

Using the convention that  $S_{\text{H}^+}^0$  is zero, and the values for  $S_{\text{Ag}}^0$  (10.0 e. u.) and  $S_{\text{H}_2}^0$  (31.2 e. u.) given by Latimer, Schutz, and Hicks,<sup>8</sup> we find from equations (6) and (7) that  $S_{\text{Ag}^+}^0$  is equal to 16.7 cal. deg.<sup>-1</sup> mol.<sup>-1</sup> at 25°.

From Skotnický's value for  $dE_{\text{Ag}}^0/dT$ , as well as from the value we have computed from the data of Kohlrausch, Brown, and MacInnes, and Harned and Wright, we find that  $\Delta S_{298}^0$  is 22.6 e. u. and that  $S_{\text{Ag}^+}^0$  is 17.0 e. u. at 25°. These values are in agreement with the values found in this study.

On the other hand, Latimer, Schutz, and Hicks<sup>8</sup> give the four values 18.5, 18.4, 18.4, and 18.3 e. u. for  $S_{\text{Ag}^+}^0$  at 25°. However, in computing the first two of these values they used the heat of solution of silver chloride at 22.5° given by Lange and Fuoss,<sup>7</sup> and they apparently assumed that this quantity had the same value at 25 as at 22.5°. It may be shown readily from the data given by Kohlrausch<sup>5</sup> (variation of the heat of solution of silver chloride with tempera-

(8) W. M. Latimer, P. W. Schutz, and J. F. Hicks, Jr., *J. Chem. Phys.*, **2**, 82 (1934).

ture) that this assumption leads to a calculated value of  $S_{\text{Ag}^+}^0$  that is too high by about 1.2 e. u. If this correction is applied, the first two values given by Latimer, Schutz, and Hicks become 17.3 and 17.2 e. u., which are in fair agreement with the values we have computed.

**Acknowledgment.**—We express our appreciation to Dr. Robert S. Livingston for his interest in this work.

### Summary

1. The temperature coefficient of the silver electrode was determined by measuring the temperature coefficients of cells of the type Pt/Quinhydrone(s),  $\text{HClO}_4(C_1)/\text{HClO}_4(C_1)$ ,  $\text{AgNO}_3(C_2)/\text{Ag}$ , in which  $C_1$  was much larger than  $C_2$ . The temperature coefficient of the standard electrode e. m. f. of silver, *i. e.*, the temperature coefficient of the cell  $\text{Ag}/\text{Ag}^+(a = 1) \parallel \text{H}^+(a = 1)/\text{H}_2$  (1 atm.), is  $+0.967 \pm 0.004$  mv. deg.<sup>-1</sup> at 25°.

2. The standard entropy of silver ion computed from this temperature coefficient is 16.7 cal. deg.<sup>-1</sup> mol.<sup>-1</sup> at 25°.

MINNEAPOLIS, MINNESOTA  
ST. PAUL, MINNESOTA

RECEIVED JULY 26, 1937

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

## The Thermodynamics of Aqueous Potassium Chloride-Lithium Chloride Mixtures at Constant Total Molalities<sup>1</sup>

BY BENTON BROOKS OWEN AND THEODORE F. COOKE, JR.

If the total ionic strength of a solution of mixed electrolytes is maintained constant and the relative concentration varied, the activity relationships of the various components are governed by specific ionic parameters and their interaction. The determination of these relationships is a very important feature of the study of specific ionic interaction. It has been established<sup>2</sup> by electromotive force measurements that the activity coefficient of hydrochloric acid in salt solutions at constant total ionic strength closely follows the equation

$$d \log \gamma_1 = \alpha_1 dm_1 \quad (1)$$

in which  $m_1$  is the molality of the acid, and the parameter  $\alpha_1$  is independent of  $m_1$ , but dependent upon the nature of the components, the total

(1) This communication embodies part of the thesis presented by Theodore F. Cooke, Jr., to the Graduate School of Yale University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Harned, *THIS JOURNAL*, **57**, 1865 (1935). Bibliography of this subject is given in his Ref. 1.

ionic strength and the temperature. If the activity coefficient of each electrolyte is known as a function of  $m$  in the pure solvent, and the plausible assumption made that

$$d \log \gamma_2 = \alpha_2 dm_2 \quad (2)$$

describes the behavior of the co-solute (salt), it is possible to evaluate  $\alpha_2$  from experimentally determined values of  $\alpha_1$ . The reciprocal relationships expressed by equations (1) and (2) are not generally valid in mixtures of salts with strong bases,<sup>3</sup> but the hydroxides are probably exceptional in this connection, as their activities are anomalous in other respects. Solubility measurements<sup>4</sup> show that the activity coefficient of silver sulfate in mixtures of magnesium and cadmium sulfates obey equation (1), but this may only be taken as presumptive evidence of its generality.

(3) Harned and Cook, *ibid.*, **59**, 1890 (1937).

(4) Åkerlöf and Thomas, *ibid.*, **56**, 593 (1934).

The determination of the osmotic coefficients of solutions by the freezing point method has enabled Scatchard<sup>5,6</sup> so to generalize and extend Brønsted's<sup>7</sup> principle of specific ion interaction that the behavior of complicated solute mixtures may now be accounted for satisfactorily. In Scatchard's treatment, allowance is made for higher terms in equations (1) and (2), and certain approximate relationships between the interaction coefficients are predictable. In the present research we are particularly concerned with the conclusions that  $\alpha_1 + \alpha_2$  is small,  $\alpha_1 - \alpha_2$  is independent of  $M$ , and the osmotic coefficient is a quadratic function of the relative composition, in solutions of two electrolytes, with a common ion, at constant ionic strength. These conclusions have been investigated<sup>6</sup> experimentally at the freezing points of solutions containing various pairs of the salts potassium nitrate, potassium chloride, lithium nitrate and lithium chloride in one-to-one, and three-to-one ratios, but in view of the importance of the general problem, it seemed worth while to study one of these salt pairs isothermally, and in a larger number of ratios. This communication is the report of such an investigation on KCl-LiCl mixtures at 25°.

The relationship between osmotic coefficient and the parameters of equations (1) and (2) is readily obtained through the Gibbs-Duhem equation. If the total molality is  $M$ , and we let the molality of lithium chloride be  $m_1 = xM$  and that of potassium chloride be  $m_2 = (1 - x)M$ , then

$$\varphi_x - \varphi_0 = -2.303\alpha_2 Mx + 1.151(\alpha_1 + \alpha_2)Mx^2 \quad (3)$$

Here  $\varphi_0$  is the osmotic coefficient when  $x = 0$ . In terms of vapor pressures, this equation can be rearranged to read

$$\frac{\log P_0 - \log P_x}{xM^2} = -0.036\alpha_2 + 0.018(\alpha_1 + \alpha_2)x \quad (3a)$$

which is the form we will employ in our calculations. If the plot of the left-hand member of this equation against  $x$  is linear, the quadratic nature of equation (3) will be established, and  $\alpha_1$  and  $\alpha_2$  can be evaluated. It should be understood at this point that equations (1) and (2) are sufficient but *not necessary* conditions for equation (3), and that our verification of the latter does not establish their simultaneous validity. For our immediate purposes, the relations (1) and (2) should be regarded merely as furnishing the sim-

plest physical interpretation of the parameters  $\alpha_1$  and  $\alpha_2$  derived from our plots.

#### Apparatus and Experimental Method

Vapor pressures were determined by the isopiestic method, which depends, in this case, upon evaluating the molality,  $m$ , of potassium chloride solutions in thermal and vapor pressure equilibrium with KCl-LiCl mixtures at given total molalities,  $M$ . The vapor pressures of the potassium chloride reference solutions are calculable from known activity coefficient data. The experimental technique has been worked out by Sinclair,<sup>8</sup> and Robinson and Sinclair,<sup>9</sup> and fully described elsewhere. Our apparatus and technique are similar to theirs except for the details noted below.

They found that attainment of vapor pressure equilibrium within a few days depends on good thermal contact between the silver solution dishes (and copper block upon which they rest), and upon removal of most of the air from the desiccator in which the system is contained. They employed a layer of potassium chloride solution to ensure contact with the block, but we found it difficult to obtain sufficiently concordant weighings by this method, and finally had to rely upon grinding the dishes and block to a very close fit. Our four dishes were milled from  $4 \times 4 \times 1.75$  cm. blocks of fine silver, and equipped with silver lids that could be operated while the desiccator was evacuated. To eliminate occasional errors due to spattering when air bubbles escape from the solutions during evacuation of the desiccator, we found it necessary to reduce the pressure in several stages during equilibration, or employ freshly boiled solutions.

Two dishes contained a given potassium chloride-lithium chloride solution, and the other two contained pure potassium chloride solution. Preliminary determinations enabled us to adjust the initial water content of the system so that loss during evacuation of the desiccator, and distillation between solutions during equilibration, would leave the total molality of the mixed salt solutions within about 1% of the desired values 1, 2, or 3  $M$ . The initial concentrations of each pair of solutions were made unequal so that final equality could be used as a criterion of the attainment of equilibrium. No results are reported unless the concordance between each pair of solutions is better than 0.1%. The short interpolation to round values of  $M$  was performed with the aid of a plot of  $m/M$  against  $M$ . To avoid smoothing the data during this process, the proper variation of  $m/M$  with  $M$  was read from the plot, and applied to each point individually. Since the uncertainty in  $m$  introduced by interpolation is much less than 0.1%, the difference between the several duplicate determinations recorded in Table I is the order of the over-all precision of the measurements.

The stock solutions were prepared from highly purified salts and analyzed gravimetrically for chloride, in triplicate, at several intervals during the course of the investigation. Vacuum corrections were taken into account, and the analyses were all better than  $\pm 0.05\%$ .

(5) Scatchard, *Chem. Rev.*, **19**, 309 (1936). Bibliography.

(6) Scatchard and Prentiss, *THIS JOURNAL*, **56**, 2320 (1934).

(7) Brønsted, *ibid.*, **45**, 2898 (1923).

(8) Sinclair, *J. Phys. Chem.*, **37**, 395 (1933).

(9) Robinson and Sinclair, *THIS JOURNAL*, **56**, 1830 (1934).

Robinson and Sinclair<sup>9</sup> have calculated the relative vapor pressure lowering of potassium chloride solutions from the available data, but they recorded their results at so few concentrations that it was necessary for us to repeat the calculation to obtain an analytical expression for vapor pressure as a function of  $m$ . For this purpose it was assumed that

$$\log \gamma = -\frac{0.506m^{1/2}}{1 + Am^{1/2}} + Bm + Cm^{3/2} - \log(1 + 0.036m) \quad (4)$$

will express the behavior of pure potassium chloride solutions with sufficient accuracy, and the parameters  $A$ ,  $B$ , and  $C$  were evaluated graphically from the same data used by Robinson and Sinclair. In dilute solutions we gave a little more weight to the electromotive force results. Combining this equation with the Gibbs-Duhem equation, we obtain

$$-\log P/P_w = \log(1 + 0.036m) - D[(1 + Am^{1/2}) - (1 + Am^{1/2})^{-1} - 4.606 \log(1 + Am^{1/2})] + Bm^2 + Cm^{5/2} \quad (5)$$

for the relative vapor pressure of potassium chloride solutions in atmospheres. The numerical value of  $P_w$ , the vapor pressure of pure water, is not needed in the calculations. The values of the parameters are:  $A = 1.145$ ,  $B = 0.00044$ ,  $C = 0.000075$ , and  $D = 0.012135$ . The value  $A$  corresponds to a distance of nearest approach,  $\delta = 3.48$ , which is consistent with values employed by other investigators.<sup>10</sup> Equation (5) yields values of the relative molal vapor pressure lowering which agree with those of Robinson and Sinclair<sup>9</sup> within 0.1% over the pertinent range 1 to 4  $m$ .

**Experimental Results and Discussion**

Table I gives the experimental data and derived vapor pressure functions used in the evaluation of  $\alpha_1$  and  $\alpha_2$ . Mixtures of total molality,  $M$ , and lithium chloride molality,  $xM$ , are isopiestic with potassium chloride solutions of molality,  $m$ . The relative vapor pressures in column four were calculated by equation (5). The fifth column contains the function plotted in Fig. 1. It is important to note that this function is rather insensitive to our selection of reference activity data for potassium chloride solutions, although the magnitude of  $-\log P_x/P_w$  is considerably affected by this choice. Thus in the neighbor-

(10) Harned, *THIS JOURNAL*, **51**, 416 (1927),  $\delta = 3.27$ . Smith and Saxton, *ibid.*, **54**, 2826 (1932),  $\delta = 3.40$ . Spencer, *idem.*, p. 4490,  $\delta = 3.58$ . Harned and Cook, *ibid.*, **59**, 1290 (1937),  $\delta = 3.60$ .

TABLE I  
VAPOR PRESSURE FUNCTIONS AT 25°

$M$	$x$	$m$	$-\log(P_x/P_w)$	$\frac{\log P_0 - \log P_x}{xm^2}$	$10^4 \Delta$
1	0	1.0000	0.014027	....	..
1	1/6	1.0160	.014256	.001360	-2
1	1/6	1.0172	.014271	.001464	+9
1	1/3	1.0340	.014512	.001455	-2
1	1/2	1.0545	.014801	.001548	0
1	2/3	1.0763	.015111	.001626	-2
1	5/6	1.1006	.015457	.001716	+1
1	1	1.1263	.015824	.001797	+1
2	0	2.0000	.028601	....	..
2	1/6	2.0547	.029423	.001233	+4
2	1/3	2.1180	.030377	.001332	+2
2	1/3	2.1182	.030380	.001334	-2
2	1/2	2.1900	.031467	.001433	-4
2	1/2	2.1908	.031478	.001439	0
2	1/2	2.1910	.031482	.001440	+1
2	2/3	2.2728	.032726	.001547	-4
2	5/6	2.3650	.034136	.001661	-3
2	5/6	2.3663	.034156	.001666	+2
2	1	2.4651	.035676	.001769	-10
2	1	2.4669	.035704	.001776	-1
3	0	3.0000	.044068	....	..
3	1/6	3.1084	.045803	.001157	+10
3	1/6	3.1108	.045841	.001182	+18
3	1/3	3.2358	.047857	.001263	+1
3	1/2	3.3912	.050386	.001404	-6
3	2/3	3.5655	.053253	.001531	-4
3	2/3	3.5660	.053260	.001532	-3
3	5/6	3.7657	.056584	.001669	-1
3	5/6	3.7664	.056595	.001670	+1
3	1	3.9888	.060352	.001809	+7

hood of  $m = 1$ , the activity coefficient of potassium chloride recently reported by Shedlovsky and MacInnes<sup>11</sup> is about 1.5% higher than values obtained from equation (4) and our values of the parameters, but the maximum effect of this discrepancy is only  $2 \times 10^{-6}$  in  $\log P_x - \log P_0$  for the 1  $M$  mixtures. This difference corresponds to an uncertainty of 0.01 to 0.02% in  $m$ . Accordingly, the linearity of the plots in Fig. 1 may be regarded as established within the limitations of our experimental data, rather than of our choice of reference.

Since the isopiestic molalities  $m$  and  $M$  are the means of duplicate determinations agreeing within 0.1%, this figure may be used as a measure of the experimental uncertainty in  $m$ . To illustrate the effect of this uncertainty upon the plotted function, the data are represented by circles whose diameters correspond to a 0.1% variation in  $m$ . The plots are evidently linear within this limit. Their slopes and intercepts are given in Table II

(11) Shedlovsky and MacInnes, *ibid.*, **59**, 503 (1937). Cf. their equation (7a).

TABLE II  
PARAMETERS OF EQUATION 3a

$M$	Slope	Intercept	$\alpha_1$	$-\alpha_2$	$\alpha_1 - \alpha_2$	$\alpha_1 + \alpha_2$
1	0.000497	0.00130	0.0637	0.0361	0.0998	0.0276
2	.000675	.00110	.0681	.0306	.0987	.0375
3	.000815	.00099	.0727	.0275	.1002	.0452

along with the corresponding values of  $\alpha_1$  and  $\alpha_2$ . These values have been used to estimate the difference between  $\varphi_x$  (obsd.), directly obtained from  $\log P_x/P_w$ , and  $\varphi_x$  (calcd.), calculated by equation (3). This difference is recorded as  $\Delta$  in the last column of Table I. The magnitude and

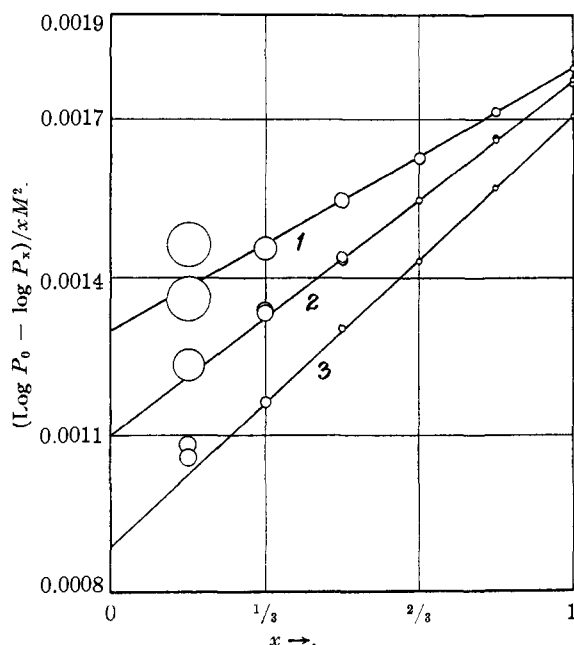


Fig. 1.—Formal verification of equations (3) and (3a). The numbers indicate the total molality  $M$  for each series. The ordinates of the 3  $M$  series have been lowered by 0.0001 to prevent overlapping.

irregularity of  $\Delta$  indicate that  $\varphi_x$  may be represented by a quadratic function of  $x$  within the accuracy of the data. This result is in formal agreement with Scatchard's<sup>5</sup> work, and the numerical values of the parameters are very close to those obtained at the freezing points of the solutions. Thus at  $M = 1$  Scatchard and Prentiss<sup>6</sup> obtained  $\alpha_1 - \alpha_2 = 0.091$ , and  $\alpha_1 + \alpha_2 = 0.026$ . Table II shows that  $\alpha_1 - \alpha_2$  is approximately independent of the concentration. This approximation seems to be of very general validity in concentrated solutions.<sup>2,4,5</sup> On the other hand,

$\alpha_1 + \alpha_2$  is neither zero, as assumed by Brønsted,<sup>7</sup> nor as small relative to  $\alpha_1 - \alpha_2$  as might be anticipated from Scatchard's considerations. In this connection it has been observed that the order of the relative magnitudes of these quantities is reversed in the system NaCl-NaOH,<sup>8</sup> but this situation is exceptional.

The difference  $\alpha_1 - \alpha_2$  can be evaluated without reference to our mixture data. Returning to equation (3a) we see that

$$(\log P_{\text{KCl}} - \log P_{\text{LiCl}}) / 0.018M^2 = (\alpha_1 - \alpha_2) \quad (6)$$

when  $x = 1$ . Hence we obtain  $\alpha_1 - \alpha_2$  by dividing values in the last column of Table I, when  $x = 1$ , by 0.018. Harned<sup>12</sup> employed an analogous equation to determine the difference in the  $\alpha$ 's in HCl-LiCl and in HCl-KCl mixtures. In combining his two series of results algebraically, the common term,  $\log P_{\text{HCl}}$  is eliminated and we obtain the relation

$$\alpha_1 - \alpha_2 = \alpha_{\text{Li}(\text{K})} - \alpha_{\text{K}(\text{Li})} = \alpha_{\text{H}(\text{K})} - \alpha_{\text{K}(\text{H})} - \alpha_{\text{H}(\text{Li})} + \alpha_{\text{Li}(\text{H})} \quad (7)$$

in which the cations of the co-solutes are inclosed by parentheses. The data in Table II of Harned's paper lead to 0.111, 0.104, and 0.100 for  $\alpha_1 - \alpha_2$  at  $M = 1, 2,$  and  $3$ , respectively. The difference between these results and ours is due to the fact that our values of  $m/M$  for pure lithium chloride and potassium chloride solutions are considerably lower than those of Robinson and Sinclair. In terms of activity coefficients, an approximate calculation shows that our results would lead to values of  $\gamma_{\text{LiCl}}/\gamma_{\text{KCl}}$  which are about 2, to 2.2% lower than theirs between 1 and 3 molal.

### Summary

The variation of the vapor pressures of solutions of lithium and potassium chlorides, in various proportions, and at constant total molalities (1, 2, and 3  $M$ ), has been determined by the isopiestic method at 25°. It was found that the osmotic coefficient is a quadratic function of the relative composition.

The results are in general agreement with relevant data in the literature, and with Scatchard's formulation of the specific ion interaction theory.

NEW HAVEN, CONN.

RECEIVED JULY 12, 1937

(12) Ref. 2. Cf. his equation (8).