous species  $i$ ;  $m_j$  and  $\gamma_j$  are the molality and activity coefficient of ionic species  $j$  at equilibrium. The values of  $m^{\circ}$  and  $p^{\circ}$  are  $1 \text{ mol} \cdot \text{kg}^{-1}$  and  $101.325 \text{ kPa}$ , respectively;  $R$ ,  $T$ , and  $F$  retain their usual meanings. Values of  $R$  and  $F$  were taken from Cohen and Taylor.<sup>(13)</sup> Values for  $K_1$ ,  $K_2$ , and  $K_s$  as functions of temperature and ionic strength are from Peiper and Pitzer's recent work.

For solutions containing  $\text{K}_2\text{CO}_3$ ,  $\text{KHCO}_3$ ,  $\text{KOH}$ , and  $\text{KCl}$ , equation (15) of Pitzer and Kim's report may be used to derive expressions for the activity coefficient ratios in equations (8) and (9) by appropriate combination of mean ionic activity coefficients as follows:

$$\begin{aligned}
\ln(\gamma_{\text{Cl}^-}/\gamma_{\text{HCO}_3^-}) &= 2 \ln \gamma_{\text{KCl}} - 2 \ln \gamma_{\text{KHCO}_3} \\
&= 2m_{\text{K}}(B_{\text{K},\text{Cl}} - B_{\text{K},\text{HCO}_3}) + 2m_{\text{K}}^2(C_{\text{K},\text{Cl}} - C_{\text{K},\text{HCO}_3}) \\
&\quad + 2(m_{\text{HCO}_3^-} - m_{\text{Cl}^-})\theta_{\text{HCO}_3,\text{Cl}} + m_{\text{K}}(m_{\text{HCO}_3^-} - m_{\text{Cl}^-})\psi_{\text{K},\text{HCO}_3,\text{Cl}} \\
&\quad + 2m_{\text{CO}_3}(\theta_{\text{CO}_3,\text{Cl}} - \theta_{\text{CO}_3,\text{HCO}_3}) + m_{\text{K}}m_{\text{CO}_3}(\psi_{\text{K},\text{CO}_3,\text{Cl}} - \psi_{\text{K},\text{CO}_3,\text{HCO}_3}) \quad (10)
\end{aligned}$$

$$\begin{aligned}
\ln(\gamma_{\text{HCO}_3^-}\gamma_{\text{Cl}^-}/\gamma_{\text{CO}_3^{2-}}) &= 2 \ln \gamma_{\text{KHCO}_3} + 2 \ln \gamma_{\text{KCl}} - 3 \ln \gamma_{\text{K}_2\text{CO}_3} \\
&= 2A_{\phi}\{I^{1/2}/(1+bI^{1/2}) + (2/b)\ln(1+bI^{1/2})\} \\
&\quad + 2m_{\text{K}}(B_{\text{K},\text{HCO}_3} + B_{\text{K},\text{Cl}} - B_{\text{K},\text{CO}_3}) + 2m_{\text{K}}^2(C_{\text{K},\text{HCO}_3} + C_{\text{K},\text{Cl}} - C_{\text{K},\text{CO}_3}) \\
&\quad - 2m_{\text{K}}(m_{\text{CO}_3^{2-}}B'_{\text{K},\text{CO}_3} + m_{\text{HCO}_3^-}B'_{\text{K},\text{HCO}_3} + m_{\text{OH}^-}B'_{\text{K},\text{OH}} + m_{\text{Cl}^-}B'_{\text{K},\text{Cl}}) \\
&\quad + 2m_{\text{CO}_3}(\theta_{\text{CO}_3,\text{HCO}_3} + \theta_{\text{CO}_3,\text{Cl}}) + m_{\text{K}}m_{\text{CO}_3}(\psi_{\text{K},\text{CO}_3,\text{HCO}_3} + \psi_{\text{K},\text{CO}_3,\text{Cl}}) \\
&\quad + 2m_{\text{HCO}_3}(\theta_{\text{HCO}_3,\text{Cl}} - \theta_{\text{CO}_3,\text{HCO}_3}) + m_{\text{K}}m_{\text{HCO}_3}(\psi_{\text{K},\text{HCO}_3,\text{Cl}} - \psi_{\text{K},\text{CO}_3,\text{HCO}_3}) \\
&\quad + 2m_{\text{OH}^-}(\theta_{\text{HCO}_3,\text{OH}} + \theta_{\text{OH}^-,\text{Cl}} - \theta_{\text{CO}_3,\text{OH}}) + m_{\text{K}}m_{\text{OH}^-}(\psi_{\text{K},\text{HCO}_3,\text{OH}} + \psi_{\text{K},\text{Cl},\text{OH}} - \psi_{\text{K},\text{CO}_3,\text{OH}}) \\
&\quad + 2m_{\text{Cl}^-}(\theta_{\text{HCO}_3,\text{Cl}} - \theta_{\text{CO}_3,\text{Cl}}) + m_{\text{K}}m_{\text{Cl}^-}(\psi_{\text{K},\text{HCO}_3,\text{Cl}} - \psi_{\text{K},\text{CO}_3,\text{Cl}}) \\
&\quad - 2m_{\text{CO}_3}(m_{\text{HCO}_3^-} + m_{\text{OH}^-} + m_{\text{Cl}^-})E_{2,1}' \quad (11)
\end{aligned}$$

Since the molality of  $\text{OH}^-$  was extremely small in solutions to which equation (9) was applied, terms involving  $\text{OH}^-$  were omitted.

The isopiestic data of Sarbar et al. (8) comprise the third set of data used in our calculations. These authors present molalities of sodium chloride or calcium chloride solutions in equilibrium with the potassium carbonate solutions. In the case of the sodium chloride reference solutions, we have used the parameters of Pitzer and Mayorga (14)

in their equation (2) to calculate osmotic coefficients for these solutions at 298.15 K. Osmotic coefficients for the calcium chloride reference solutions were calculated using the results of the fit of Rard, Habenschuss and Spedding<sup>(15)</sup> in their equation (14). Osmotic coefficients for the potassium carbonate solutions in equilibrium with these reference solutions were calculated using the relation

$$v_s m_s \phi_s = v_r m_r \phi_r \quad (12)$$

where  $v_i$ ,  $m_i$  and  $\phi_i$  are the stoichiometric number of ions, molality and osmotic coefficient of the sample and reference solutions.

The hydrolysis and disproportionation equilibria (1) introduce small but nonnegligible concentrations of bicarbonate and hydroxide ions into these carbonate solutions; in order to explicitly take these ions into consideration we use the applicable mixed electrolyte equation for the osmotic coefficient

$$\begin{aligned} \phi_{K_2CO_3} = & 1 + \left( \sum_i m_i \right)^{-1} \left\{ -2A_\phi \left[ I^{3/2} / (1 + 1.2 I^{1/2}) \right] \right. \\ & + 2m_K \left[ m_{CO_3} B_{K,CO_3}^\phi + m_{HCO_3} B_{K,HCO_3}^\phi + m_{OH} B_{K,OH}^\phi + m_K \left( C_{K,CO_3}^\phi / \sqrt{2} + C_{K,HCO_3}^\phi + C_{K,OH}^\phi \right) \right] \\ & + 2m_{CO_3} m_{HCO_3} \left( \theta_{CO_3,HCO_3} + m_K \psi_{K,CO_3,HCO_3} \right) + 2m_{CO_3} m_{OH} \left( \theta_{CO_3,OH} + m_K \psi_{K,CO_3,OH} \right) \\ & \left. + 2m_{HCO_3} m_{OH} \left( \theta_{HCO_3,OH} + m_K \psi_{K,HCO_3,OH} \right) + 2m_{CO_3} \left( m_{OH} + m_{HCO_3} \right) I_{2,1}^{E\theta'} \right\} \quad (13) \end{aligned}$$

In equations (9), (10), and (12), the coefficients  $B_{c,a}^\phi$ ,  $C_{c,a}^\phi$  and  $B_{c,a}^\phi$ ,  $C_{c,a}^\phi$  are second and third virial coefficients for the electrolyte ca for activity coefficient and osmotic coefficient expansions, respectively.

These coefficients are defined as

$$B_{c,a} = \beta_{c,a}^{(0)} + \beta_{c,a}^{(1)} (2/\alpha^2 I) \{1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})\} \quad (14)$$

$$B_{c,a}^{\phi} = \beta_{c,a}^{(0)} + \beta_{c,a}^{(1)} \exp(-\alpha I^{1/2}) \quad (15)$$

$$C_{c,a} = C_{c,a}^{\phi} / (2 |z_c z_a|^{1/2}). \quad (16)$$

Also,

$$B'_{c,a} = \beta_{c,a}^{(1)} (2/\alpha^2 I^2) \{-1 + (1 + \alpha I^{1/2} + \frac{1}{2} \alpha^2 I) \exp(-\alpha I^{1/2})\} \quad (17)$$

where  $I$  is the molality-based ionic strength,  $z_i$  is the charge on ionic species  $i$ ; also  $b = 1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$  and  $\alpha = 2.0 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ . Values of the Debye-Hückel slope of the osmotic coefficient,  $A_{\phi}$ , were taken from Bradley and Pitzer.<sup>(16)</sup> The coefficients  $\theta_{i,j}$  are second virial coefficients representing the difference between the interaction of two different ions of like sign from the appropriate mean of interactions of like pairs of ions. Similarly  $\psi_{i,j,k}$  are third virial coefficients representing differences in interactions among three different ions not all of like sign. These terms are discussed in more detail by Pitzer and Kim.

The terms in equations (11) and (13) involving  $E_{\theta', 2,1}$  arise from consideration of the higher-order electrostatic terms derived by Pitzer.<sup>(17,18)</sup> In general, these effects should be taken into account in systems involving asymmetric mixing; that is, for 2-1 and higher charge type electrolyte mixtures. In this treatment, the terms  $\theta_{i,j}$  for the interaction of two ions of like sign but different charge numbers may be written as

$$\theta_{i,j} = E_{\theta_{i,j}} + S_{\theta_{i,j}}. \quad (18)$$

The  $E_{\theta_{i,j}}$  terms are functions of ionic strength, temperature and the charges on the ions. The only cases arising for this system involve

$\text{CO}_3^{-2}$  with singly charged anions and, therefore, require  $E_{\theta_{2,1}}$  and  $E_{\theta'_{2,1}}$ , its ionic strength derivative. The latter appears explicitly while the former is included as part of  $\theta_{\text{CO}_3, \text{HCO}_3}$ , etc., in accordance with equation (18). Both  $E_{\theta}$  and  $E_{\theta'}$  may be calculated a priori as described in references 17 and 18 and do not represent adjustable parameters. The coefficients  $S_{\theta_{i,j}}$  are assumed to be independent of ionic strength and are evaluated empirically.

For many practical applications the small improvement in the accuracy of osmotic and activity coefficients calculated using the full electrostatic formulation over that obtained using the simpler equations neglecting the higher-order effects does not justify the additional complexity of the calculations required. In view of this, we have determined values of the mixed electrolyte virial coefficients  $\theta_{i,j}$  and  $\psi_{i,j,k}$  both with and without the inclusion of higher order electrostatic effects.

In all, 25 parameters are included in equations (10), (11), and (13). Of these, ten are reliably and accurately known from previous work. Seven were found to be unnecessary to the adequate representation of the experimental data when higher-order electrostatic effects were included in the calculations; one additional parameter was found to be important when these effects were not considered. Of the remaining parameters,  $\beta^{(0)}$  and  $\beta^{(1)}$  for  $\text{KHCO}_3$  are reported in reference (3), and  $\beta^{(0)}$ ,  $\beta^{(1)}$  and  $C^\phi$  for  $\text{K}_2\text{CO}_3$  are reported by Sarbar et al. However, as Sarbar et al. do not consider the changes in solution composition introduced by the equilibria (1), and as the uncertainties in the second virial coefficients for  $\text{KHCO}_3$  calculated by Roy et al. are rather large, these five parameters have been redetermined. The other parameters,  $\theta_{\text{CO}_3, \text{HCO}_3}$ ,  $\psi_{\text{K}, \text{CO}_3, \text{HCO}_3}$ ,  $\psi_{\text{K}, \text{CO}_3, \text{Cl}}$  and  $\psi_{\text{K}, \text{HCO}_3, \text{Cl}}$ , have not been previously determined.

In a combined fit involving data of different types, both the overall quality of fit and the final parameter values are dependent to a degree on the weights assigned to the data. As an aid in assigning weights as consistently as possible, three separate least-squares routines were employed in an iterative process to determine values of the parameters consistent with all three types of data available. The parameters  $\beta_{K,CO_3}^{(0)}$  and  $C_{K,CO_3}^\phi$  were determined by fitting to the isopiestic data. The data of this study for cell (2) were used to determine  $\beta_{K,HCO_3}^{(0)}$ ,  $\beta_{K,CO_3}^{(1)}$ ,  $S_{\theta_{CO_3,HCO_3}}^{(0)}$ ,  $\psi_{K,CO_3,HCO_3}$ , and  $\psi_{K,CO_3,Cl}$ , leaving  $\beta_{K,HCO_3}^{(1)}$  to be calculated from the electromotive force measurements of cell (4). This process was repeated until convergence of all parameters was achieved, using the full electrostatic formulation in all three routines.

The mixed electrolyte interaction parameters  $\theta_{CO_3,HCO_3}$ ,  $\psi_{K,CO_3,HCO_3}$ ,  $\psi_{K,CO_3,Cl}$  and  $\psi_{K,HCO_3,Cl}$  were redetermined, neglecting all higher-order electrostatic terms, by fitting to the data of this study using the previously determined pure electrolyte virial coefficients for potassium carbonate and bicarbonate. Applicability of these parameters to the isopiestic data and the data of cell (4) was checked by comparing calculated osmotic coefficients and cell potentials with experimental values for these systems.

The pure electrolyte second and third virial coefficients  $B_{c,a}$  and  $C_{c,a}$  are temperature dependent. Over a fairly limited range in temperature, this dependence may be written as

$$P_t = P_r + (\partial P/\partial T)(T-T_r) + \frac{1}{2}(\partial^2 P/\partial T^2)(T-T_r)^2 \quad (19)$$

where  $P_t$  and  $P_r$  are values of  $\beta_{c,a}^{(0)}$ ,  $\beta_{c,a}^{(1)}$  or  $C_{c,a}^\phi$  at arbitrary temperature  $T$  and reference temperature  $T_r$  respectively. Enthalpy and heat capacity data from which the first and second temperature derivatives of the parameters could be calculated directly are not available for this system. In view of the limited temperature range of the available data, we take  $\partial^2 P / \partial T^2 = 0$  for all coefficients.

As the isopiestic measurements are limited to 298.15 K only, these data could not be used in determining temperature coefficients; therefore, we take  $\partial C^\phi / \partial T = 0$ . The very low carbonate molalities present in experiments involving cells (4) and (6) imply that these data are rather insensitive to small changes in the values of the carbonate virial parameter temperature coefficients. Also, the structure of equation (10) prevents independent determination of  $\beta_{K,CO_3}^{(0)}$  and  $\beta_{K,HCO_3}^{(0)}$  based on the data of this study alone. In consideration of these restrictions, we adopt the first temperature derivatives of the bicarbonate second virial coefficients for  $NaHCO_3$  determined by Peiper and Pitzer as  $\partial \beta^{(0)} / \partial T$  and  $\partial \beta^{(1)} / \partial T$  for  $KHCO_3$ . The work of Roy *et al.*<sup>(3)</sup> has shown that these results may be applied to potassium bicarbonate solutions.

Temperature derivatives for the carbonate second virial coefficients were determined by fitting  $\beta_{K,CO_3}^{(0)}$  and  $\beta_{K,CO_3}^{(1)}$  to the data of this study in four isothermal fits, using values for the other parameters as determined in the previously described iterative fit. The resulting values of  $\partial \beta^{(0)} / \partial T$  and  $\partial \beta^{(1)} / \partial T$  for  $K_2CO_3$  were checked for consistency by recalculating bicarbonate parameters using the bicarbonate/chloride cell data.

The values of all parameters necessary for the calculation of thermodynamic properties of the mixed potassium carbonate/bicarbonate/chloride solutions using the higher-order electrostatic interaction terms are

presented in Table 2. Table 3 lists values of the mixed electrolyte interaction parameters to be used in calculations in which the higher-order electrostatic interactions are omitted. The uncertainties shown in Tables 2 and 3 are those given statistically; the actual uncertainties are larger by amounts not readily determinable. The standard error of fit to the 77 data points of the  $\text{KHCO}_3 + \text{KCl}$  cell data was 0.7 mV, the same overall fit quality reported by Roy et al. in their treatment of these data. The 26 points of the isopiestic data of Sarbar et al. were fit with standard error of 0.0059 in the osmotic coefficient, while these authors report 0.0050 in their fit. As these authors included fourth, fifth and sixth virial coefficients in their fit, and did not consider the hydrolysis equilibrium, our results do not necessarily imply any significant decrease in fit quality.

Of the 160 points which comprise the data of this study, the 8 points of Run 5 at 310.15 and 318.15 K were not fitted satisfactorily, showing deviations of 2-3 mV. The data within each temperature set show fairly consistent deviations; additional data leading to precise determination of temperature dependences of one or more of the mixed electrolyte interaction parameters may lead to acceptable fits of these data. However, we have not included these points in our overall fit of this system. The remaining data of this study, comprising 152 points, were fit with a standard error of 0.5 mV when higher order electrostatic terms are included. When these effects are not included, the standard error of fit increases slightly to 0.55 mV. This error is slightly greater than the 0.4 mV deviation reported by Peiper and Pitzer for sodium carbonate and bicarbonate; however, in view of the lack of enthalpy and heat capacity data for the potassium salts and the subsequent approximations required in determining temperature coefficients for the second virial



parameters, we feel that our results provide a satisfactory and accurate representation of the thermodynamic properties of these solutions.

Table 4 lists the osmotic coefficient  $\phi$  and activity coefficients  $\gamma_{\pm}$  for mixed and nominally pure  $\text{KHCO}_3$  and  $\text{K}_2\text{CO}_3$  solutions at selected concentrations at 298.15 K. Equilibrium concentrations of carbonate, bicarbonate and hydroxide ions, the equilibrium carbon dioxide pressure over the solutions and the activity of water are also given. In addition, the stoichiometric activity and osmotic coefficients  $\gamma^{\text{st}}$  and  $\phi^{\text{st}}$  are tabulated for nominally pure solutions. They are defined as

$$\phi^{\text{st}} = \sum_i m_i \phi / m^{\text{st}} \quad (20)$$

$$\gamma_{\pm}^{\text{st}} = (m_x / m_x^{\text{st}})^{1/\nu} \gamma_{\pm} \quad (21)$$

where  $m_x$  and  $m_x^{\text{st}}$  are the equilibrium and stoichiometric molalities of carbonate or bicarbonate ion and  $\nu$  is the number of ions generated on dissociation of the electrolyte. All quantities were calculated using the full electrostatic formulation of Pitzer<sup>(17)</sup> and the parameters listed in Table 2.

## 5. Discussion

It is noteworthy that the present measurements extended to ionic strengths above  $6 \text{ mol} \cdot \text{kg}^{-1}$  and that the ion interaction equations fitted these data very well. These are much higher ionic strengths than have been studied for the analogous sodium system, and this gives greater precision of determination of some parameters.

Ion interaction parameters for  $\text{K}_2\text{CO}_3$  and  $\text{KHCO}_3$  have been reported by Harvie<sup>(19)</sup> from studies of the solubility of solid salts in electrolyte mixtures. Although his individual parameters differ from ours by

a few hundredths, the signs of these differences are such that the net effect on activity coefficients is not large. In each case his  $\beta^{(1)}$  and  $C^\phi$  are smaller and his  $\beta^{(0)}$  is larger than ours.

Chen, Britt, Boston and Evans<sup>(20)</sup> report ion interaction parameters for  $K_2CO_3$  and  $KHCO_3$  based on equilibrium vapor pressure data at temperatures ranging from 343.15 to 403.15 K. The values of  $\beta^{(0)}$  and  $\beta^{(1)}$  for  $K_2CO_3$  and  $KHCO_3$  at 383.15 K reported by these authors differ only slightly from those obtained by extrapolation of the interaction parameters determined in this work using the temperature coefficients listed in Table 2.

The earlier investigation of  $KHCO_3$  using only the data for cell (4) gave values of  $\beta^{(0)}$  and  $\beta^{(1)}$  for  $KHCO_3$  which were much more uncertain than the present values. The new results fall within the old ranges of uncertainty. It is interesting that we find non-zero values for the carbonate-bicarbonate and potassium-carbonate-bicarbonate mixing parameters  $S_{CO_3, HCO_3}^\theta$  and  $\psi_{K, CO_3, HCO_3}$  of  $0.089 \pm 0.011$  and  $0.024 \pm 0.004$ , respectively, whereas Peiper and Pitzer concluded that for the sodium system these parameters were not needed. The higher molalities studied in this research provide the basis for determining these parameters.

The results of this study and of the work of Peiper and Pitzer on the related carbonate/bicarbonate/chloride system with sodium cation represent significant steps toward a practical model for the calculation of thermodynamic properties of systems of mixed electrolytes including carbonate and bicarbonate ions. Measurements on the magnesium and calcium analogues of cell (4), yet to be carried out, could be treated by the general procedure of this report. Such data together with the existing knowledge would allow calculation of activity coefficients of all major components of various natural waters.

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Table 1. Experimental Cell Potentials, Corrected to Unit Fugacity of  $H_2$ , and Solution Molalities  $m_1(K_2CO_3)$ ,  $m_2(KHCO_3)$ , and  $m_3(KCl)$  in  $mol \cdot kg^{-1}$

Run 1

$m_1$	0.010094	0.019977	0.029594	0.039896	0.049864	0.063894	0.069367	0.080096
$m_2$	0.0099946	0.020627	0.027970	0.040041	0.049767	0.060743	0.070172	0.079925
$m_3$	0.0099967	0.019579	0.031663	0.039926	0.050262	0.059835	0.070339	0.079830
I	0.050273	0.10014	0.14842	0.19966	0.24962	0.31226	0.34861	0.40004
5°C, E/V	0.91780	0.90038	0.88941	0.88170	0.87506	0.87161	0.86554	0.86236
25°C, E/V	0.94237	0.92249	0.91083	0.90251	0.89590	0.89222	0.88581	0.88228
37°C, E/V	0.05605	0.93631	0.92428	0.91570	0.90845	0.90467	0.89831	-
45°C, E/V	-	0.94564	0.93337	0.92472	0.91743	0.91337	0.90644	-

Run 2

$m_1$	0.039927	0.079740	0.11966	0.15950	0.19919	0.23921	0.27923	0.31959
$m_2$	0.039946	0.079777	0.11972	0.15958	0.19928	0.23932	0.27936	0.31974
$m_3$	0.040093	0.080071	0.12016	0.16017	0.20002	0.24020	0.28039	0.32092
I	0.19982	0.39907	0.59886	0.79825	0.99687	1.19715	1.39744	1.59943
5°C, E/V	0.88188	0.86270	0.85149	0.84357	0.83706	0.83215	0.82807	0.82447
25°C, E/V	0.90237	0.88225	0.86999	0.86149	0.85470	0.84929	0.84502	0.84105
37°C, E/V	-	0.89496	0.88250	0.87341	-	0.86030	0.85598	0.85196
45°C, E/V	0.92393	0.90232	0.88982	0.88031	-	0.86680	0.86213	0.85763

Run 3

$m_1$	0.15974	0.31949	0.47915	0.63910	0.79885	0.95788	1.11830	1.27696
$m_2$	0.15987	0.31976	0.47954	0.63960	0.79950	0.95866	1.11921	1.27800
$m_3$	0.15971	0.31942	0.47903	0.63894	0.79866	0.95764	1.11803	1.27665
I	0.79880	1.59765	2.39602	3.19584	3.99471	4.78994	5.59214	6.38553
5°C, E/V	0.84360	0.82507	0.81472	0.80778	0.80323	0.79910	0.79629	0.79360
25°C, E/V	0.86177	0.84157	0.83014	0.82262	0.81754	0.81253	0.80920	0.80637

Table 1. (continued)

Run 3 (continued)

37°C,E/V	0.87330	0.85221	0.84019	0.83182	-	0.82077	0.81729	0.81379
45°C,E/V	0.88083	0.85957	0.84724	0.83803	-	0.82640	0.82275	0.81889

Run 4

m <sub>1</sub>	0.059909	0.11982	0.17972	0.23963	0.29952	0.35955	0.41948	0.47920
m <sub>2</sub>	0.17967	0.35935	0.53900	0.71867	0.89826	1.0783	1.2580	1.4372
m <sub>3</sub>	0.059924	0.11985	0.17977	0.23983	0.29959	0.35964	0.41959	0.47933
I	0.41932	0.83866	1.2579	1.6774	2.0964	2.5166	2.9361	3.3541
5°C,E/V	-	0.82583	0.81425	0.80723	0.80113	0.79611	0.79206	0.78841
25°C,E/V	-	0.84244	-	0.82204	0.81501	0.80986	0.80543	0.80147
37°C,E/V	-	0.85413	-	-	0.82565	0.82021	0.81539	0.81074
45°C,E/V	-	0.86204	-	-	0.83334	0.82747	-	-

Run 5

m <sub>1</sub>	0.53891	0.71874	0.89846	1.0786	1.2575	1.4366	1.6175	1.7970
m <sub>2</sub>	0.18038	0.24057	0.30072	0.36102	0.42089	0.48086	0.54140	0.60148
m <sub>3</sub>	0.17982	0.23482	0.29979	0.35989	0.41957	0.47936	0.53971	0.59960
I	1.9769	2.6316	3.2959	3.9566	4.6128	5.2701	5.9336	6.5921
5°C,E/V	0.86592	0.85890	0.85401	0.85062	0.84738	0.84529	0.84342	0.84168
25°C,E/V	0.88501	0.87737	0.87196	0.86780	0.86422	0.86175	0.85948	0.85735
37°C,E/V	0.89700	0.88852	0.88263	0.87855	0.87446	0.87186	0.86926	0.86711
45°C,E/V	0.90428	0.89618	0.88997	0.88561	0.88116	0.87852	0.87573	0.87347

Table 1. (continued)

Run 6

$m_1$	1.4960	1.4836	1.4973	0.0059050	0.0058907	0.0078760
$m_2$	0.99661	0.99077	0.99879	0.0061130	0.0071338	0.0081537
$m_3$	0.50075	0.98809	1.4977	0.0059749	0.0069728	0.0079701
I	5.9854	6.4297	6.9884	0.029803	0.034779	0.039752
5°C,E/V	0.82283	0.81099	0.80113	-	0.92671	0.92388
25°C,E/V	0.84294	0.82494	0.81419	0.95470	0.95076	-
37°C,E/V	0.85214	0.83356	0.82196	0.96979	0.96510	-
45°C,E/V	0.85821	0.83944	0.82689	0.97955	0.97604	-



Table 2. Ion Interaction Parameters for Solutions of  $K^+$  with  $CO_3^{2-}$ ,  $HCO_3^-$ ,  $OH^-$ , and  $Cl^-$

	$K_2CO_3$	$KHCO_3$	KOH	KCl
$\beta^{(0)}/(kg \cdot mol^{-1})$	$0.1288 \pm 0.0009^a$	$-0.0107 \pm 0.0015^a$	$0.1298^b$	$0.04835^b$
$\beta^{(1)}/(kg \cdot mol^{-1})$	$1.433 \pm 0.015^a$	$0.0478 \pm 0.0085^a$	$0.320^b$	$0.2122^b$
$C^\phi/(kg^2 \cdot mol^{-2})$	$0.00050 \pm 0.00013^a$		$0.0041^b$	$-0.00084^b$
$\frac{\partial \beta^{(0)}}{\partial T} \times 10^3/(kg \cdot mol^{-1} \cdot K^{-1})$	$1.1^a$	$1.0^c$	-	$0.58^d$
$\frac{\partial \beta^{(1)}}{\partial T} \times 10^3/(kg \cdot mol^{-1} \cdot K^{-1})$	$4.36^a$	$1.1^c$	-	$1.1^d$
$\frac{\partial C^\phi}{\partial T} \times 10^3/(kg^2 \cdot mol^{-2} \cdot K^{-1})$	-	-	-	$-0.05^d$

$$S_{\theta_{CO_3, HCO_3}} = 0.089 \pm 0.011^a$$

$$\psi_{K, CO_3, Cl} = 0.024 \pm 0.004^a$$

$$\psi_{K, CO_3, HCO_3} = -0.036 \pm 0.008^a$$

$$\theta_{HCO_3, Cl} = 0.0359^c$$

$$S_{\theta_{CO_3, Cl}} = -0.053^c$$

$$\theta_{OH, Cl} = -0.050^e$$

$$\psi_{K, OH, Cl} = -0.008^e$$

<sup>a</sup> Determined in this research.

<sup>b</sup> Taken from Pitzer and Mayorga<sup>(14)</sup>.

<sup>c</sup> Taken from Peiper and Pitzer<sup>(2)</sup>.

<sup>d</sup> Taken from Silvester and Pitzer<sup>(18)</sup>.

<sup>e</sup> Taken from Pitzer and Kim<sup>(5)</sup>.

Table 3. Mixed Electrolyte Interaction Parameters, Not Including Higher Order Electrostatic Terms for Unsymmetrical Mixing

$$\begin{array}{ll} \theta_{\text{CO}_3, \text{HCO}_3} = -0.063 \pm 0.012^{\text{a}} & \theta_{\text{CO}_3, \text{Cl}} = -0.092^{\text{b}} \\ \psi_{\text{K}, \text{CO}_3, \text{HCO}_3} = 0.013 \pm 0.009^{\text{a}} & \psi_{\text{K}, \text{CO}_3, \text{Cl}} = 0.0073 \pm 0.0041^{\text{a}} \\ \psi_{\text{K}, \text{HCO}_3, \text{Cl}} = -0.0037 \pm 0.0008^{\text{a}} & \end{array}$$

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<sup>a</sup> Determined in this research.

<sup>b</sup> Taken from Peiper and Pitzer<sup>(2)</sup>.

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