

# THE ACTIVITY COEFFICIENT OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTION AS MEASURED WITH A CATION-SENSITIVE GLASS ELECTRODE<sup>1</sup>

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## INTRODUCTION

Glass electrodes which respond to monovalent cations such as Na<sup>+</sup> and K<sup>+</sup> are now commercially available. Such electrodes have been used to measure the activity coefficient of NaCl in various media (1, 2, 3). In the present work the activity coefficient of KCl in aqueous solution has been measured in the range 0.01 *m* to 2.5 *m* at temperatures from 15° to 55° using a cation-sensitive glass electrode. The study was undertaken to determine how well the activity coefficients so measured would agree with those measured by other methods.

## EXPERIMENTAL

The glass electrodes used were Beckman cationic 39137 electrodes, while the reference electrodes were Ag, AgCl electrodes of the thermal type. The reference electrodes were shorted together and allowed to equilibrate in KCl solution prior to use.

A vibrating reed electrometer, in conjunction with a Rubicon K-2 potentiometer and a Brown recorder, was used for measurement of the emf of the cell. The precision of individual measurements was of the order of a few hundredths of a millivolt, but reproducibility between experiments was sometimes no better than a millivolt. Equilibrium was attained in a few hours with solutions of low concentration and in 6-8 hours with the solutions of high concentration.

The solutions were prepared by weight from reagent grade KCl and triply distilled water. The emf cell was immersed in a constant temperature bath controlled to a few hundredths of a degree. The entire bath and electrode assembly were surrounded by an aluminum shield to minimize external effects on the emf readings.

## RESULTS AND DISCUSSION

The fundamental equation relating the measured emf *E* of the cell, the "standard potential" *E*<sup>o</sup> of the electrode couple, and the activity *a* of the KCl in solution is

$$E = E^{\circ} - \frac{RT}{F} \ln a. \quad (1)$$

Since  $a_{\text{KCl}}$  may be expressed as  $m_{\text{K}^+} \gamma_{\text{K}^+} m_{\text{Cl}^-} \gamma_{\text{Cl}^-}$ , where  $\gamma_{\text{K}^+}$  and  $\gamma_{\text{Cl}^-}$  are the activity coefficients of the K<sup>+</sup> and the Cl<sup>-</sup> ions and the *m*'s are molalities, eq. (1) may be written

$$E = E^{\circ} - \frac{2RT}{F} \ln m - \frac{2RT}{F} \ln \gamma_{\pm}, \quad (2)$$

where  $\gamma_{\pm} = \sqrt{\gamma_{\text{K}^+} \gamma_{\text{Cl}^-}}$  is the mean ionic activity coefficient of the KCl. It is assumed that the concen-

tration dependence of  $\ln \gamma_{\pm}$  is given by an extended Debye-Huckel equation of the type

$$\ln \gamma_{\pm} = -\frac{S_T \sqrt{m}}{1 + A \sqrt{m}} + B m + C m^2, \quad (3)$$

then substitution of eq. (3) into eq. (2) gives eq. (4)

$$E = E^{\circ} - \frac{2RT}{F} \ln m - \frac{2RT}{F} \left[ \frac{-S_T \sqrt{m}}{1 + A \sqrt{m}} + B m + C m^2 \right] \quad (4)$$

in which the temperature dependence of the *B* and *C* coefficients may be expressed as

$$B = b_1 + \frac{b_2}{T} \quad (5a)$$

and

$$C = c_1 + \frac{c_2}{T}. \quad (5b)$$

The form of eqs. (5a) and (5b) is consistent with the assumption that  $\Delta C_p = 0$  for the KCl in solution over the temperature range studied.

Since the *E*<sup>o</sup> values of many cell combinations vary quadratically with temperature, we may further assume that

$$E^{\circ} = a_1 + a_2 T + a_3 T^2 \quad (6)$$

In treating the data the individual emf values (measured with a given electrode combination) at each temperature and concentration were averaged. The averaged values for each electrode combination were then fitted by the method of least squares to eq. (4), with the temperature dependence of *B*, *C*, and *E*<sup>o</sup> given by eqs. (5a), (5b), and (6) and with the appropriate Debye-Huckel limiting slope *S*<sub>T</sub> used at each temperature. In carrying out the calculations all the data (at all temperatures and concentrations) were used simultaneously in determining the values of *a*<sub>1</sub>, *a*<sub>2</sub>, *a*<sub>3</sub>, *b*<sub>1</sub>, *b*<sub>2</sub>, *c*<sub>1</sub>, and *c*<sub>2</sub> for each electrode combination separately.

Three different glass electrode-reference electrode combinations were used in this study. It was found that, whereas each electrode pair had a different *E*<sup>o</sup> value, all three pairs gave essentially the same activity coefficient values for the KCl solutions. The average maximum deviation between the *E*<sup>o</sup>-*E* values for all concentrations and temperatures for all three electrodes was 1.6 mv, while the average deviation was 1.0 mv. Since the activity coefficient values obtained with the three different glass electrodes were not significantly different, only the values obtained with one electrode will be presented here.

In carrying out the calculations it was found that when the value of *A* in eq. (4) was taken as 1.45 the best overall fit of the data was obtained, i.e., that the average deviations between the observed and calculated values were the smallest. The activity coefficient values

<sup>1</sup> Research sponsored by The Office of Saline Water, U. S. Department of the Interior under Union Carbide Corporation's contract with the U. S. Atomic Energy Commission.

computed with  $A = 1.45$  are shown in column 4 of Table I. Also included in the table are values of the

TABLE I

THE ACTIVITY COEFFICIENT OF KCl

$t^{\circ}\text{C}$	$m_{\text{KCl}}$	E	$\gamma^1_{\text{KCl}}$	$\gamma^2_{\text{KCl}}$	$\gamma^3_{\text{KCl}}$
15	0.01	-.0456 +17	.904	.903	
	.1	-.1507 + 3	.776	.769	
	.5	-.2217 + 1	.653	.650	
	1.0	-.2524 + 6	.601	.601	
	2.5	-.2946	.571	.562	
	25	0.01	-.0370 -13	.903	.901
.1		-.1471 -13	.772	.769	.769
.5		-.2208 -12	.649	.651	.649
1.0		-.2524 -11	.598	.606	.603
2.5		-.2969 -11	.573	.572	.567
40		0.01	-.0305 + 9	.900	.900
	.1	-.1447 - 4	.767	.765	
	.5	-.2231 + 9	.643	.646	
	1.0	-.2564 +14	.592	.603	
	2.5	-.3046 +21	.574	.575	
	55	0.01	-.0218 +14	.897	
.1		-.1399 -13	.761		
.5		-.2230 + 4	.639		
1.0		-.2557 - 5	.586		
2.5		+.3055 -10	.572		

<sup>1</sup> Present work (glass electrode)  
<sup>2</sup> Harned and Cook (amalgam cell)  
<sup>3</sup> Based on data of Robinson and Sinclair

activity coefficients obtained with amalgam cells (4) and with the isopiestic method (5). The values given in column 6 of Table I have been recomputed from the original isopiestic data using a newer technique (6) than that used in the original paper. As can be seen the activity coefficient values obtained with the cation-sensitive glass electrodes agree in most cases to within 1% with the values obtained by the other methods.

As a further check on the reproducibility of the glass electrode measurements the smoothest values of the activity coefficients and the  $E^{\circ}$  values were substituted into eq. (2) at each concentration and temperature to back-calculate the emf values. The deviations between the observed values and the calculated values are shown in column 3 of Table I immediately below the observed emf values. A positive deviation indicates that the observed value is numerically higher than the calculated value. The greatest deviation is 2.1 mv at 40° in the 2.5 m solution.

Measurements were also made at 5° in all the above solutions and in .001 m KCl solutions from 5° to 55°. However, the observed values were more erratic than those reported and the resulting activity coefficients were 15 to 40% different from those in the literature.

Recently the activity coefficient of KCl was measured from 0° to 50°C in the concentration range .05 to 4.0 m using an amalgam cell.<sup>7</sup> When these values are extrapolated to 55°, then excellent agreement is observed with the values reported in this paper. The greatest deviation (2.3%) is at 1.0 m where it appears that our value is more consistent.

The authors wish to express their sincere appreciation to Walter J. Stevens, Jr., and Richard Shea for performing the experimental measurements.

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