[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Conductivity of Concentrated Mixtures of Alkali Chlorides

BY PIERRE VAN RYSSELBERGHE AND LEE NUTTING

Introduction

In two recent papers[1] we have interpreted migration data obtained with concentrated mixtures of alkali chlorides by means of a hypothesis which, when generalized, is of the same nature as that proposed by Guggenheim and Unmack:[2] "The ratio of the mobility of a given ion in one solution to its mobility in another solution is the same for all ions." As shown by Guggenheim and Unmack[2] this same hypothesis is involved in Longsworth's computation of moving boundary measurements.[3] It is however clear that the strict application of this assumption would lead, in the case of solutions of pure salts, to transport numbers independent of concentration. Therefore, as in our previous work,[1] we shall restrict the assumption of proportionality to solutions of the same total concentration and, for the time being at least, to mixtures of alkali chlorides.

In a certain mixture of the chlorides ACl and BCl (concentration of ACl = xC moles per liter, concentration of BCl = $(1 - x)C$ moles per liter) the mobilities of the various ions are u_{A}, u_{B}, u_{Cl}. In a solution of pure ACl of concentration C the mobilities are u°_{A}, $u^{\circ}_{\mathrm{Cl,A}}$; in a solution of pure BCl of concentration C they are u°_{B}, $u^{\circ}_{\mathrm{Cl,B}}$. Comparing the mobilities in the mixture with those in pure ACl we have, according to the hypothesis

$$u_{\mathrm{A}}/u^{\circ}_{\mathrm{A}} = u_{\mathrm{Cl}}/u^{\circ}_{\mathrm{Cl,A}} \qquad (1.1)$$

or

$$u_{\mathrm{A}}/u_{\mathrm{Cl}} = u^{\circ}_{\mathrm{A}}/u^{\circ}_{\mathrm{Cl,A}} = T^{\circ}_{\mathrm{A}}/T^{\circ}_{\mathrm{Cl,A}} \qquad (1.2)$$

T°_{A} and $T^{\circ}_{\mathrm{Cl,A}}$ being the transport numbers in pure ACl at the concentration C. In the same way, comparing the mobilities in the mixture with those in pure BCl, we have

$$u_{\mathrm{B}}/u^{\circ}_{\mathrm{B}} = u_{\mathrm{Cl}}/u^{\circ}_{\mathrm{Cl,B}} \qquad (2.1)$$

or

$$u_{\mathrm{B}}/u_{\mathrm{Cl}} = u^{\circ}_{\mathrm{B}}/u^{\circ}_{\mathrm{Cl,B}} = T^{\circ}_{\mathrm{B}}/T^{\circ}_{\mathrm{Cl,B}} \qquad (2.2)$$

T°_{B} and $T^{\circ}_{\mathrm{Cl,B}}$ being the transport numbers in pure BCl at the concentration C. We have previously shown[1] that (1.2) and (2.2) lead to the following formula for the transport number of the ion A^+ in the mixture

$$T_{\mathrm{A}} = \left(x\,\frac{T^{\circ}_{\mathrm{A}}}{T^{\circ}_{\mathrm{Cl,A}}}\right)\Bigg/\left(x\,\frac{T^{\circ}_{\mathrm{A}}}{T^{\circ}_{\mathrm{Cl,A}}} + (1 - x)\,\frac{T^{\circ}_{\mathrm{B}}}{T^{\circ}_{\mathrm{Cl,B}}} + 1\right) \qquad (3)$$

which is a generalization for all concentrations of the formula established by MacInnes[4] for concentrations lower than 0.1 mole per liter. The derivation of (3) implies that the degrees of dissociation of ACl and BCl are the same in all mixtures and in solutions of the pure salts of the same total concentration.

Equivalent Conductivity of a Mixture of Alkali Chlorides.—Calling Λ the equivalent conductivity of the mixture, we have

$$\Lambda = \alpha F[xu_{\mathrm{A}} + (1 - x)u_{\mathrm{B}} + u_{\mathrm{Cl}}] \qquad (4)$$

α being the degree of dissociation, F one faraday of electricity. Using the formulas (1.2) and (2.2) we have

$$\Lambda = \alpha F u_{\mathrm{Cl}}\left[x\,\frac{T^{\circ}_{\mathrm{A}}}{T^{\circ}_{\mathrm{Cl,A}}} + (1 - x)\,\frac{T^{\circ}_{\mathrm{B}}}{T^{\circ}_{\mathrm{Cl,B}}} + 1\right] \qquad (5)$$

This equation enables us to calculate the quantity $\alpha F u_{\mathrm{Cl}} = \Lambda_{\mathrm{Cl}}$ when the total equivalent conductivity Λ is known. It was found, on the basis of the experimental values of Λ obtained by Stearn[5] and by Ruby and Kawai,[6] that the quantity Λ_{Cl} deduced from equation (5) is, within the limits of experimental error, a linear function of the mixing ratio x given by

$$\Lambda_{\mathrm{Cl}} = x\Lambda^{\circ}_{\mathrm{Cl,A}} + (1 - x)\Lambda^{\circ}_{\mathrm{Cl,B}} \qquad (6)$$

$\Lambda_{\mathrm{Cl,A}}$ and $\Lambda_{\mathrm{Cl,B}}$ being the equivalent conductivities of the chloride ion in solutions of pure ACl and BCl of the same concentration as the total concentration of the mixture. (6) could also be written in terms of the transport numbers in solutions of the pure salts

$$\Lambda_{\mathrm{Cl}} = x\Lambda^{\circ}_{\mathrm{ACl}}\,T^{\circ}_{\mathrm{Cl,A}} + (1 - x)\Lambda\,T^{\circ}_{\mathrm{Cl,B}} \qquad (7)$$

(5) becomes then

$$\Lambda = [x\Lambda^{\circ}_{\mathrm{ACl}}\,T^{\circ}_{\mathrm{Cl,A}} + (1 - x)\Lambda^{\circ}_{\mathrm{BCl}}\,T^{\circ}_{\mathrm{Cl,B}}]\left[x\,\frac{T^{\circ}_{\mathrm{A}}}{T^{\circ}_{\mathrm{Cl,A}}} + (1 - x)\,\frac{T^{\circ}_{\mathrm{B}}}{T^{\circ}_{\mathrm{Cl,B}}} + 1\right] \qquad (8)$$

a formula giving the equivalent conductivity of the mixture in terms of the conductivities and transport numbers of the pure salts at a concentration equal to the total concentration of the mixture. In order to show the high degree of

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(1) Van Rysselberghe, THIS JOURNAL, **55**, 990 (1933); Van Rysselberghe and Nutting, *ibid.*, **55**, 996 (1933).

(2) Guggenheim and Unmack, *Det. Kgl. Danske Videnskab. Selskab*, X, **14**, 16 (1931).

(3) Longsworth, THIS JOURNAL, **52**, 1897 (1930).

(4) MacInnes, *ibid.*, **47**, 1922 (1925).

(5) Stearn, *ibid.*, **44**, 670 (1922).

(6) Ruby and Kawai, *ibid.*, **48**, 1119 (1926).

accuracy of this formula and to compare it to the old mixture rule

$$\Lambda = x\Lambda^{\circ}_{\mathrm{ACl}} + (1 - x)\,\Lambda^{\circ}_{\mathrm{BCl}} \qquad (9)$$

we have presented in Table I for the various mixtures studied by Stearn[5] and by Ruby and Kawai,[6] respectively: the total concentration, the ratio x of the concentration of potassium chloride to the total concentration, the measured equivalent conductivity and the values calculated according to formulas (8) and (9). The conductivities for the pure salts used in the calculations are those of Stearn and of Ruby and Kawai. The transport numbers used at 0.1 and 0.25 are those of Longsworth.[7] At higher concentrations the transport numbers of potassium chloride were obtained from the data of MacInnes and Dole.[8] The transport numbers of sodium chloride were obtained by drawing the best possible curve through all the available data.[9]

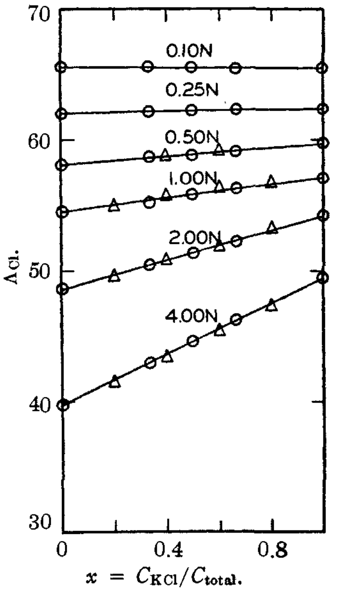

Fig. 1.—Conductivity of the chloride ion in mixtures of potassium and sodium chlorides at 25°: ○, Stearn; △, Ruby and Kawai.

The values calculated according to formula (8) agree remarkably well with the measured conductivities throughout the whole range of concentrations. Those calculated according to formula (9), satisfactory at low concentrations, exhibit large departures from the measured ones at higher concentrations. It is to be noted that the mixture law (9) is never strictly valid except at zero total concentration. It happens to be sufficiently accurate at concentrations lower than 0.1 for which

$$\Lambda_{\mathrm{Cl}} = \Lambda^{\circ}_{\mathrm{Cl,A}} = \Lambda^{\circ}_{\mathrm{Cl,B}} \qquad (10)$$

It is easy to see that (8) and (9) become mathematically equivalent when (10) holds.

On Fig. 1 are plotted against the mixing ratio x the values of Λ_{Cl} deduced from the measurements of Stearn and of Ruby and Kawai by means of formula (5). This diagram justifies equation (6).

TABLE I

CONDUCTIVITIES OF MIXTURES OF POTASSIUM CHLORIDE AND SODIUM CHLORIDE AT 25°

Data of Stearn

Total concn., moles per 1000 g. of water	x	Λ measured	Λ calcd. form. (8)	Λ calcd. form. (9)
0.10	1/3	114.12	114.01	113.99
.10	1/2	117.46	117.60	117.58
.10	2/3	120.97	121.18	121.16
.25	1/3	107.02	107.38	107.40
.25	1/2	110.69	111.02	111.05
.25	2/3	114.58	114.65	114.69
.50	1/3	101.51	101.49	101.63
.50	1/2	105.16	105.32	105.50
.50	2/3	109.10	109.25	109.35
1.00	1/3	94.14	94.58	94.77
1.00	1/2	98.75	98.74	98.98
1.00	2/3	102.82	102.95	103.19
2.00	1/3	85.17	85.43	85.83
2.00	1/2	90.12	90.26	90.80
2.00	2/3	95.20	95.47	95.77
4.00	1/3	71.21	71.20	72.16
4.00	1/2	77.06	77.13	78.18
4.00	2/3	83.31	83.29	84.20
Data of Ruby and Kawai				
0.50	2/5	103.08	103.24	103.37
.50	3/5	107.80	107.93	108.09
1.00	1/5	91.14	91.14	91.31
1.00	2/5	96.24	96.29	96.56
1.00	3/5	101.54	101.50	101.80
1.00	4/5	106.88	106.84	107.05
2.00	1/5	81.25	81.19	81.53
2.00	2/5	87.02	87.05	87.60
2.00	3/5	93.05	93.12	93.66
2.00	4/5	99.45	99.36	99.73
4.00	1/5	66.30	66.33	67.03
4.00	2/5	73.22	73.27	74.30
4.00	3/5	80.52	80.55	81.58
4.00	4/5	88.13	88.17	88.85

Other measurements on mixtures, like those of Bray and Hunt,[10] of Dewey,[11] etc., were found to

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(7) Longsworth, THIS JOURNAL, **54**, 2741 (1932).

(8) MacInnes and Dole, *ibid.*, **53**, 1357 (1931).

(9) "International Critical Tables;" Landolt-Börnstein-Roth, Tables; McBain, *Proc. Washington Acad. Sci.*, **9**, 1-78 (1907).

(10) Bray and Hunt, THIS JOURNAL, **33**, 781 (1911).

(11) Dewey, *ibid.*, **47**, 1927 (1925).

be less suitable for our purpose (presence of hydrochloric acid as one of the constituents, total concentration too low to obtain significant departures from the old mixture rule, etc.).

Remarks.—(6) could also be written in terms of mobilities

$$u_{\text{Cl}} = xu^{\circ}_{\text{Cl,A}} + (1 - x)u^{\circ}_{\text{Cl,B}} \qquad (11)$$

From (1.2), (2.2) and (11) we deduce the interesting relations

$$u_{\text{A}} = [xu^{\circ}_{\text{Cl,A}} + (1 - x)u^{\circ}_{\text{Cl,B}}]\,(T^{\circ}_{\text{A}}/T^{\circ}_{\text{Cl,A}}) \qquad (12.1)$$

$$u_{\text{B}} = [xu^{\circ}_{\text{Cl,A}} + (1 - x)u^{\circ}_{\text{Cl,B}}]\,(T^{\circ}_{\text{B}}/T^{\circ}_{\text{Cl,B}}) \qquad (12.2)$$

and the limiting mobilities of ion A$^+$ at infinite dilution in BCl and of ion B$^+$ at infinite dilution in ACl

$$[\lim u_{\text{A}}]_{x=0} = u^{\circ}_{\text{Cl,B}} \cdot \frac{T^{\circ}_{\text{A}}}{T^{\circ}_{\text{Cl,A}}} = u^{\circ}_{\text{A}}\,\frac{u^{\circ}_{\text{Cl,B}}}{u^{\circ}_{\text{Cl,A}}} \qquad (13.1)$$

$$[\lim u_{\text{B}}]_{x=1} = u^{\circ}_{\text{Cl,A}} \cdot \frac{T^{\circ}_{\text{B}}}{T^{\circ}_{\text{Cl,B}}} = u^{\circ}_{\text{B}}\,\frac{u^{\circ}_{\text{Cl,A}}}{u^{\circ}_{\text{Cl,B}}} \qquad (13.2)$$

Figure 2 gives the ratios $u_{\text{K}}/u^{\circ}_{\text{K}}$ and $u_{\text{Na}}/u^{\circ}_{\text{Na}}$ in terms of x for mixtures of potassium chloride and sodium chloride of a total concentration of 2 moles per liter. We notice that in the mixture the potassium ion moves more slowly and the sodium ion more rapidly than in solutions of the pure salts. This is in qualitative agreement with the theoretical deductions of Onsager and Fuoss for very dilute solutions.[12]

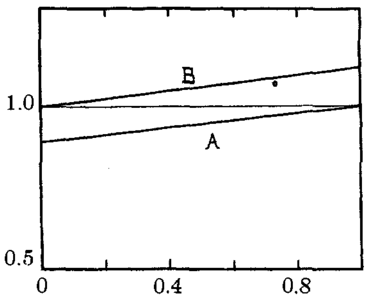

Fig. 2.—Mobility ratios $u_{\text{K}}/u^{\circ}_{\text{K}}$(A) and $u_{\text{Na}}/u^{\circ}_{\text{Na}}$ (B) in 2 M mixtures of KCl and NaCl.

Summary

1. A formula is obtained giving the equivalent conductivity of a mixture of alkali chlorides in terms of the conductivities and transport numbers of the pure salts at the same concentration as the total concentration of the mixture.

2. Measured and calculated conductivities of mixtures of potassium and sodium chloride agree remarkably well up to as high a total concentration as 4 moles per liter.

3. It is shown that at concentrations of the order of 0.1 mole per liter the new formula and the old mixture rule give the same results.

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[12] Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Activity Coefficients of Sulfuric Acid in Aqueous Solutions of Ammonium Sulfate at 25°

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Electromotive force data on solutions of various sulfates in sulfuric acid have been obtained by Harned and Sturgis[1] from a study of cells of the type

$$\text{H}_2 \mid \text{H}_2\text{SO}_4\ (m_1),\ \text{M}_2\text{SO}_4\ (m_2) \mid \text{Hg}_2\text{SO}_4 \mid \text{Hg}$$

wherein m_2 represents potassium or sodium and m_1 (H_2SO_4) = 0.1 and 0.01. Measurements were also made with magnesium sulfate. Åkerlöf[2] extended the measurements to m_1 (H_2SO_4) = 0.05 and 0.005, and included lithium sulfate as an added salt. Randall and Langford[3] have extended the data with sodium sulfate up to concentrations of 2 molal in various acid concentrations. All the above work was carried out at 25°.

In this paper are given data for the above cell with ammonium sulfate as the added salt and with m_1 (H_2SO_4) = 0.1 and 0.01 and at a temperature of 25°. These results are directly comparable to those obtained by Harned and Sturgis with sodium and potassium sulfates at these acid concentrations. From the results the activity coefficients of the acid have been calculated.

Experimental Procedure

All reagents employed were purified carefully and where necessary were analyzed according to the accepted methods. All electrical measuring instruments had been calibrated by the Bureau of Standards. The temperature was accurate to ±0.03°. The usual experimental procedure was followed.

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[1] Harned and Sturgis, THIS JOURNAL, **47**, 945 (1925).

[2] Åkerlöf, *ibid.*, **48**, 1160 (1926); *Physik. Z.*, **27**, 411 (1926).

[3] Randall and Langford, THIS JOURNAL, **49**, 1445 (1927).