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Rabindra N. Roy, James J. Gibbons, Mark D. Wood,
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October 1981

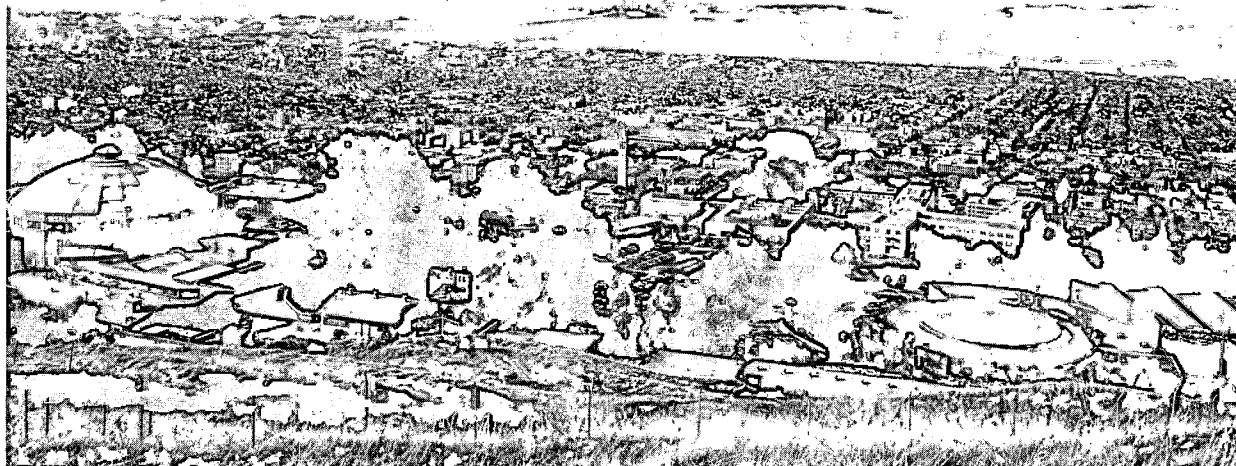
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THE FIRST IONIZATION OF CARBONIC ACID IN AQUEOUS SOLUTIONS
OF POTASSIUM CHLORIDE INCLUDING THE ACTIVITY COEFFICIENTS
OF POTASSIUM BICARBONATE

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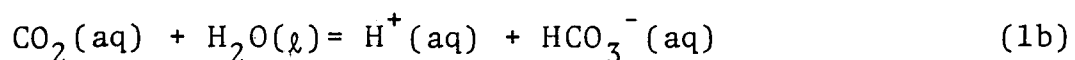
Abstract

The electrochemical cell without liquid junction $\text{Pt}, \text{H}_2 / \text{KHCO}_3(m_1), \text{KCl}(m_2), \text{CO}_2(m_3) / \text{AgCl}, \text{Ag}$ has been used to determine the first ionization constant of carbonic acid and the activity coefficient of KHCO_3 in potassium chloride solutions and in water at 278.15, 298.15, and 318.15 K. The molality ratios $m_1:m_2$ were approximately 1:1, 2:1, 3:1, 4:1, and 6:1. The range of molality for KHCO_3 varied from 0.015 to about 1 mol kg^{-1} , whereas that for KCl ranged from 0.01 to about 0.34 mol kg^{-1} . Certified primary grade gas mixtures (H_2 and CO_2) were used. The average value of $\text{p}K_1$ for all different ratios of m_1/m_2 at 298.15 K is 6.360, which is the same as the previous result of 6.360 for the $\text{NaHCO}_3 + \text{NaCl} + \text{H}_2\text{O}$ system. The data were also treated by fitting to the Pitzer equations for mixed electrolytes. All parameters reliably and accurately known from other systems were adopted leaving only the KHCO_3 parameters to be determined. From these results, values are calculated for activity and osmotic coefficients of pure KHCO_3 at selected molalities and temperatures as well as the trace activity coefficient of KHCO_3 in KCl .

1. Introduction

The importance of thermodynamic studies involving carbonic acid and its mixtures with strong electrolytes (e.g., NaCl, KCl, CaCl₂ etc.) is well-known in the fields of chemical oceanography, biology,⁽¹⁾ industrial chemistry,⁽²⁾ and geological chemistry.⁽³⁾ While carbonic acid-bicarbonate - carbonate properties at infinite dilution are well-known, the primary practical interest lies in mixtures at finite concentration with other ions such as chloride. In view of the presence of a substantial vapor pressure of carbon dioxide, isopiestic investigation of bicarbonates is not straightforward. However, the success of the virial coefficient equations of Pitzer⁽⁴⁾ and of Pitzer and Kim⁽⁵⁾ for mixed electrolytes opened the opportunity of using certain electrochemical cell measurements to determine the desired properties. This method was applied successfully⁽⁶⁻⁸⁾ for systems involving the species Na⁺, Cl⁻, HCO₃⁻, CO₃⁼, and CO₂ or H₂CO₃. It would be of interest to use similar methods for bicarbonate systems with other important positive ions such as K⁺, Mg⁺⁺, and Ca⁺⁺. The present paper is the first step; it relates to potassium as the positive ion. Included are (1) the experimental electrochemical cell measurements, (2) their simple interpretation by extrapolation to zero ionic strength, and (3) the more complex interpretation with the mixed-electrolyte equations of Pitzer and Kim.⁽⁵⁾

The solubility of CO₂(g) and first ionization of carbonic acid can be expressed as



with the thermodynamic equations

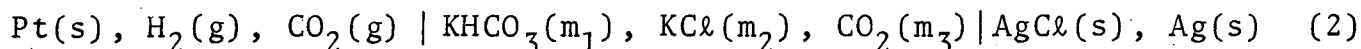
$$K_S = m(\text{CO}_2)\gamma(\text{CO}_2)/f(\text{CO}_2) \quad (1c)$$

and

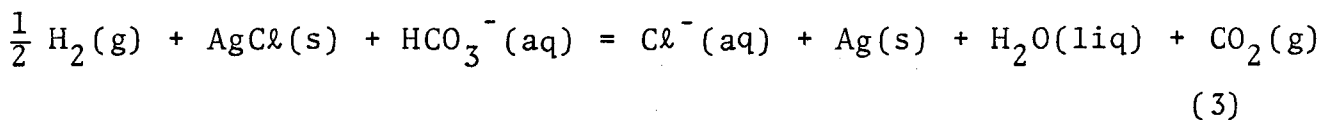
$$K_1 = \frac{m(\text{H}^+)m(\text{HCO}_3^-)\gamma(\text{H}^+)\gamma(\text{HCO}_3^-)}{a(\text{H}_2\text{O})m(\text{CO}_2)\gamma(\text{CO}_2)} \quad (1d)$$

where $m(\text{CO}_2)$ is the total molality of unionized CO_2 in the solution; $\gamma(\text{H}^+)$, $\gamma(\text{HCO}_3^-)$ and $\gamma(\text{CO}_2)$ are the activity coefficients of H^+ , HCO_3^- and CO_2 , respectively. Also $a(\text{H}_2\text{O})$ and $f(\text{CO}_2)$ are the water activity and the carbon dioxide fugacity in the gas phase, respectively.

The experimental data presented here include e.m.f. measurements at 278.15, 298.15, and 318.15 K of the cell without liquid junction



with reaction

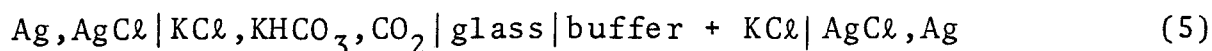


The hydrogen and silver-silver chloride electrodes are reversible in H^+ and Cl^- . The potential of this cell is given by

$$E = E^\circ - \frac{RT}{F} \left[\ln(K_1 K_S) + \ln \left\{ \frac{a(\text{H}_2\text{O}) f(\text{CO}_2)}{f^{1/2}(\text{H}_2)} \right\} + \ln \left\{ \frac{m(\text{Cl}^-)\gamma(\text{Cl}^-)}{m(\text{HCO}_3^-)\gamma(\text{HCO}_3^-)} \right\} \right] \quad (4)$$

wherein K_1 , the conventional dissociation constant, and K_s , the Henry's law constant for CO_2 solubility in H_2O , were defined above, and $f(\text{H}_2)$ represents the fugacity of $\text{H}_2(\text{g})$ while $m(\text{Cl}^-)$ and $m(\text{HCO}_3^-)$ are the equilibrium molalities of Cl^- and HCO_3^- , with $m(\text{Cl}^-) = m_2$ and $m(\text{HCO}_3^-) \approx m_1$. Also, $E^\circ = E^\circ(\text{Ag}, \text{AgCl})$, the standard potential of the silver-silver chloride electrode. R , T and F retain their usual meanings; values of R and F may be taken from Cohen and Taylor⁽⁹⁾ and $R/F = 8.61736 \text{ (abs V)} \cdot \text{K}^{-1}$.

There are no measurements reported for KHCO_3 in cell (2), but MacInnes and Belcher⁽¹⁰⁾ determined the value of the constant K_1 using the related cell

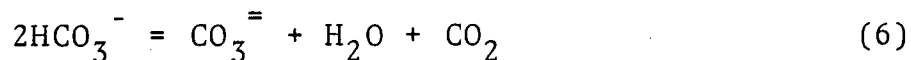


where CO_2 in the solution is in equilibrium with the gas at a known partial pressure. The range of ionic strengths studied by them was 0.002 to 0.25 mol kg^{-1} and with equal Cl^- and HCO_3^- molalities. Also, they maintained the partial pressure of CO_2 above the solution near 10 kPa. Their value of $\text{p}K_1$ at 298.15 K is 6.343, which does not agree well with other values,^(6-8,11) even though the internal precision of their data is good. This conflict is a direct result of their assignment of an incorrect value to the Henry's law constant and to a lesser extent the use of the value of E° then available. Cell (5) differs from cell (2) only in the substitution of a glass electrode for a hydrogen electrode. The potential of cell (5) is given by equation (4) but with $E^\circ = E^\circ(\text{Ag}, \text{AgCl}) - E^\circ(\text{glass})$. For cells (2) and (5), the quantity determined by extrapolation of the

difference $E - E^\circ$ to zero ionic strength and zero CO_2 molality is the product K_1K_s . From MacInnes and Belcher,⁽¹⁰⁾ $p(K_1K_s) = +7.818$, whereas Peiper and Pitzer⁽⁸⁾ found $p(K_1K_s) = +7.820$, and Harned and Davis⁽¹¹⁾ obtained $p(K_1K_s) = +7.816$.

In view of the good agreement of MacInnes and Belcher's value of K_1K_s with the best recent values, we will make full use of their data which, however, are limited to 298.15 K and very low molalities. The new experiments reported below (for cell (2)) extend to much higher molality and to 278.15 and 318.15 K.

The full interpretation of the experimental results at finite molality requires equations for mixed electrolytes not only because of the presence of the added chloride but also in view of the disproportion equilibrium



This reaction reduces the molality of HCO_3^- . Also the presence of the $\text{CO}_3^{=}$ has a small influence on the activity coefficients of the other species. All of these effects are readily included in the equations of Pitzer and Kim.⁽⁵⁾

2. Experimental

CHEMICALS

Potassium chloride and potassium bicarbonate were ACS certified-grade from Fisher. The salts were used as purchased after drying the KCl and without further purification of KHCO_3 . Each solution was made by weighing solid potassium chloride,

solid potassium bicarbonate, and carbon dioxide-free doubly distilled water. Vacuum corrections were applied to all weighings. Weighing inaccuracy should not exceed ± 0.04 percent. There is some possibility, however, that the bicarbonate was slightly impure by loss of CO_2 and H_2O or by being not completely dry. This is discussed further below.

The primary standard-grade hydrogen-carbon dioxide mixtures obtained from Air Products and Chemicals, Inc. (LaPorte, Texas) were within ± 0.02 mol percent. The mol percent values of CO_2 were 80.163 and 19.655.

APPARATUS AND METHOD

Dissolved air was removed from the solution by gently passing the hydrogen-carbon dioxide gas for about 1/2 h just before the e.m.f. cells were filled. The design of the cells, preparation of the silver - silver chloride and hydrogen electrodes, maintenance of the constant temperature bath in which the cells were immersed, further purification (i.e., removal of traces of oxygen) of the gas mixture, and other experimental details, have been discussed previously. (6,12,13)

Measurements of the e.m.f. of cell (2) were made by means of a Leeds and Northrup type K-3 potentiometer, in conjunction with a Leeds and Northrup D.C. null detector (Model 9829) in the sensitivity range of 250 to 25 μV . The values of E° , the standard electrode potential of the silver-silver chloride electrode on the molal scale, at 278.15, 298.15, and 318.15 K were 0.23431, 0.22259, and 0.20857 V. These values were obtained

using the usual standardization procedure, as recommended by Bates, et al.⁽¹⁴⁾

EXPERIMENTAL RESULTS

After appropriate corrections for barometric pressure and water vapor (see Ref. 6 for details) the partial pressures of H₂ and CO₂ were calculated and used without adjustment as the fugacities. The effect of the H₂ fugacity was introduced as the term $E_c = (-RT/2F) \ln f(H_2)$. Values of E_c for various experimental series are given in Table 1.

Tables 2-6 present the experimental solution molalities, carbon dioxide pressures, and cell e.m.f. values. The further calculations will be discussed in the next sections.

3. Calculations of K_1 by Extrapolation

In this section the data are treated by the method of Harned and Davis,⁽¹¹⁾ i.e., by an appropriate extrapolation to zero ionic strength to yield pK_1 . The apparent pK_1' is defined as

$$\begin{aligned} -\log_{10} K_1' &= -[\log_{10} K_1 + \log_{10} (\gamma_{Cl} / \gamma_{HCO_3})] \\ &= [E + E_c - E^\circ(Ag, AgCl)] / k + \log_{10} SP(CO_2) + \log_{10} (m_2 / m_1) \quad (7) \end{aligned}$$

where $k = \ln(10) RT/F$ and the molality of dissolved CO₂ is given by $SP(CO_2)$. In the limit of zero ionic strength all activity coefficients become unity and S becomes K_s , the Henry's law constant for CO₂ in pure water. Then K_1' becomes the thermodynamic constant K_1 for the first dissociation of carbonic acid at the temperature T . There is no contribution from the Debye-Hückel limiting law since chloride and bicarbonate ions have the

same charge. Thus one expects a linear dependence of $-\log K_1'$ on ionic strength in dilute solutions.

The values of S , Henry's law constant, listed in Tables 2-6, at the experimental temperatures and the molalities of KCl were obtained by using an interpolation and extrapolation procedure from a large linear plot of $-\log S$ against the molality of KCl . The values of S at round molalities of KCl were first calculated from the data of Markham and Kobe⁽¹⁵⁾ in terms of α , the Bunsen coefficient, and the equation recommended by Davis⁽¹⁶⁾

$$S = \frac{1.977}{44.01} \cdot \frac{\alpha}{d_{\text{H}_2\text{O}}} \quad (8)$$

where the actual density of CO_2 at 273.15 K is 1.977 g-lit^{-1} and $d_{\text{H}_2\text{O}}$ is the density of H_2O at the experimental temperature. It is of interest to mention that the value of S at 298.15 K obtained from the above treatment is in agreement with the value obtained from the Ostwald coefficient data of Yasunishi and Yoshida,⁽¹⁷⁾ interpreted using the apparent molal volume data of Vaslow.⁽¹⁸⁾

The values of $-\log K_1'$ from Tables 2-6 do show an essentially linear dependence on ionic strength and the intercepts are shown as $-\log_{10} K_1$ in Table 7. At each of the temperatures the various series yield concordant values of $\text{p}K_1$. For a single series of data with a given ratio (m_1/m_2) the precision is within 0.25 mV. At 298.15 K we find $\text{p}K_1 = 6.360$ from these data for KHCO_3 which is exactly the same value as was obtained from a similar treatment⁽⁶⁾ of data for sodium bicarbonate and agrees well with the value 6.355 from the more comprehensive treatment of Peiper and

Pitzer.⁽⁸⁾ It is not possible to derive activity coefficients for pure KHCO_3 from these data alone. The more comprehensive treatment of the next section yields that information.

4. Calculations with General Equations for Mixed Electrolytes

In this section the data for KHCO_3 are treated by the methods used previously^(7,8) for NaHCO_3 which are based on the general equations of Pitzer and Kim⁽⁵⁾ for mixed electrolytes. This procedure is useful provided the parameters for KCl are already known as they are.

Of the quantities in equation (4), the K_1K_s product, as a function of temperature, was taken from Peiper and Pitzer.⁽⁸⁾ The ratio $\gamma(\text{Cl}^-)/\gamma(\text{HCO}_3^-)$ is the quantity primarily determined. In addition the activity of water and the exact molality of HCO_3^- are needed. The latter departs slightly from m_1 because of the second ionization to $\text{CO}_3^{=}$; this is calculated in the usual manner using the second dissociation constant K_2 , also from reference (8), and the appropriate expression for activity coefficients. Activity and osmotic coefficient expressions were derived from the general equations of Pitzer and Kim⁽⁵⁾ We give, explicitly, only the expression for $\gamma(\text{Cl}^-)/\gamma(\text{HCO}_3^-)$ in equation (9) and for $a(\text{H}_2\text{O})$ in equation (10).

$$\begin{aligned} \ln \frac{\gamma(\text{Cl}^-)}{\gamma(\text{HCO}_3^-)} &= 2 \ln \gamma(\text{KCl}) - 2 \ln \gamma(\text{KHCO}_3) \\ &= 2 m(\text{K}) (B_{\text{K},\text{Cl}} - B_{\text{K},\text{HCO}_3}) \\ &\quad + 2(m(\text{HCO}_3) - m(\text{Cl})) \theta_{\text{HCO}_3,\text{Cl}} \end{aligned} \quad (9)$$

$$+ 2m(\text{CO}_3) (\theta_{\text{CO}_3, \text{Cl}} - \theta_{\text{CO}_3, \text{HCO}_3})$$

and

$$\begin{aligned} \frac{1000}{M_w} \ln a(\text{H}_2\text{O}) &= (\Sigma m_i) \phi \\ &= \Sigma m_i + 2I f^\phi \\ &+ 2m(\text{K})m(\text{CO}_3) \left[\beta_{\text{K}, \text{CO}_3}^{(0)} + \beta_{\text{K}, \text{CO}_3}^{(1)} e^{-2I^{1/2}} \right] \\ &+ 2m(\text{K})m(\text{HCO}_3) \left[\beta_{\text{K}, \text{HCO}_3}^{(0)} + \beta_{\text{K}, \text{HCO}_3}^{(1)} e^{-2I^{1/2}} \right] \\ &+ 2m(\text{K})m(\text{Cl}) \left[\beta_{\text{K}, \text{Cl}}^{(0)} + \beta_{\text{K}, \text{Cl}}^{(1)} e^{-2I^{1/2}} \right] \quad (10) \\ &+ 2m(\text{CO}_3)m(\text{HCO}_3) \theta_{\text{CO}_3, \text{HCO}_3} \\ &+ 2m(\text{CO}_3)m(\text{Cl}) \theta_{\text{CO}_3, \text{Cl}} \\ &+ 2m(\text{HCO}_3)m(\text{Cl}) \theta_{\text{HCO}_3, \text{Cl}}. \end{aligned}$$

In equations (9) and (10),

$$f^\phi = -A_\phi \frac{I^{1/2}}{I + 1.2I^{1/2}} \quad (11)$$

$$B_{c,a} = \beta_{c,a}^{(0)} + \frac{\beta_{c,a}^{(1)}}{2I} [1 - (1 + 2I^{1/2}) e^{-2I^{1/2}}]. \quad (12)$$

The quantities $B_{c,a}$ are the second virial coefficients for the electrolytes ca , and f^ϕ is the Debye-Hückel function for the osmotic coefficient with parameter A_ϕ . Values of A_ϕ are given by Bradley and Pitzer⁽¹⁹⁾ for a wide range of temperatures and

pressures; at 298.15 K, $A_\phi = 0.3915$. Also, M_w is the formula weight of water, taken as $18.01533 \text{ g mol}^{-1}$, I is the molal ionic strength, and Σm_i is the sum of all solute molalities, including uncharged species. The mixing parameters $\theta_{a,a'}$ are described by Pitzer and Kim.⁽⁵⁾ While the presence of doubly charged carbonate ions makes these solutions, in principle, asymmetric mixtures, the carbonate molality is always small, and the net effect of the higher order electrostatic terms for asymmetric mixing⁽²⁰⁾ is negligible. Hence these terms are omitted.

The equations for osmotic and activity coefficients require the second-virial-coefficient parameters for KCl , KHCO_3 , and K_2CO_3 . The values of $\beta^{(0)}$ and $\beta^{(1)}$ for KCl are given by Pitzer and Mayorga⁽²¹⁾ and their temperature dependence by Silvester and Pitzer⁽²²⁾. The parameters for K_2CO_3 were determined very recently by Sarbar, *et al.*,⁽²³⁾ and those for KHCO_3 are determined in the present calculation. The temperature dependence of the K_2CO_3 and KHCO_3 parameters is not known at present; however, previous results^(8,22) for a wide variety of systems including NaHCO_3 indicate they should be small. Therefore we have used the temperature dependences of the corresponding sodium salts as an approximation. The anion mixing parameters are available from the analogous system⁽⁸⁾ with Na^+ instead of K^+ . These various parameters are listed in Table 8.

The least-squares calculation included the results of MacInnes and Belcher⁽¹⁰⁾ and comprised 77 data points at ionic strengths from 0.002 to 1.2 mol kg^{-1} , and at 273.15, 298.15, and 318.15 K. The newly determined parameters are

$$\beta_{K,HCO_3}^{(0)} = -0.022 \pm 0.014$$

$$\beta_{K,HCO_3}^{(1)} = 0.09 \pm 0.04$$

These β values are within the overall pattern found by Pitzer and Mayorga⁽²¹⁾ for other 1-1 electrolytes.

The standard error of fit was 0.7 mV which is somewhat higher than the 0.4 mV found for the corresponding data for the sodium bicarbonate system. The deviations are often in the same direction for measurements of a single series but are not regular with respect to chloride-bicarbonate ratio. Our only explanation is that the potassium bicarbonate sample was subject to more deviation from exact $KHCO_3$ composition by excess H_2O or loss of H_2O and CO_2 than was the sodium bicarbonate. The agreement is, nevertheless, reasonably good and gives us confidence that the final results are quite accurate.

While the parameters given for K_2CO_3 by Sarbar, et al.,⁽²³⁾ are probably accurate enough for the present purpose, it may be noted that further work is needed for that system. Accurate measurements are needed for dilute solutions and the hydrolysis equilibrium should be considered in interpretation (it was ignored by Sarbar, et al.).

The parameters here obtained were used to calculate values for γ , the mean molal activity coefficient of $KHCO_3$, and ϕ , the osmotic coefficient of the solution, at 278.15 K, 298.15 K and 318.15 K and selected molalities. These values are listed in Table 9. Also given are γ^{st} , the stoichiometric activity coefficient of $KHCO_3$, and γ^{tr} , the trace activity coefficient of

KHCO_3 in solutions of KCl . The stoichiometric activity coefficient is defined by

$$\gamma^{\text{st}} = \left(\frac{m_{\text{HCO}_3}}{m_{\text{HCO}_3}^{\text{st}}} \right)^{1/2} \gamma \quad (13)$$

wherein $m_{\text{HCO}_3}^{\text{st}}$ and m_{HCO_3} are the stoichiometric and equilibrium molalities of HCO_3^- , respectively. The precision of all quantities in Table 9 is 0.002, except at 318.15 K where a precision of 0.004 is indicated. The activity coefficient is also given in figure 1.

There are no published values of the KHCO_3 activity coefficient against which the values of Table 9 may be compared. However, it is useful to note that $\gamma(\text{KHCO}_3)$ is everywhere smaller than $\gamma(\text{NaHCO}_3)$, which may be expected on the basis of a similar comparison for other anions.

Unlike the sodium systems, reliable measurements of the enthalpy and heat capacity of KHCO_3 and K_2CO_3 solutions are not available. Also lacking are measurements leading directly to the K_2CO_3 activity coefficient, which may be obtained from experiments similar to those of Harned and Scholes.⁽²⁵⁾ These measurements, even if made only at 298.15 K, with the experimental data presented herein, would significantly increase thermodynamic understanding of the KHCO_3 and K_2CO_3 aqueous systems in the important 273.15 - 323.15 K temperature range.

Also of great importance in understanding the chemistry of natural waters is a knowledge of the activity coefficients of aqueous $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$. Work is currently being undertaken to determine these quantities at 298.15 K using cells similar to (2) above.

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Table 1. Summary of the Information Necessary to Calculate $-\log_{10}K_1$ for the $\text{KHCO}_3(m_1) + \text{KCl}(m_2) + \text{H}_2\text{O}$ System

<u>Mol % $\text{CO}_2 = 80.163$, Mol % $\text{H}_2 = 19.837$; Approx. Ratio $(m_1/m_2) = 1:1$</u>			
T/K	278.15	298.15	
B.P./kPa	96.259	96.309	
P_{total} /kPa	95.387	43.148	
E_c/V	0.02011	0.02186	
<u>Mol % $\text{CO}_2 = 19.655$, Mol % $\text{H}_2 = 80.345$; Approx. Ratio $(m_1/m_2) = 2:1$</u>			
T/K	278.15	298.15	
B.P./kPa	96.127	96.259	
P_{total} /kPa	95.256	93.087	
E_c/V	0.003363	0.003901	
<u>Mol % $\text{CO}_2 = 19.655$, Mol % $\text{H}_2 = 80.345$; Approx. Ratio $(m_1/m_2) = 3:1$</u>			
T/K	278.15	298.15	318.15
B.P./kPa	96.988	96.725	96.593
P_{total} /kPa	96.127	93.553	87.048
E_c/V	0.003254	0.003836	0.004443

Table 1 (continued)

<u>Mol % CO₂ = 19.655, Mol % H₂ = 80.345; Approx. Ratio (m₁/m₂) = 4:1</u>		
T/K	278.15	298.15
B.P./kPa	97.191	97.191
P _{total} /kPa	96.320	94.019
E _c /V	0.003229	0.003772
<u>Mol % CO₂ = 19.655, Mol % H₂ = 80.345; Approx. Ratio (m₁/m₂) = 6:1</u>		
T/K		298.15
B.P./kPa		96.796
P _{total} /kPa		93.624
E _c /V		0.003826

Table 2. Quantities Leading to the Calculation of $-\log_{10}K_1$ for Solutions of $\text{KHCO}_3(m_1) + \text{KCl}(m_2) + \text{H}_2\text{O}$ at 278.15 and 298.15 K ($m_1/m_2 \approx 1:1$; Mol % $\text{CO}_2 = 80.163$)

$m_1/\text{mol kg}^{-1}$	0.052840	0.048898	0.042334	0.037450	0.027517	0.015223
$m_2/\text{mol kg}^{-1}$	0.054390	0.050430	0.043696	0.038654	0.027370	0.015713
<u>T/K = 278.15</u>						
E_{obs}/V	0.64510	0.64510	0.64525	0.64533	0.64555	0.64578
$-\log_{10}S$	1.1935	1.1930	1.1925	1.1919	1.1908	1.1900
$(E_{\text{obs}} + E_c - E^\circ)/k$	7.8077	7.8077	7.8104	7.8119	7.8158	7.8200
$\log_{10}SP(\text{CO}_2)$	-1.3157	-1.3152	-1.3147	-1.3141	-1.3130	-1.3122
$-\log_{10}K_1'$	6.5058	6.5062	6.5095	6.5115	6.5165	6.5216
<u>T/K = 298.15</u>						
E_{obs}/V	0.67028	0.67032	0.67047	0.67062	0.67092	0.67124
$(E_{\text{obs}} + E_c - E^\circ)/k$	7.9373	7.9380	7.9406	7.9431	7.9482	7.9536
$-\log_{10}S$	1.4735	1.4732	1.4730	1.4727	1.4718	1.4710
$\log_{10}SP(\text{CO}_2)$	-1.6061	-1.6058	-1.6056	-1.6053	-1.6044	-1.6036
$-\log_{10}K_1'$	6.3450	6.3459	6.3488	6.3515	6.3576	6.3637

Table 3. Quantities Leading to the Calculation of $-\log_{10}K_1$ for Solutions of $\text{KHCO}_3(m_1)$ + $\text{KCl}(m_2)$ + H_2O at 278.15 and 298.15 K ($m_1/m_2 \approx 2:1$ Ratio; Mol % $\text{CO}_2 = 19.655$)

$m_1/\text{mol kg}^{-1}$	0.67085	0.59765	0.52249	0.30309	0.19368	0.13098
$m_2/\text{mol kg}^{-1}$	0.33151	0.29928	0.26166	0.15178	0.096995	0.065547
<u>T/K = 278.15</u>						
E_{obs}/V	0.70817	0.70844	0.70955	0.71112	0.71155	0.71229
$-\log_{10}S$	1.2185	1.2158	1.2120	1.2022	1.1970	1.1945
$(E_{\text{obs}} + E_c - E^\circ)/k$	8.6471	8.6520	8.6721	8.7005	8.7083	8.7217
$\log_{10}^{\text{SP}}(\text{CO}_2)$	-1.9518	-1.9491	-1.9453	-1.9355	-1.9303	-1.9278
$-\log_{10}K_1'$	6.3892	6.4025	6.4265	6.4646	6.4777	6.4936
<u>T/K = 298.15</u>						
E_{obs}/V	0.73769	0.73826	0.73912	0.74122	0.74186	0.74218
$-\log_{10}S$	1.4920	1.4900	1.4866	1.4799	1.4762	1.4643
$(E_{\text{obs}} + E_c - E^\circ)/k$	8.7733	8.7829	8.7975	8.8330	8.8438	8.8492
$\log_{10}^{\text{SP}}(\text{CO}_2)$	2.2353	2.2333	2.2299	2.2232	2.2195	2.2076
$-\log K_1'$	6.2319	6.2492	6.2673	6.3095	6.3240	6.3413

Table 4. Quantities Leading to the Calculation of $-\log_{10} K_1$ for Solutions of $\text{KHCO}_3(m_1) + \text{KCl}(m_2) + \text{H}_2\text{O}(m_1/m_2 \approx 3:1 \text{ Ratio; Mol } \% \text{ CO}_2 = 19.655)$

$m_1/\text{mol kg}^{-1}$	0.74277	0.51479	0.44768	0.40465	0.28162	0.16052	0.11681	0.055480
$m_2/\text{mol kg}^{-1}$	0.25029	0.17347	0.15085	0.13635	0.094897	0.054091	0.039362	0.018695
<u>T/K = 278.15</u>								
E_{obs}/V		0.71715	0.71790		0.71961	0.72039		0.72127
$-\log_{10} S$		1.2044	1.2027		1.1981	1.1935		1.1900
$(E_{\text{obs}} + E_c - E^\circ)/k$		8.8078	8.8214		8.8524	8.8665		8.8825
$\log_{10} \text{SP}(\text{CO}_2)$		-1.9337	-1.9320		-1.9274	-1.9228		-1.9193
$-\log_{10} K_1'$		6.4017	6.4170		6.4526	6.4713		6.4908
<u>T/K = 298.15</u>								
E_{obs}/V	0.74431	0.74716	0.74782	0.74830	0.75019	0.75135	0.75246	0.75244
$-\log_{10} S$	1.4867	1.4814	1.4796	1.4788	1.4763	1.4734	1.4726	1.4713
$(E_{\text{obs}} + E_c - E^\circ)/k$	8.8841	8.9323	8.9434	8.9515	8.9835	9.0031	9.0219	9.0215
$\log_{10} \text{SP}(\text{CO}_2)$	-2.2278	-2.2225	-2.2207	-2.2199	-2.2174	-2.2145	-2.2137	-2.2124
$-\log_{10} K_1'$	6.1839	6.2374	6.2503	6.2592	6.2937	6.3162	6.3358	6.3367
<u>T/K = 318.15</u>								
E_{obs}/V		0.77698	0.77819	0.77937	0.78157			
$-\log_{10} S$		1.7000	1.6988	1.6977	1.6950			
$(E_{\text{obs}} + E_c - E^\circ)/k$		9.0748	0.0939	0.1126	9.1475			
$\log_{10} \text{SP}(\text{CO}_2)$		-2.4724	-2.4712	-2.4701	-2.4674			
$-\log_{10} K_1'$		6.1300	6.1503	6.1701	6.2050			

Table 5. Quantities Leading to the Calculation of $-\log_{10}K_1$ for Solutions of $\text{KHCO}_3(m_1) + \text{KCl}(m_2) + \text{H}_2\text{O}$ ($m_1/m_2 \approx 4:1$ Ratio; Mol % $\text{CO}_2 = 19.655$)

$m_1/\text{mol kg}^{-1}$	0.98557	0.88078	0.75570	0.67532	0.46425	0.28658	0.18452	0.090147
$m_2/\text{mol kg}^{-1}$	0.24985	0.22328	0.19158	0.17120	0.11769	0.072652	0.046779	0.022853
<u>T/K = 278.15</u>								
E_{obs}/V	0.72229	0.72299	0.72366	0.72401	0.72569	0.72649	0.72727	0.72775
$-\log_{10}S$	1.2110	1.2086	1.2067	1.2038	1.1989	1.1950	1.1926	1.1904
$(E_{\text{obs}} + E_c - E^\circ)/k$	8.9005	8.9131	8.9253	8.9317	8.9521	8.9766	8.9908	8.9994
$\log_{10}\text{SP}(\text{CO}_2)$	-1.9396	-1.9372	-1.9342	-1.9324	-1.9275	-1.9236	-1.9212	-1.9190
$-\log_{10}K_1'$	6.3649	6.3799	6.3951	6.4033	6.4386	6.4570	6.4736	6.4844
<u>T/K = 298.15</u>								
E_{obs}/V	0.75207	0.75370	0.75412	0.75495	0.75650	0.75821	0.75914	0.76022
$-\log_{10}S$	1.4876	1.4847	1.4825	1.4813	1.4785	1.4738	1.4732	1.4715
$(E_{\text{obs}} + E_c - E^\circ)/k$	9.0143	9.0417	9.0488	9.0629	9.0891	9.1180	9.1337	9.1519
$\log_{10}\text{SP}(\text{CO}_2)$	-2.2297	-2.2237	-2.2215	-2.2203	-2.2175	-2.2128	-2.2122	-2.2105
$-\log_{10}K_1'$	6.1886	6.2220	6.2313	6.2466	6.2756	6.3092	6.3255	6.3454

Table 6. Quantities Leading to the Calculation of $-\log_{10}K_1$ for Solutions of $\text{KHCO}_3(m_1) + \text{KCl}(m_2) + \text{H}_2\text{O}$ at 298.15 K ($m_1/m_2 \approx 6:1$, Mol % $\text{CO}_2 = 19.655$)

$m_1/\text{mol kg}^{-1}$	0.53868	0.41706	0.28919	0.15782	0.053149
$m_2/\text{mol kg}^{-1}$	0.091413	0.070775	0.049530	0.026783	0.008943
<u>T/K = 298.15</u>					
E_{obs}/V	0.76511	0.76614	0.76776	0.76894	0.77075
$-\log_{10}S$	1.4759	1.4746	1.4732	1.4718	1.4707
$(E_{\text{obs}} + E_c - E^\circ)/k$	9.2355	9.2529	9.2803	9.3003	9.3309
$\log_{10}SP(\text{CO}_2)$	-2.2168	-2.2155	-2.2141	-2.2127	-2.2116
$-\log_{10}K_1'$	6.2484	6.2671	6.2999	6.3173	6.3453

Table 7. Extrapolated values of $-\log_{10} K_1$ for $\text{KHCO}_3(m_1) + \text{KCl}(m_2) + \text{H}_2\text{O}$ at 278.15, 298.15 and 318.15 K.

m_1/m_2	mol % CO_2	$-\log_{10} K_1$	std. dev.
<u>T = 278.15 K</u>			
1:1	80.163	6.528	0.006
2:1	19.655	6.518	0.006
3:1	19.655	6.503	0.004
4:1	19.655	6.497	0.002
<u>T = 298.15 K</u>			
1:1	80.163	6.371	0.007
2:1	19.655	6.366	0.005
3:1	19.655	6.355	0.005
4:1	19.655	6.357	0.003
6:1	19.655	6.353	0.004
<u>T = 318.15 K</u>			
3:1	19.655	6.298	0.009

Table 8. Ion Interaction Parameters at 298.15 K

	K_2CO_3	$KHCO_3$	KCl
$\beta^{(0)}$	0.138 ^a	-0.022 ± 0.014 ^b	0.04835 ^c
$\beta^{(1)}$	1.481 ^a	0.09 ± 0.04 ^b	0.2122 ^c
$\frac{\partial \beta^{(0)}}{\partial T} \times 10^3$	1.788 ^d	0.996 ^d	0.5794 ^e
$\frac{\partial \beta^{(1)}}{\partial T} \times 10^3$	2.051 ^d	1.104 ^d	1.071 ^e

$$\theta_{HCO_3, Cl} = 0.0359^d \quad \theta_{CO_3, Cl} = -0.092^d$$

^a Taken from Sarbar, et al.⁽²³⁾

^b Determined in this research.

^c Taken from Pitzer and Mayorga⁽²¹⁾

^d Taken from Peiper and Pitzer⁽⁸⁾

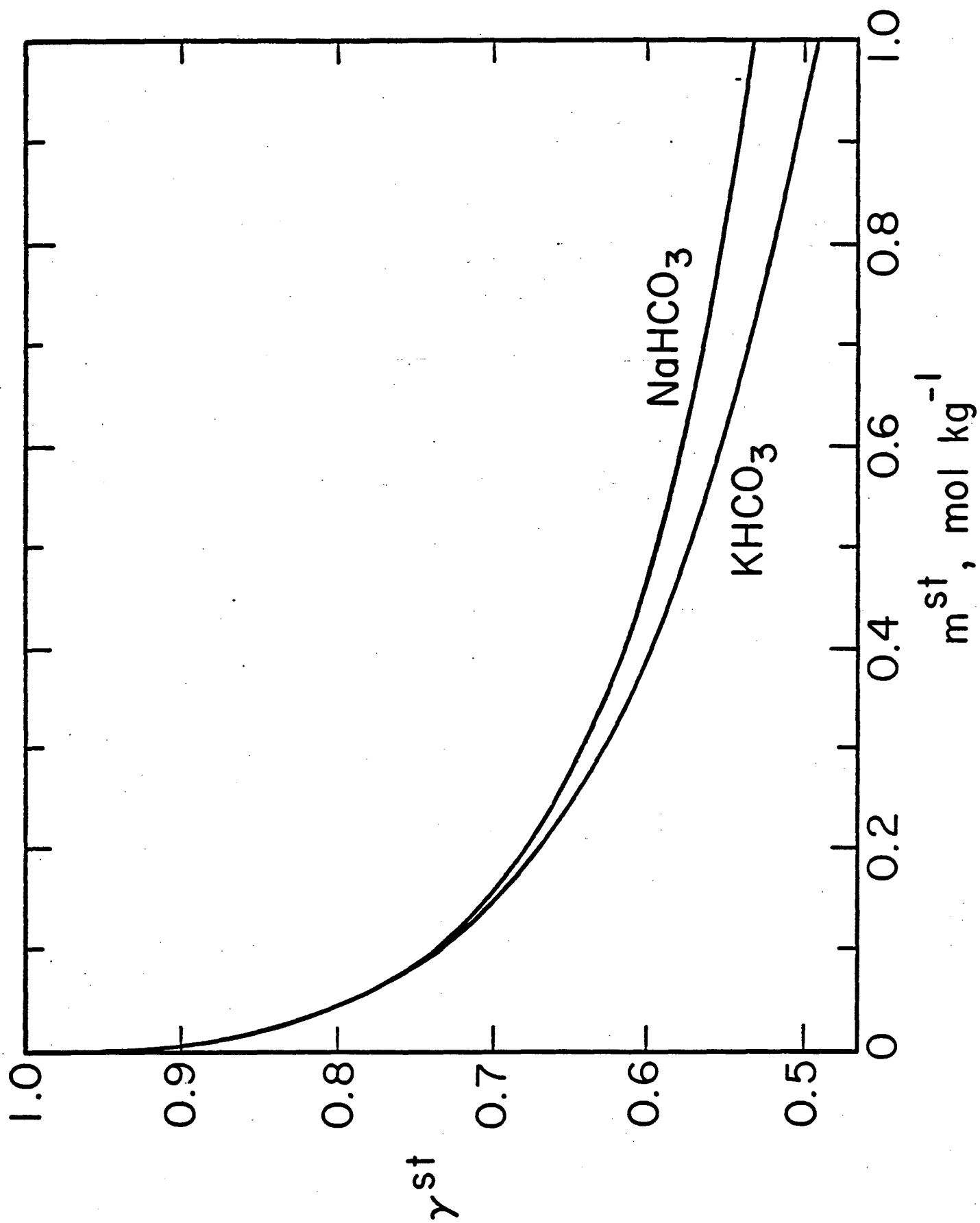
^e Taken from Silvester and Pitzer⁽²²⁾

Table 9. Activity and Osmotic Coefficients for Solutions of KHCO_3 at 278.15 K, 298.15 K and 318.15 K. γ , γ^{st} and ϕ are given for nominally pure KHCO_3 solutions; γ^{tr} is given for a trace amount of KHCO_3 in a solution of KCl . γ^{st} is the stoichiometric activity coefficient⁽⁸⁾ and γ^{tr} is the trace activity coefficient.

I	278.15 K				298.15 K				318.15 K			
	γ	γ^{st}	γ^{tr}	ϕ	γ	γ^{st}	γ^{tr}	ϕ	γ	γ^{st}	γ^{tr}	ϕ
0.001	0.965	0.956	0.966	0.989	0.964	0.954	0.965	0.988	0.963	0.953	0.964	0.988
0.002	0.952	0.942	0.953	0.984	0.951	0.941	0.951	0.983	0.949	0.939	0.950	0.983
0.005	0.926	0.917	0.928	0.975	0.925	0.915	0.926	0.974	0.922	0.912	0.923	0.974
0.010	0.900	0.890	0.902	0.966	0.897	0.887	0.900	0.965	0.894	0.884	0.897	0.964
0.020	0.865	0.856	0.869	0.954	0.862	0.852	0.866	0.954	0.859	0.848	0.863	0.952
0.050	0.805	0.796	0.813	0.933	0.802	0.792	0.810	0.932	0.798	0.788	0.806	0.931
0.10	0.748	0.739	0.762	0.912	0.745	0.736	0.759	0.912	0.742	0.732	0.755	0.912
0.20	0.680	0.672	0.703	0.886	0.680	0.671	0.702	0.888	0.678	0.668	0.699	0.890
0.30	0.636	0.628	0.667	0.868	0.638	0.629	0.667	0.873	0.638	0.629	0.665	0.876
0.40	0.602	0.594	0.640	0.854	0.606	0.598	0.642	0.860	0.608	0.599	0.642	0.865
0.50	0.575	0.568	0.619	0.842	0.581	0.573	0.622	0.850	0.585	0.576	0.623	0.856
0.60	0.552	0.545	0.601	0.831	0.560	0.552	0.606	0.841	0.565	0.556	0.609	0.849
0.70	0.533	0.526	0.587	0.821	0.542	0.535	0.593	0.833	0.549	0.541	0.597	0.843
0.80	0.515	0.509	0.574	0.812	0.526	0.519	0.581	0.825	0.534	0.526	0.587	0.837
0.90	0.499	0.493	0.563	0.803	0.511	0.504	0.572	0.818	0.521	0.513	0.578	0.832
1.00	0.484	0.478	0.553	0.794	0.498	0.491	0.563	0.812	0.510	0.502	0.571	0.827

Figure Captions

Figure 1. The stoichiometric activity coefficients of NaHCO_3 and KHCO_3 at 298.15 K. Values of γ^{st} for NaHCO_3 are taken from reference (8); m^{st} is the stoichiometric molality of HCO_3^- .



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