

Submitted to the Journal of Physical Chemistry

UC-4  
LBL-10298 02  
Preprint

THE ACTIVITY COEFFICIENT OF AQUEOUS  $\text{NaHCO}_3$

Kenneth S. Pitzer and J. Christopher Peiper

December 1979

RECEIVED  
LAWRENCE  
BERKELEY LABORATORY

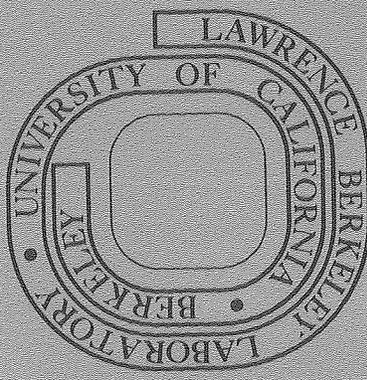
FEB 25 1980

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

LIBRARY AND  
DOCUMENTS SECTION

**TWO-WEEK LOAN COPY**

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 6782.*



LBL-10298 02

## DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

# The Activity Coefficient of Aqueous $\text{NaHCO}_3$

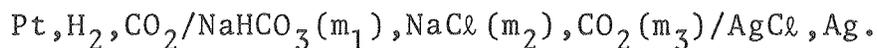
Kenneth S. Pitzer and J. Christopher Peiper

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

## Abstract

The determination of the activity coefficient and related properties of sodium bicarbonate presents special problems because of the appreciable vapor pressure of  $\text{CO}_2$  above such solutions. With the development of reliable equations for the thermodynamic properties of mixed electrolytes, it is possible to determine the parameters for  $\text{NaHCO}_3$  from cell measurements or  $\text{NaCl}$ - $\text{NaHCO}_3$  mixtures. Literature data are analyzed to illustrate the method and provide interim values, but it is noted that further measurements over a wider range of concentrations would yield more definitive results. An estimate is also given for the activity coefficient of  $\text{KHCO}_3$ .

The activity coefficient of aqueous  $\text{NaHCO}_3$  is not known with accuracy comparable to that for other simple salts. The results of Han and Kesler<sup>1</sup> and of Han and Bernardin<sup>2</sup> were based on old experiments of limited precision and were presented only on small graphs which are presumably representative of their accuracy. The isopiestic method, which is widely applicable to most salts, fails (or is complicated) by the significant vapor pressure of  $\text{CO}_2$  as well as  $\text{H}_2\text{O}$  for  $\text{NaHCO}_3$  solutions. In view of the importance of bicarbonate in various solutions with  $\text{Na}^+$  the principal cation, we have sought other methods of determination of the activity coefficient for  $\text{NaHCO}_3$ . The effectiveness of the equations of Pitzer and Kim<sup>3</sup> for mixed electrolytes makes it feasible to use experiments on rather complex mixtures provided all important parameters for other solutes are accurately known. With this strategy in mind we examined the excellent experiments of Harned and Davis<sup>4</sup> and of Harned and Bonner<sup>5</sup> with the electrochemical cell



These investigators extrapolated their results to zero molality to obtain the first dissociation constant of carbonic acid. We shall use the data for finite molalities to determine the ion interaction parameters (virial coefficients) for  $\text{Na}^+$ ,  $\text{HCO}_3^-$  in this mixed electrolyte. This is feasible because the corresponding parameters for  $\text{Na}^+$ ,  $\text{Cl}^-$  are accurately known and any other parameters are expected to have very little effect.

The chemical reaction for this electrochemical cell is



and the corresponding equation for the cell potential is

$$E_A = E_A^0 - \frac{RT}{F} \left[ \ln \left( \frac{m_{\text{Cl}^-} a_{\text{H}_2\text{O}}^f \text{CO}_2}{m_{\text{HCO}_3^-} f_{\text{H}_2}^{1/2}} \right) + \ln \left( \frac{\gamma_{\text{Cl}^-}}{\gamma_{\text{HCO}_3^-}} \right) \right] \quad (1)$$

The standard potential of this cell is related to other quantities by

$$E_A^0 = E^0(\text{Ag}, \text{AgCl}) - (RT/F) \ln(K_1 K_S) \quad (2)$$

where  $E^0(\text{Ag}, \text{AgCl})$  is the standard potential for the Ag, AgCl electrode,  $K_1$  is the first dissociation constant of carbonic acid as usually defined and  $K_S$  is the Henry's law constant for solubility of  $\text{CO}_2$ . The product  $K_1 K_S$  is the equilibrium constant for the reaction



Also  $m_{\text{Cl}^-} = m_2$  and in adequate approximation for these solutions  $m_{\text{HCO}_3^-} = m_1$ .

It is then convenient to rearrange equation (1) to

$$\ln \left( \frac{\gamma_{\text{Cl}^-}}{\gamma_{\text{HCO}_3^-}} \right) - \ln(K_1 K_S) = \ln \left( \frac{m_1 f_{\text{H}_2}^{1/2}}{m_2 a_{\text{H}_2\text{O}}^f \text{CO}_2} \right) + \left( \frac{F}{RT} \right) [E_A - E^0(\text{Ag}, \text{AgCl})] \quad (3)$$

Now all quantities on the right side are known to sufficient accuracy for each experiment. Hence the limit at zero ionic strength yields  $K_1 K_S$ ; this was the original treatment. We shall

use the same data to evaluate also  $\ln(\gamma_{\text{Cl}^-}/\gamma_{\text{HCO}_3^-})$  as a function of  $m_1$  and  $m_2$ .

The solutions investigated by Harned and Bonner<sup>5</sup> do not extend much above an ionic strength of 1M while those of Harned and Davis<sup>4</sup> are more dilute. In this range Pitzer and Mayorga<sup>6</sup> found that third virial coefficients could be neglected. Then equation (17) of Pitzer and Kim<sup>3</sup> yields

$$\ln(\gamma_{\text{Cl}^-}/\gamma_{\text{HCO}_3^-}) = 2m_{\text{Na}}(B_{\text{NaCl}} - B_{\text{NaHCO}_3}) + 2\theta_{\text{Cl},\text{HCO}_3}(m_{\text{HCO}_3^-} - m_{\text{Cl}^-}) \quad (4)$$

where the virial coefficients related to dissolved  $\text{CO}_2$  are omitted since their effect is believed to be negligible. The coefficients  $B_{\text{MX}}$  are given by

$$B_{\text{MX}} = \beta_{\text{MX}}^{(0)} + \beta_{\text{MX}}^{(1)} g(I) \quad (5)$$

$$g(I) = (1/2I)[1 - (1+2I^{1/2}) \exp(-2I^{1/2})] \quad (6)$$

where  $I$  is the ionic strength and  $\beta^{(0)}$  and  $\beta^{(1)}$  are the two parameters primarily related to the short range forces between  $\text{M}^+$  and  $\text{X}^-$  ions. Also we note that in this case

$m_{\text{Na}} = I = m_1 + m_2$  and  $(m_{\text{HCO}_3^-} - m_{\text{Cl}^-}) = m_1 - m_2$ . Then

$$\ln(\gamma_{\text{Cl}^-}/\gamma_{\text{HCO}_3^-}) = 2I[\Delta\beta^{(0)} + \Delta\beta^{(1)} g(I)] + 2(m_1 - m_2)\theta \quad (7)$$

$$\Delta\beta^{(i)} = \beta_{\text{NaCl}}^{(i)} - \beta_{\text{NaHCO}_3}^{(i)}, \quad i = 0, 1 \quad (8)$$

also the subscripts are omitted hereafter from  $\theta$ .

In view of the characteristics of the silver-silver chloride electrode<sup>7</sup> it seemed best to use the  $E^0(\text{Ag}, \text{AgCl})$  values from the

same laboratory.<sup>8</sup> Modern physical constants<sup>9</sup> were used (F and R) with the conversion factor 1.00033 included since the original measurements were in the International volts in use at that time. The resulting factor is  $(R/F) = 8.61451 \times 10^{-5}$  Int.V/K.

All of the experimental values of Harned and Davis<sup>4</sup> and of Harned and Bonner,<sup>5</sup> 678 in all, were included in a least squares calculation. Each set of data at a given temperature was assigned a weight inversely related to the standard deviation of fit of that set treated separately. No experimental point showed excessive deviation, hence none was discarded. Preliminary calculations indicated that the temperature dependence of  $\Delta\beta^{(0)}$ ,  $\Delta\beta^{(1)}$ , and  $\theta$  was negligible over the temperature range 0-50°C and in view of the accuracy of the data. This is consistent with the very small temperature coefficients of such parameters determined by Silvester and Pitzer<sup>10</sup> for similar solutes.

A familiar three-term expression was used for the temperature dependence of  $\ln(K_1K_S)$  with the result

$$\ln(K_1K_S) = -\frac{5023.23}{T} + 119.330 - 21.1469 \ln T \quad (10)$$

The other parameters were found to be

$$\Delta\beta^{(0)} = 0.048_8 \quad (11a)$$

$$\Delta\beta^{(1)} = 0.225_3 \quad (11b)$$

$$\theta_{\text{Cl}_2, \text{HCO}_3} = 0.030 \quad (11c)$$

The statistically indicated uncertainty in each of these last three quantities is 0.01. However,  $\Delta\beta^{(0)}$  and  $\theta$  are rather closely coupled for the presently available data where  $m_1$  is never large. Thus, for the more concentrated solutions I and  $(m_2 - m_1)$  have similar values, and, from equation (7), one notes that  $(\Delta\beta^{(0)} - \theta)$  is determined much more accurately than either parameter individually. This particular uncertainty could be removed if the same type of cell measurements were extended to solutions with higher  $m_1$ ; indeed, with data for still higher  $m$  values, third virial coefficients could also be determined.

If we now introduce the parameters<sup>6</sup> for NaCl,  $\beta^{(0)} = 0.0765$ ,  $\beta^{(1)} = 0.2664$ , the resulting values for NaHCO<sub>3</sub> are

$$\beta_{\text{NaHCO}_3}^{(0)} = 0.027_7 \quad (12)$$

$$\beta_{\text{NaHCO}_3}^{(1)} = 0.041_1 \quad (13)$$

Since the accuracy of the NaCl values is high, the uncertainties of these values corresponds to those stated above for the  $\Delta\beta$  values. These  $\beta$  values are within the pattern of values found for other simple 1-1 electrolytes.<sup>6</sup>

These results allow the calculation of the activity coefficient of NaHCO<sub>3</sub> in mixtures with NaCl. Equation (15) of Pitzer and Kim<sup>3</sup> simplifies to

$$\ln \gamma_{\text{NaHCO}_3} = -A_\phi \left[ I^{1/2} / (1 + 1.2I^{1/2}) + (2/1.2) \ln(1 + 1.2I^{1/2}) \right] + I \left[ (1+y)B_{\text{NaHCO}_3} + (1-y)(B_{\text{NaCl}} + \theta) \right] + I^2 \left[ yB'_{\text{NaHCO}_3} + (1-y)B'_{\text{NaCl}} \right] \quad (14)$$

$$B_j = \beta_j^{(0)} + \beta_j^{(1)} g(I) \quad (15)$$

$$B'_j = (\beta_j^{(1)}/2I^2) [-1 + (1 + 2I^{1/2} + 2I) \exp(-2I^{1/2})] \quad (16)$$

Here  $y$  is the solute fraction of bicarbonate. The Debye-Hückel parameter  $A_\phi$  was taken from Bradley and Pitzer;<sup>11</sup> the value is 0.391 at 25°C.

In Table I the resulting activity coefficient of  $\text{NaHCO}_3$  is given for  $y=0$  (the trace activity of  $\text{NaHCO}_3$  in  $\text{NaCl}$ ) and for  $y=1$  (pure bicarbonate). For the trace activity  $\beta_{\text{NaHCO}_3}^{(0)}$  and  $\theta$  appear as a simple sum; hence the special uncertainty discussed above disappears and the results should be quite accurate. For the pure bicarbonate, however,  $\theta$  disappears and the term  $2I\beta_{\text{NaHCO}_3}^{(0)}$  remains, yielding somewhat greater uncertainty.

The activity coefficient of 0.53<sub>g</sub> at 1M for pure bicarbonate in Table I may be compared with Han and Kesler's value<sup>1</sup> of 0.56. The agreement is as good as could be expected in view of the data upon which Han and Kesler's calculations were based.

The osmotic coefficient of pure  $\text{NaHCO}_3$  is also given in Table I as calculated from the equation

$$\phi - 1 = -A_\phi m^{1/2} / (1 + 1.2m^{1/2}) + m[\beta^{(0)} + \beta^{(1)} \exp(-2m^{1/2})] \quad (17)$$

The value of  $\ln(K_1 K_s)$  from equation (10) is -18.004 at 25°C which agrees reasonably well with the original interpretation of the data of Harned and Davis<sup>4</sup> yielding -17.995. Also  $(\Delta H^0/R)$  for chemical reaction(B) is -1282 K from equation (10) while Harned and Davis reported values yielding  $(\Delta H/R) = -1238$  K. Recently Berg and Vanderzee<sup>12</sup> made calorimetric measurements on carbonate systems and reviewed the available literature; their

value for  $(\Delta H^0/R)$  is  $1274 \pm 20$  K and they recommend for  $\ln(K_1K_s)$  the value  $-18.001$ . The agreement of the  $\Delta H^0/R$  values is significant since we made no use of their calorimetric data. For  $\ln(K_1K_s)$ , however, Berg and Vanderzee were dealing with essentially the same data which we considered and which Harned, et al, interpreted originally.

There are no experimental data for  $\text{KHCO}_3$  of accuracy equal to those discussed above for  $\text{NaHCO}_3$ . However, Mac Innes and Belcher<sup>13</sup> did measure at  $25^\circ\text{C}$  a similar cell with a glass electrode instead of the hydrogen electrode. While their absolute accuracy is less and the absolute agreement with the values from Harned's laboratory is not very good, the precision of measurement of Mac Innes and Belcher seems good. Their results indicate that the quantity  $\ln(\gamma_{\text{Cl}}/\gamma_{\text{HCO}_3})$  is the same for solutions of  $\text{K}^+$  as for  $\text{Na}^+$  to their precision of measurement. Thus our values for  $\Delta\beta^{(0)}$  and  $\Delta\beta^{(1)}$  can be used as an estimate for solutions of  $\text{K}^+$ , yielding for  $\text{KHCO}_3$   $\beta^{(0)} = -0.0005$  and  $\beta^{(1)} = -0.013$ , at  $25^\circ\text{C}$ .

In summary, we have presented a method for the determination of the activity coefficient and related properties of aqueous bicarbonates from cell measurements on mixtures with the corresponding chlorides. Cell data from the literature yield reasonably good values for the parameters defining  $\text{NaHCO}_3$  properties and excellent agreement with recent calorimetric measurements of the heat of ionization of carbonic acid. Cell measurements designed with this method in view could yield much more accurate parameters for the thermodynamic properties of aqueous bicarbonates.

## Acknowledgement

This research was supported by the U. S. Department of Energy through Contract W-7405-Eng-48.

## References

1. S. T. Han and R. B. Kesler, *Tappi*, 46, 308 (1963).
2. S. T. Han and L. J. Bernardin, *Tappi*, 41, 540 (1958).
3. K. S. Pitzer and J. J. Kim, *J. Am. Chem. Soc.*, 96, 5701 (1974).
4. H. S. Harned and R. Davis, Jr., *J. Am. Chem. Soc.*, 65, 2030 (1943).
5. H. S. Harned and F. T. Bonner, *J. Am. Chem. Soc.*, 67, 1026 (1945); F. T. Bonner, Ph.D. Dissertation, Yale University, June 1944.
6. K. S. Pitzer and G. Mayorga, *J. Phys. Chem.*, 77, 2300 (1973).
7. R. G. Bates, et al., *J. Chem. Phys.*, 25, 361 (1956); see also R. G. Bates and V. E. Bower, *J. Res. Nat. Bur. Stand. Sect. A*, 53, 283 (1954).
8. H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, 54, 1350 (1932); 55, 3179 (1933).
9. E. R. Cohen and B. N. Taylor, *J. Phys. Chem. Ref. Data*, 2, 663 (1973).
10. L. F. Silvester and K. S. Pitzer, *J. Solution Chem.*, 7, 327 (1978).
11. D. J. Bradley and K. S. Pitzer, *J. Phys. Chem.*, 83, 1599 (1979).

12. R. L. Berg and C. E. Vanderzee, *J. Chem. Thermodynamics*, 10, 1113 (1978).
13. D. A. MacInnes and D. Belcher, *J. Am. Chem. Soc.*, 55, 2630 (1933).

Table I. The Activity Coefficient of  $\text{NaHCO}_3$  at Solute Fraction  $y$  in Mixture with  $\text{NaCl}$  and the Osmotic Coefficient of  $\text{NaHCO}_3$  (at  $25^\circ\text{C}$ ).

$m$	$\gamma(y=1)$	$\gamma(y=0)$	$\phi(y=1)$
0.01	.898	.900	.966
0.02	.863	.868	.954
0.05	.804	.813	.934
0.1	.749	.764	.915
0.2	.688	.712	.895
0.3	.650	.681	.883
0.4	.62 <sub>3</sub>	.659	.875
0.5	.60 <sub>1</sub>	.643	.869
0.6	.58 <sub>4</sub>	.631	.865
0.7	.57 <sub>0</sub>	.621	.862
0.8	.55 <sub>8</sub>	.613	.859
0.9	.54 <sub>8</sub>	.606	.857
1.0	.53 <sub>9</sub>	.601	.856

