LBL-13482
Preprint

# Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

## EARTH SCIENCES DIVISION

Submitted to the Journal of Chemical Thermodynamics

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Rabindra N. Roy, James J. Gibbons, Mark D. Wood,
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Kenneth S. Pitzer

October 1981

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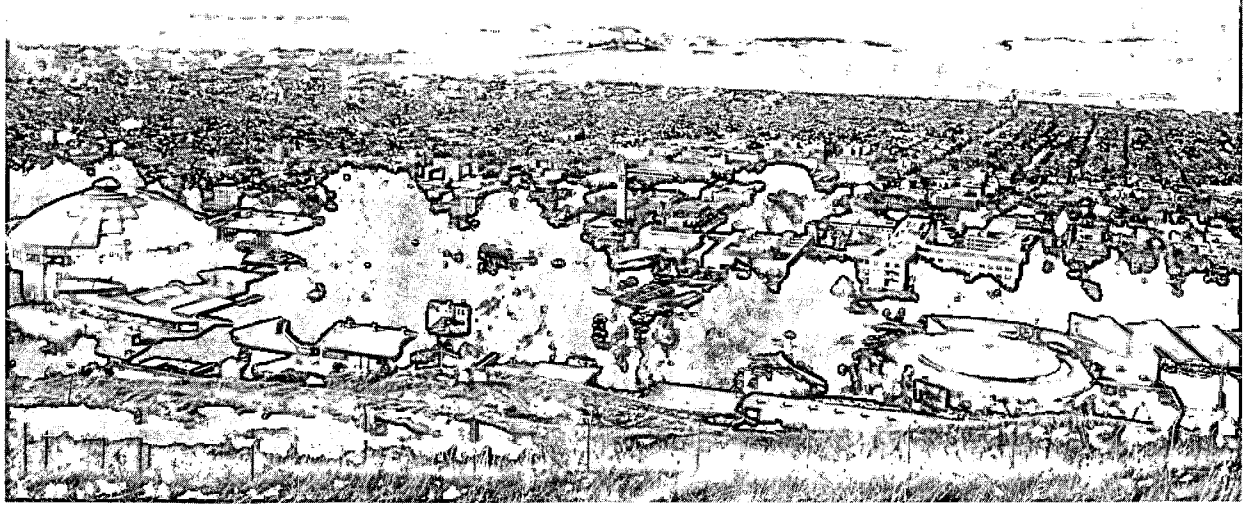

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

LBL-13482 c.2

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

Rabindra N. Roy*, James J. Gibbons, Mark D. Wood
and
Rick W. Williams

Department of Chemistry
Drury College
Springfield, Missouri 65802 U.S.A.

and

J. Christopher Peiper and Kenneth S. Pitzer

Department of Chemistry
and
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720 U.S.A.

"Prepared for 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 W-7405-ENG-48."

* Also visiting scientist at the Lawrence Berkeley Laboratory while on sabbatical leave from Drury College

Abstract

The electrochemical cell without liquid junction $Pt,H_2/KHCO_3(m_1)$, $KC\ell(m_2)$, $CO_2(m_3)/AgC\ell,Ag$ 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 $KC\ell$ 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 $pK_1$ 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 $NaHCO_3 + NaC\ell + H_2O$ 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 $KC\ell$.

## 1. Introduction

The importance of thermodynamic studies involving carbonic acid and its mixtures with strong electrolytes (e.g., $NaC\ell$, $KC\ell$, $CaC\ell_2$ 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 $Na^+$, $C\ell^-$, $HCO_3^-$, $CO_3^=$, and $CO_2$ or $H_2CO_3$. 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 $CO_2(g)$ and first ionization of carbonic acid can be expressed as

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

$$CO_2(aq) + H_2O(\ell) = H^+(aq) + HCO_3^-(aq) \tag{1b}$$

with the thermodynamic equations

$$K_s = m(CO_2)\gamma(CO_2)/f(CO_2) \tag{1c}$$

and

$$K_1 = \frac{m(H^+)m(HCO_3^-)\gamma(H^+)\gamma(HCO_3^-)}{a(H_2O)m(CO_2)\gamma(CO_2)} \tag{1d}$$

where $m(CO_2)$ is the total molality of unionized $CO_2$ in the solution; $\gamma(H^+)$, $\gamma(HCO_3^-)$ and $\gamma(CO_2)$ are the activity coefficients of $H^+$, $HCO_3^-$ and $CO_2$, respectively. Also $a(H_2O)$ and $f(CO_2)$ 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

$$Pt(s),\ H_2(g),\ CO_2(g)\ |\ KHCO_3(m_1),\ KC\ell(m_2),\ CO_2(m_3)\ |\ AgC\ell(s),\ Ag(s) \tag{2}$$

with reaction

$$\frac{1}{2}H_2(g) + AgC\ell(s) + HCO_3^-(aq) = C\ell^-(aq) + Ag(s) + H_2O(liq) + CO_2(g) \tag{3}$$

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

$$E = E^\circ - \frac{RT}{F}\left[\ell n(K_1K_s) + \ell n\left\{\frac{a(H_2O)f(CO_2)}{f^{1/2}(H_2)}\right\} + \ell n\left\{\frac{m(C\ell^-)\gamma(C\ell^-)}{m(HCO_3^-)\gamma(HCO_3^-)}\right\}\right] \tag{4}$$

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 $f(H_2)$ represents the fugacity of $H_2(g)$ while $m(C\ell^-)$ and $m(HCO_3^-)$ are the equilibrium molalities of $C\ell^-$ and $HCO_3^-$, with $m(C\ell^-) = m_2$ and $m(HCO_3^-) \approx m_1$. Also, $E° = E°(Ag,AgC\ell)$, 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 $R/F = 8.61736$ (abs V)$\cdot K^{-1}$.

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

$$Ag,AgC\ell|KC\ell,KHCO_3,CO_2|glass|buffer + KC\ell|AgC\ell,Ag \qquad (5)$$

where $CO_2$ in the solution is in equllibrium 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 $C\ell^-$ and $HCO_3^-$ molalities. Also, they maintained the partial pressure of $CO_2$ above the solution near 10 kPa. Their value of $pK_1$ 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 $E° = E°(Ag,AgC\ell) - E°$ (glass). For cells (2) and (5), the quantity determined by extrapolation of the

difference E - E° 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

$$2HCO_3^- = CO_3^= + H_2O + CO_2 \qquad (6)$$

This reaction reduces the molality of $HCO_3^-$. Also the presence of the $CO_3^=$ 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 $E^\circ$, 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 $H_2$ and $CO_2$ were calculated and used without adjustment as the fugacities. The effect of the $H_2$ fugacity was introduced as the term $E_c = (-RT/2F)\ \ell n\ f(H_2)$. 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

$$-\log_{10}K_1' = -[\log_{10}K_1 + \log_{10}(\gamma_{C\ell}/\gamma_{HCO_3})]$$

$$= [E+E_c-E^\circ(Ag,AgC\ell)]/k + \log_{10}SP(CO_2) + \log_{10}(m_2/m_1) \quad (7)$$

where $k = \ell n(10)\ RT/F$ and the molality of dissolved $CO_2$ 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 $CO_2$ 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]

$$S = \frac{1.977}{44.01} \cdot \frac{\alpha}{d_{H_2O}} \qquad (8)$$

where the actual density of $CO_2$ at 273.15 K is 1.977 g-lit$^{-1}$ and $d_{H_2O}$ 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 $pK_1$. 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 $pK_1 = 6.360$ 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 parmeters for $KC\ell$ 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 $\gamma(C\ell^-)/\gamma(HCO_3^-)$ 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 $CO_3^=$; 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 $\gamma(C\ell^-)/\gamma(HCO_3^-)$ in equation (9) and for $a(H_2O)$ in equation (10).

$$\ell n \frac{\gamma(C\ell^-)}{\gamma(HCO_3^-)} = 2\ \ell n\ \gamma(KC\ell) - 2\ \ell n\ \gamma(KHCO_3)$$

$$= 2\ m(K)(B_{K,C\ell} - B_{K,HCO_3})$$

$$+ 2(m(HCO_3) - m(C\ell))\ \theta_{HCO_3,C\ell} \qquad (9)$$

$$+ \quad 2m(CO_3)(\theta_{CO_3,C\ell} - \theta_{CO_3,HCO_3})$$

and

$$\frac{1000}{M_W} \ln a(H_2\mathring{O}) = (\Sigma m_i)\phi$$

$$= \Sigma m_i + 2If^{\phi}$$

$$+ 2m(K)m(CO_3)\left[\beta^{(0)}_{K,CO_3} + \beta^{(1)}_{K,CO_3} e^{-2I^{1/2}}\right]$$

$$+ 2m(K)m(HCO_3)\left[\beta^{(0)}_{K,HCO_3} + \beta^{(1)}_{K,HCO_3} e^{-2I^{1/2}}\right]$$

$$+ 2m(K)m(C\ell)\left[\beta^{(0)}_{K,C\ell} + \beta^{(1)}_{K,C\ell} e^{-2I^{1/2}}\right] \qquad (10)$$

$$+ 2m(CO_3)m(HCO_3)\ \theta_{CO_3,HCO_3}$$

$$+ 2m(CO_3)m(C\ell)\ \theta_{CO_3,C\ell}$$

$$+ 2m(HCO_3)m(C\ell)\ \theta_{HCO_3,C\ell}.$$

In equations (9) and (10),

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

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

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

pressures; at 298.15 K, $A_\phi = 0.391_5$. Also, $M_w$ is the formula weight of water, taken as 18.01533 g $mol^{-1}$, I is the molal ionic strength, and $\Sigma m_i$ 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 prinicple, 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

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

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

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 $\gamma$, the mean molal activity coefficient of $KHCO_3$, and $\phi$, 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 $\gamma^{st}$, the stoichiometric activity coefficient of $KHCO_3$, and $\gamma^{tr}$, the trace activity coefficient of

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

$$\gamma^{st} = \left(\frac{m_{HCO_3}}{m^{st}_{HCO_3}}\right)^{1/2} \gamma \qquad (13)$$

wherein $m^{st}_{HCO_3}$ 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 $\gamma(KHCO_3)$ is everywhere smaller than $\gamma(NaHCO_3)$, 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 $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. Work is currently being undertaken to determine these quantities at 298.15 K using cells similar to (2) above.

ACKNOWLEDGMENT

The research at Drury College was supported by NIH 1 RO 1 GM 26809-03 BMT and by the Petroleum Research Fund, administered by the American Chemical Society ACS-PRF #12520-B5. The authors are grateful to high school students Janette, Laurie, Shelley, Lenny, and Howard (Project Seed).

The research at the University of California 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 W-7405-ENG-48.

We thank Dr. R. N. Goldberg for communicating the results for $K_2CO_3$ in advance of publication.

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Table 1. Summary of the Information Necessary to Calculate $-\log_{10}K_1$ for the $KHCO_3(m_1) + KC\ell(m_2) + H_2O$ System

| | | | |
|---|---|---|---|
| | Mol % $CO_2$ = 80.163, Mol % $H_2$ = 19.837; Approx. Ratio $(m_1/m_2)$ = 1:1 | | |
| 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 | |
| | Mol % $CO_2$ = 19.655, Mol % $H_2$ = 80.345; Approx. Ratio $(m_1/m_2)$ = 2:1 | | |
| 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 | |
| | Mol % $CO_2$ = 19.655, Mol % $H_2$ = 80.345; Approx. Ratio $(m_1/m_2)$ = 3:1 | | |
| 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)

| | Mol % $CO_2$ = 19.655, Mol % $H_2$ = 80.345; Approx. Ratio ($m_1/m_2$) = 4:1 | |
|---|---|---|
| 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 |

| | Mol % $CO_2$ = 19.655, Mol % $H_2$ = 80.345; Approx. Ratio ($m_1/m_2$) = 6:1 |
|---|---|
| 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 $KHCO_3(m_1)$ + $KC\ell(m_2)$ + $H_2O$ at 278.15 and 298.15 K ($m_1/m_2 \approx 1:1$; Mol % $CO_2$ = 80.163)

| | | | | | | |
|---|---|---|---|---|---|---|
| $m_1$/mol kg$^{-1}$ | 0.052840 | 0.048898 | 0.042334 | 0.037450 | 0.027517 | 0.015223 |
| $m_2$/mol kg$^{-1}$ | 0.054390 | 0.050430 | 0.043696 | 0.038654 | 0.027370 | 0.015713 |
| T/K = 278.15 | | | | | | |
| $E_{obs}$/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 |
| $(E_{obs}+E_c-E°)/k$ | 7.8077 | 7.8077 | 7.8104 | 7.8119 | 7.8158 | 7.8200 |
| $\log_{10}SP(CO_2)$ | -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 |
| T/K = 298.15 | | | | | | |
| $E_{obs}$/V | 0.67028 | 0.67032 | 0.67047 | 0.67062 | 0.67092 | 0.67124 |
| $(E_{obs}+E_c-E°)/k$ | 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 |
| $\log_{10}SP(CO_2)$ | -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 $KHCO_3(m_1)$ + $KC\ell(m_2)$ + $H_2O$ at 278.15 and 298.15 K ($m_1/m_2$ ≈ 2:1 Ratio; Mol % $CO_2$ = 19.655)

| | | | | | | |
|---|---|---|---|---|---|---|
| $m_1$/mol $kg^{-1}$ | 0.67085 | 0.59765 | 0.52249 | 0.30309 | 0.19368 | 0.13098 |
| $m_2$/mol $kg^{-1}$ | 0.33151 | 0.29928 | 0.26166 | 0.15178 | 0.096995 | 0.065547 |
| T/K = 278.15 | | | | | | |
| $E_{obs}$/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 |
| $(E_{obs}+E_c-E°)/k$ | 8.6471 | 8.6520 | 8.6721 | 8.7005 | 8.7083 | 8.7217 |
| $\log_{10}SP(CO_2)$ | -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 |
| T/K = 298.15 | | | | | | |
| $E_{obs}$/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 |
| $(E_{obs}+E_c-E°)/k$ | 8.7733 | 8.7829 | 8.7975 | 8.8330 | 8.8438 | 8.8492 |
| $\log_{10}SP(CO_2)$ | 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 $KHCO_3(m_1)$ + $KC\ell(m_2)$ + $H_2O$($m_1/m_2$ ≈ 3:1 Ratio; Mol % $CO_2$ = 19.655)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $m_1$/mol kg$^{-1}$ | 0.74277 | 0.51479 | 0.44768 | 0.40465 | 0.28162 | 0.16052 | 0.11681 | 0.055480 |
| $m_2$/mol kg$^{-1}$ | 0.25029 | 0.17347 | 0.15085 | 0.13635 | 0.094897 | 0.054091 | 0.039362 | 0.018695 |
| T/K = 278.15 | | | | | | | | |
| $E_{obs}$/V | | 0.71715 | 0.71790 | | 0.71961 | 0.72039 | | 0.72127 |
| $-\log_{10}S$ | | 1.2044 | 1.2027 | | 1.1981 | 1.1935 | | 1.1900 |
| $(E_{obs}+E_c-E°)/k$ | | 8.8078 | 8.8214 | | 8.8524 | 8.8665 | | 8.8825 |
| $\log_{10}SP(CO_2)$ | | -1.9337 | -1.9320 | | -1.9274 | -1.9228 | | -1.9193 |
| $-\log_{10}K_1'$ | | 6.4017 | 6.4170 | | 6.4526 | 6.4713 | | 6.4908 |
| T/K = 298.15 | | | | | | | | |
| $E_{obs}$/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 |
| $(E_{obs}+E_c-E°)/k$ | 8.8841 | 8.9323 | 8.9434 | 8.9515 | 8.9835 | 9.0031 | 9.0219 | 9.0215 |
| $\log_{10}SP(CO_2)$ | -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 |
| T/K = 318.15 | | | | | | | | |
| $E_{obs}$/V | | 0.77698 | 0.77819 | 0.77937 | 0.78157 | | | |
| $-\log_{10}S$ | | 1.7000 | 1.6988 | 1.6977 | 1.6950 | | | |
| $(E_{obs}+E_c-E°)/k$ | | 9.0748 | 0.0939 | 0.1126 | 9.1475 | | | |
| $\log_{10}SP(CO_2)$ | | -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 $KHCO_3(m_1)$ + $KC\ell(m_2)$ + $H_2O$ ($m_1/m_2 \approx 4:1$ Ratio; Mol % $CO_2$ = 19.655)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $m_1$/mol kg$^{-1}$ | 0.98557 | 0.88078 | 0.75570 | 0.67532 | 0.46425 | 0.28658 | 0.18452 | 0.090147 |
| $m_2$/mol kg$^{-1}$ | 0.24985 | 0.22328 | 0.19158 | 0.17120 | 0.11769 | 0.072652 | 0.046779 | 0.022853 |
| T/K = 278.15 | | | | | | | | |
| $E_{obs}$/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 |
| $(E_{obs}+E_c-E°)/k$ | 8.9005 | 8.9131 | 8.9253 | 8.9317 | 8.9521 | 8.9766 | 8.9908 | 8.9994 |
| $\log_{10}SP(CO_2)$ | -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 |
| T/K = 298.15 | | | | | | | | |
| $E_{obs}$/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 |
| $(E_{obs}+E_c-E°)/k$ | 9.0143 | 9.0417 | 9.0488 | 9.0629 | 9.0891 | 9.1180 | 9.1337 | 9.1519 |
| $\log_{10}SP(CO_2)$ | -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 $KHCO_3(m_1) + KC\ell(m_2) + H_2O$ at 298.15 K ($m_1/m_2 \approx 6:1$, Mol % $CO_2$ = 19.655)

| | | | | | |
|---|---|---|---|---|---|
| $m_1$/mol kg$^{-1}$ | 0.53868 | 0.41706 | 0.28919 | 0.15782 | 0.053149 |
| $m_2$/mol kg$^{-1}$ | 0.091413 | 0.070775 | 0.049530 | 0.026783 | 0.008943 |
| T/K = 298.15 | | | | | |
| $E_{obs}$/V | 0.76511 | 0.76614 | 0.76776 | 0.76894 | 0.77075 |
| $-\log_{10}S$ | 1.4759 | 1.4746 | 1.4732 | 1.4718 | 1.4707 |
| $(E_{obs}+E_c-E°)/k$ | 9.2355 | 9.2529 | 9.2803 | 9.3003 | 9.3309 |
| $\log_{10}SP(CO_2)$ | -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 $KHCO_3(m_1)$ + $KC\ell(m_2)$ + $H_2O$ at 278.15, 298.15 and 318.15 K.

| $m_1/m_2$ | mol % $CO_2$ | $-\log_{10} K_1$ | std. dev. |
|---|---|---|---|
| T = 278.15 K | | | |
| 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 |
| T = 298.15 K | | | |
| 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 |
| T = 318.15 K | | | |
| 3:1 | 19.655 | 6.298 | 0.009 |

Table 8. Ion Interaction Parameters at 298.15 K

| | $K_2CO_3$ | $KHCO_3$ | $KC\ell$ |
|---|---|---|---|
| $\beta^{(0)}$ | 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] |

$\theta_{HCO_3,C\ell} = 0.0359$[d] $\theta_{CO_3,C\ell} = -0.092$[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]

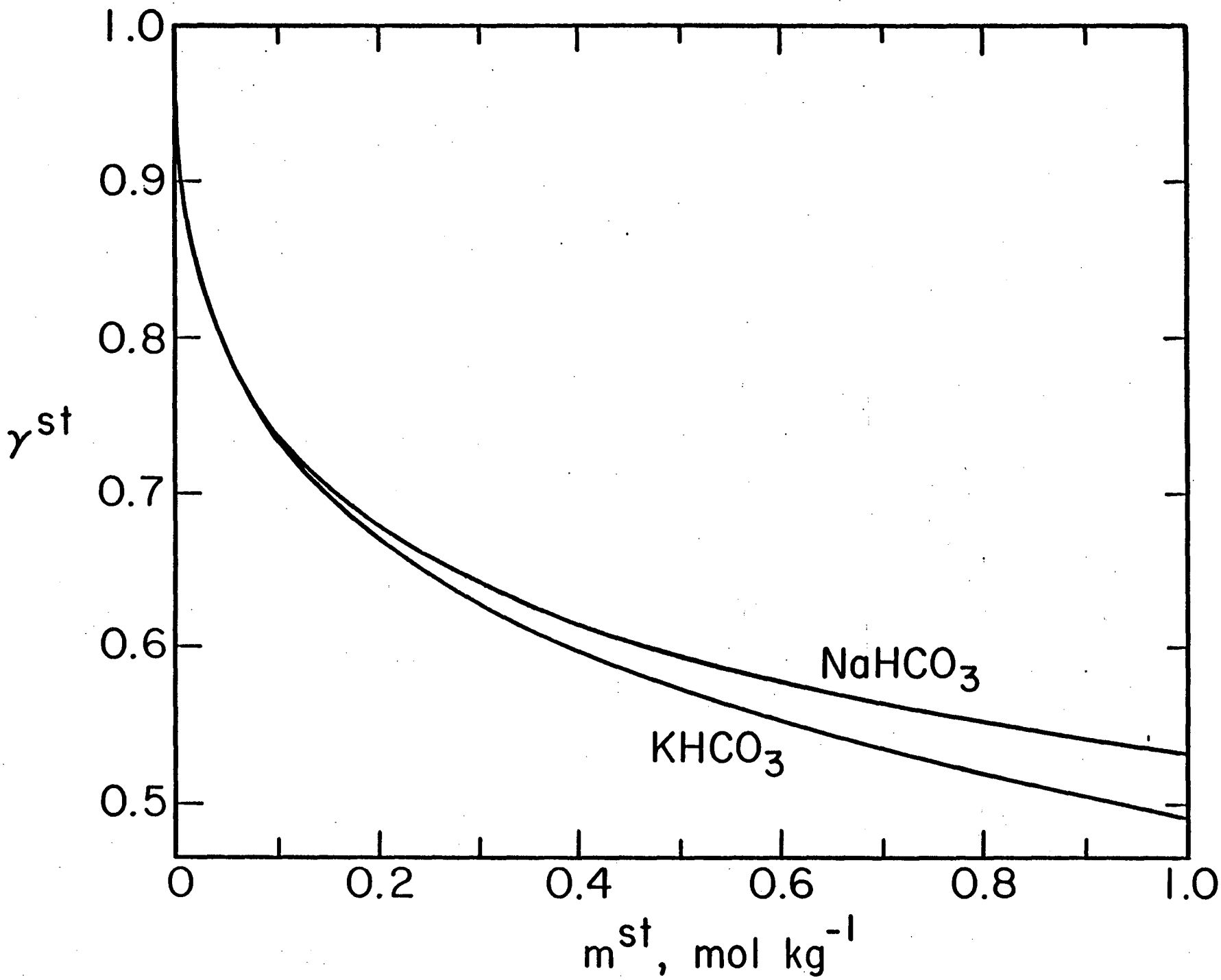
[e] Taken from Silvester and Pitzer[22]

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

| | 278.15 K | | | | 298.15 K | | | | 318.15 K | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I | $\gamma$ | $\gamma^{st}$ | $\gamma^{tr}$ | $\phi$ | $\gamma$ | $\gamma^{st}$ | $\gamma^{tr}$ | $\phi$ | $\gamma$ | $\gamma^{st}$ | $\gamma^{tr}$ | $\phi$ |
| 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 $\gamma^{st}$ for $NaHCO_3$ are taken from reference (8); $m^{st}$ is the stoichiometric molality of $HCO_3^-$.


1.0
0.9
0.8
0.7
0.6
0.5
$\gamma^{st}$
0
0.2
0.4
0.6
0.8
1.0
$m^{st}$, mol $kg^{-1}$
$NaHCO_3$
$KHCO_3$

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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*TECHNICAL INFORMATION DEPARTMENT*
*LAWRENCE BERKELEY LABORATORY*
*UNIVERSITY OF CALIFORNIA*
*BERKELEY, CALIFORNIA 94720*