[Contribution from the Department of Chemistry, Stanford University]

Transport Numbers in Mixed Aqueous Solutions of Alkali Chlorides. I. Theoretical Remarks

By Pierre Van Rysselberghe

Introduction

In recent years various authors have reported or discussed results of migration experiments on mixed aqueous solutions of potassium and sodium chlorides.[1-7] The general conclusion one is entitled to draw from these papers is that when the total concentration is not too high the transport numbers of the two metallic ions are in satisfactory agreement with those calculated by applying MacInnes' formula.[3] This shows that only simple ions are present in those solutions and that, at equal concentrations, potassium and sodium chlorides are dissociated to the same extent. In order to test further the validity of these conclusions McBain and Van Rysselberghe carried out migration experiments with mixed solutions of potassium and sodium chloride of high total concentration and high ratio between the concentration of sodium chloride and that of potassium chloride.[8] They interpreted their results on the basis of incomplete dissociation. This interpretation is discussed in the present note. In a subsequent paper experimental results obtained with mixtures of cesium and sodium chlorides, potassium and lithium chlorides, rubidium and sodium chlorides and new results obtained with mixtures of potassium and sodium chlorides will be presented and discussed.

Transport Number of One of the Two Metallic Ions in a Binary Mixture of Alkali Chlorides.—Let us call ACl and BCl the two chlorides, C the total concentration in gram molecules per liter, x the ratio of the concentration of ACl to the total concentration C, Λ_{ACl}, Λ_{BCl}, Λ_A, Λ_B, $\Lambda_{Cl,A}$, $\Lambda_{Cl,B}$ the equivalent conductivities of the salts and ions at the concentration C, T_A, T_B, T_{Cl} the transport numbers of the ions in the mixture, T°_{A}, T°_{B}, $T^{\circ}_{Cl,A}$, $T^{\circ}_{Cl,B}$ the transport numbers of the ions in solutions of the pure salts at the concentration C. We have the following relations between these various quantities

$$\Lambda_A = \Lambda_{ACl} \times T^{\circ}_{A} \quad (1)$$

$$\Lambda_B = \Lambda_{BCl} \times T^{\circ}_{B} \quad (2)$$

$$\Lambda_{Cl,A} = \Lambda_{ACl} \times T^{\circ}_{Cl,A} \quad (3)$$

$$\Lambda_{Cl,B} = \Lambda_{BCl} \times T^{\circ}_{Cl,B} \quad (4)$$

$$T^{\circ}_{A} + T^{\circ}_{Cl,A} = 1 \quad (5)$$

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(1) Braley and Hall, This Journal, **42**, 1770 (1920).

(2) Schneider and Braley, *ibid.*, **45**, 1121 (1923).

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

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

(5) Bjerrum and Ebert, *Det. Kgl. Danske Videnskabernes Selskab.* VI, **9**, p. 5 (1925).

(6) Braley and Rippie, This Journal, **49**, 1493 (1927).

(7) See also: Taylor, *ibid.*, **48**, 599 (1926).

(8) McBain and Van Rysselberghe, *ibid.*, **52**, 2336 (1930).

$$T^\circ_{\mathrm{B}} + T^\circ_{\mathrm{Cl,B}} = 1 \qquad (6)$$

$$T_{\mathrm{A}} + T_{\mathrm{B}} + T_{\mathrm{Cl}} = 1 \qquad (7)$$

If we assume that the degrees of dissociation and the mobilities of the ions of the two salts in the mixture are the same as those in pure solutions of each of the two salts at the same concentration as the total concentration of the mixture, we have for the transport number of the ion A in the mixture

$$T_{\mathrm{A}} = \frac{x\Lambda_{\mathrm{A}}}{x\Lambda_{\mathrm{A}} + (1 - x)\Lambda_{\mathrm{B}} + x\Lambda_{\mathrm{Cl,A}} + (1 - x)\,\Lambda_{\mathrm{Cl,B}}} \qquad (8)$$

Making use of equations (1), (2), (3), (4), (5) and (6) we obtain

$$T_{\mathrm{A}} = \frac{x\Lambda_{\mathrm{ACl}}\,T^\circ_{\mathrm{A}}}{x\Lambda_{\mathrm{ACl}} + (1 - x)\,\Lambda_{\mathrm{BCl}}} \qquad (9)$$

We may consider equation (9) as a mathematical expression of the so-called "isohydric principle."

At concentrations not exceeding 0.1 mole per liter the alkali chlorides may be considered as dissociated to the same extent at equal concentrations.[8,9] We have then

$$\Lambda_{\mathrm{Cl,A}} = \Lambda_{\mathrm{Cl,B}} = \Lambda_{\mathrm{Cl}} \qquad (10)$$

or, according to equations (3) and (4)

$$\Lambda_{\mathrm{ACl}} \times T^\circ_{\mathrm{Cl,A}} = \Lambda_{\mathrm{BCl}} \times T^\circ_{\mathrm{Cl,B}} \qquad (11)$$

or, according to equations (5) and (6)

$$\Lambda_{\mathrm{Cl}} = \Lambda_{\mathrm{ACl}} \times (1 - T^\circ_{\mathrm{A}}) = \Lambda_{\mathrm{BCl}} \times (1 - T^\circ_{\mathrm{B}}) \qquad (12)$$

The transport number of the ion A in the mixture, given by equation (8), becomes according to equation (10)

$$T_{\mathrm{A}} = \frac{x\Lambda_{\mathrm{A}}}{x\Lambda_{\mathrm{A}} + (1 - x)\Lambda_{\mathrm{B}} + \Lambda_{\mathrm{Cl}}} \qquad (13)$$

or, according to equation (1), (2) and (12)

$$T_{\mathrm{A}} = \frac{x\Lambda_{\mathrm{Acl}}\,T^\circ_{\mathrm{A}}}{x\Lambda_{\mathrm{ACl}}\,T^\circ_{\mathrm{A}} + (1 - x)\,\Lambda_{\mathrm{ACl}}\cdot\dfrac{1 - T^\circ_{\mathrm{A}}}{1 - T^\circ_{\mathrm{B}}}\cdot T^\circ_{\mathrm{B}} + \Lambda_{\mathrm{ACl}}\,(1 - T^\circ_{\mathrm{A}})} \qquad (14)$$

or

$$T_{\mathrm{A}} = \frac{T^\circ_{\mathrm{A}}\,(1 - T^\circ_{\mathrm{B}})}{T^\circ_{\mathrm{A}} - T^\circ_{\mathrm{B}} + \dfrac{1 - T^\circ_{\mathrm{A}}}{x}} \qquad (15)$$

This formula has been established by MacInnes[3] and has been found to agree with certain experimental results of Schneider and Braley,[2] Dewey,[4] and Braley and Rippie.[6] It must be kept in mind that equation (9) is general as long as the isohydric principle holds and that equation (15) is valid only in the range of concentrations for which relation (12) holds. In the case of potassium and sodium chloride relation (12) holds strictly up to concentrations of about 0.1 gram molecule per liter.

The transport number T_{A} as given by equation (9) or (15) is, by definition, the number of gram equivalents of A^+ migrated to the cathode when

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(9) MacInnes and Cowperthwaite, *Trans. Faraday Soc.*, **23**, 400 (1927).

one faraday of current has passed through the solution. In order to compare the state of dissociation of the salt ACl in the mixture with its state of dissociation when present alone, it is convenient to compare the number of equivalents of A^+ migrated to the cathode when one faraday of current has been carried by the salt ACl in the mixture with the transport number of A^+ in a solution of ACl alone of the same concentration as the total concentration of the mixture.

If the salts ACl and BCl are dissociated to practically the same extent in solutions of equal concentration, the fraction of the total current carried by ACl can be calculated by means of the isohydric principle. This fraction is

$$\gamma = \frac{x\Lambda_{\mathrm{ACl}}}{x\Lambda_{\mathrm{ACl}} + (1 - x)\,\Lambda_{\mathrm{BCl}}} \tag{16}$$

As expected, dividing T_{A} as given by (9) by γ, we obtain

$$T_{\mathrm{A}} \times \frac{1}{\gamma} = T_{\mathrm{A}}^{\circ} \tag{17}$$

If the isohydric principle really holds in these mixed solutions, the experimental value of T_{A} should always obey equation (9) and dividing it by γ one should always find T_{A}° the transport number of A^+ in a solution of ACl alone of the same concentration as the total concentration of the mixture.[10] The results of McBain and Van Rysselberghe[8] at the concentrations 2 and 5 N ($x = 0.10, 0.04, 0.02$) and those of Schneider and Braley[2] at the concentrations 0.8 and 1.6 N ($x = 0.75, 0.67, 0.50, 0.33, 0.25$) show that at these concentrations the isohydric principle as embodied in equation (9) does not hold.

McBain and Van Rysselberghe[8] developed a qualitative reasoning in which γ is calculated by supposing that the salts are independent and the decrease in the transport number of K^+ is considered as due to the change in the degree of dissociation of potassium chloride caused by the addition of a large amount of sodium chloride. This reasoning can be summed up by the formula

$$T_{\mathrm{A}} \times \frac{1}{\gamma} = T_{\mathrm{A}}' \times \frac{\alpha}{\alpha'} \tag{18}$$

in which T_{A}' is the transport number of A^+ in a solution of ACl at the concentration xC, α' the degree of dissociation at this same concentration and α the degree of dissociation of ACl in the mixture. It was found that by using degrees of dissociation deduced from the Nernst theory[11,12] of electrolytic dissociation the experimental results could be satisfactorily accounted for.

The problem, however, deserves a more detailed scrutiny. In order to account for the measured values of T_{A} various lines of theoretical reasoning

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(10) McBain and Van Rysselberghe (Ref. 8) use $T_{\mathrm{A}} \times 1/\gamma$ instead of T_{A}.

(11) Nernst, *Z. physik. Chem.*, **135**, 237 (1928).

(12) Orthmann, *Ergebnisse der exakten Naturwissenschaften*, **6**, 155 (1927).

might be followed. One might suppose that dissociation is complete at all concentrations and calculate the mobilities according to the Debye–Hückel–Onsager theory.[13] Such an attempt has been made by Bennewitz, Wagner and Küchler.[14] Since the Onsager conductivity theory gives at most the limiting slope of a mobility or conductivity curve and since appreciable departures from equation (9) (at least in the case of alkali chlorides) appear at concentrations where the theory certainly does not hold, such attempts can hardly be considered as significant.

Empirical equations for the variation of transport numbers with concentration have been established by Jones and Dole[15] and by Longsworth.[16] They are useful for interpolation but it is evident that they do not help the solution of our problem.

Since the direct calculation of mobilities in concentrated mixtures is probably theoretically impossible, we shall try to base the interpretation of experimental data upon the following hypothesis: *in any mixture of two alkali chlorides the mobilities of the various ions are proportional to their values in solutions of the two salts alone of the same concentration as the total concentration of the mixture.* This hypothesis is obviously different from the isohydric principle (see equation 9).

Let us call u_{A}, u_{B}, u_{Cl} the mobilities of the three ions in the mixture of total concentration C; $\overset{\circ}{u}_{\mathrm{A}}$, $\overset{\circ}{u}_{\mathrm{Cl,\,A}}$, $\overset{\circ}{u}_{\mathrm{B}}$, $\overset{\circ}{u}_{\mathrm{Cl,\,B}}$ the mobilities of these ions in solutions of ACl and BCl of concentration C; α and β the degrees of dissociation of ACl and BCl in the mixture. The transport number T_{A} in the mixture is given by

$$T_{\mathrm{A}} = \frac{\alpha x u_{\mathrm{A}}}{\alpha x\,(u_{\mathrm{A}} + u_{\mathrm{Cl}}) + \beta\,(1 - x)\,(u_{\mathrm{B}} + u_{\mathrm{Cl}})} \tag{19}$$

or

$$T_{\mathrm{A}} = \frac{\alpha x \dfrac{u_{\mathrm{A}}}{u_{\mathrm{Cl}}}}{\alpha x \left(1 + \dfrac{u_{\mathrm{A}}}{u_{\mathrm{Cl}}}\right) + \beta\,(1 - x)\left(1 + \dfrac{u_{\mathrm{B}}}{u_{\mathrm{Cl}}}\right)} \tag{20}$$

According to our hypothesis

$$\frac{u_{\mathrm{A}}}{u_{\mathrm{Cl}}} = \frac{\overset{\circ}{u}_{\mathrm{A}}}{\overset{\circ}{u}_{\mathrm{Cl,\,A}}} = \frac{\overset{\circ}{T}_{\mathrm{A}}}{\overset{\circ}{T}_{\mathrm{Cl,\,A}}} \tag{21}$$

and

$$\frac{u_{\mathrm{B}}}{u_{\mathrm{Cl}}} = \frac{\overset{\circ}{u}_{\mathrm{B}}}{\overset{\circ}{u}_{\mathrm{Cl,\,B}}} = \frac{\overset{\circ}{T}_{\mathrm{B}}}{\overset{\circ}{T}_{\mathrm{Cl,\,B}}}$$

Hence

$$T_{\mathrm{A}} = \frac{\alpha x \dfrac{\overset{\circ}{T}_{\mathrm{A}}}{\overset{\circ}{T}_{\mathrm{Cl,\,A}}}}{\alpha x \left(1 + \dfrac{\overset{\circ}{T}_{\mathrm{A}}}{\overset{\circ}{T}_{\mathrm{Cl,\,A}}}\right) + \beta\,(1 - x)\left(1 + \dfrac{\overset{\circ}{T}_{\mathrm{B}}}{\overset{\circ}{T}_{\mathrm{Cl,\,B}}}\right)} \tag{22}$$

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(13) Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

(14) Bennewitz, Wagner and Küchler, *ibid.*, **30**, 623 (1929).

(15) Jones and Dole, THIS JOURNAL, **51**, 1073 (1929).

(16) Longsworth, *ibid.*, **54**, 2741 (1932).

It can easily be shown that if $\alpha = \beta$ this relation reduces to the MacInnes formula (15), as one would naturally expect.

From (22) we deduce

$$\frac{\alpha}{\beta} = \frac{1-x}{x}\,\frac{T_{\text{A}}}{T^{\circ}_{\text{A}} - T_{\text{A}}}\,\frac{T^{\circ}_{\text{Cl, A}}}{T^{\circ}_{\text{Cl, B}}} \tag{23}$$

It can also be shown that T_{A} and T_{B} obey the relation

$$T_{\text{A}} \times T_{\text{B}} = (T^{\circ}_{\text{A}} - T_{\text{A}})\,(T^{\circ}_{\text{B}} - T_{\text{B}}) \tag{24}$$

which is equivalent to

$$\frac{T_{\text{A}}}{T^{\circ}_{\text{A}}} + \frac{T_{\text{B}}}{T^{\circ}_{\text{B}}} = 1 \tag{25}$$

This shows that for a given total concentration the points having T_{A} and T_{B} as coördinates lie on a straight line whose intercepts on the axes are T°_{A} and T°_{B}.

This property is of course verified at low concentrations, where the MacInnes formula is found to hold. Even at the concentration 1.6, investigated by Schneider and Braley,[2] relation (24) is approximately verified. In a subsequent paper it will be shown that at still higher concentrations (2, 4 and 5 *N*) and even when x becomes very small the MacInnes formula (or formula (22) with $\alpha = \beta$) holds rather well, a result indicating that alkali chlorides are probably dissociated to the same extent at all concentrations and in all mixtures.

Let us now examine two other ways of interpreting migration data on mixtures of alkali chlorides.

1. The *isohydric principle* as embodied in equation (9) implies that

$$\alpha\,(u_{\text{A}} + u_{\text{Cl}}) = \alpha^{\circ}\,(u^{\circ}_{\text{A}} + u^{\circ}_{\text{Cl, A}}) \tag{26}$$

and

$$\beta\,(u_{\text{B}} + u_{\text{Cl}}) = \beta^{\circ}\,(u^{\circ}_{\text{B}} + u^{\circ}_{\text{Cl, B}})$$

α° and β° being the degrees of dissociation of ACl and BCl in solutions of concentration C. At low concentrations

$$\alpha^{\circ}\,u^{\circ}_{\text{Cl, A}} = \beta^{\circ}\,u^{\circ}_{\text{Cl, B}} \tag{27}$$

and supposing that

$$u^{\circ}_{\text{Cl, A}} = u^{\circ}_{\text{Cl, B}} \tag{28}$$

one finds

$$\alpha^{\circ} = \beta^{\circ} \tag{29}$$

From the fact that at these low concentrations equation (9) is verified one deduces that $\alpha = \beta$.

At high concentrations (larger than 0.1 N) relation (27) does not hold and neither the isohydric principle (26) nor equation (9) can be considered as significant.

2. The *principle of independency of the two salts in the mixture* gives

$$T_{\text{A, i}} = \frac{\alpha' x u'_{\text{A}}}{\alpha' x\,(u'_{\text{A}} + u'_{\text{Cl, A}}) + \beta'\,(1 - x)\,(u'_{\text{B}} + u_{\text{Cl, B}})} \tag{30}$$

in which the primes refer to the concentration xC for ACl and to the concentration $(1-x)C$ for BCl. Taking the ratio of T_A as given by (19) to $T_{A,i}$ as given by (30) we have

$$\frac{T_A}{T_{A,i}} = \frac{\alpha}{\alpha'} \cdot \frac{u_A}{u'_A} \cdot \frac{\alpha' x(u'_A + u'_{Cl,A}) + \beta'(1-x)(u'_B + u'_{Cl,B})}{\alpha x(u_A + u_{Cl}) + \beta(1-x)(u_B + u_{Cl})} \qquad (31)$$

When x tends toward zero, this ratio tends toward

$$\lim \left[\frac{T_A}{T_{A,i}}\right]_{x=0} = \frac{\alpha u_A}{\alpha' u'_A} \qquad (32)$$

Dividing both terms of the ratio by u_A^∞, the mobility of A^+ at infinite dilution, we have

$$\lim \left[\frac{T_A}{T_{A,i}}\right]_{x=0} = \frac{\alpha \dfrac{u_A}{u_A^\infty}}{\alpha' \dfrac{u'_A}{u_A^\infty}} \qquad (33)$$

$\alpha(u_A/u_A^\infty)$ might be considered as a *dynamic degree of dissociation.* We have then

$$\lim \left[\frac{T_A}{T_{A,i}}\right]_{x=0} = \frac{\alpha_d}{\alpha'_d} \qquad (34)$$

a relation analogous to equation (18) used by McBain and Van Rysselberghe in the case of very small values of x. Their interpretation of the values of T_K in mixtures of potassiuim chloride and sodium chloride suggests the possibility of establishing a set of dissociation constants in terms of the α'_ds. It will be shown, however, in subsequent papers that within the limits of experimental error the MacInnes formula, based on our general hypothesis, accounts satisfactorily for most of the experimental data and that any further calculation of degrees of dissociation or dissociation constants is rendered hardly significant on account of the rather small degree of accuracy of the experimental results.

1. If the fraction γ of the current carried by ACl is calculated according to the hypothesis of proportionality of the mobilities to their values in solutions of ACl and BCl alone of the same concentration as the total concentration of the mixture, relation (17) is always satisfied. Hence the transport numbers of the positive ions in the mixture are the same as in solutions of the pure salts of the same concentration as the mixture, when the transport is expressed in terms of one faraday carried by the respective chlorides.

2. It has come to our attention that Guggenheim and Unmack(17) in their studies of cells with liquid junctions propose a hypothesis of the same type as ours. They state it as follows: "...the ratio of the mobility of a given ion in one solution to its mobility in another solution is the same for all ions..."

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(17) Guggenheim and Unmack, *Det. Kgl. Danske Videnskabernes Selskab*, X, **14**, p. 16 (1931).

Summary

1. The following hypothesis is suggested as the basis of the interpretation of transport numbers in mixtures of alkali chlorides: *The mobilities of the various ions are proportional to their values in solutions of the two salts alone of the same concentration as the total concentration of the mixture.*

2. The MacInnes formula for the transport number of one of the two positive ions in a mixture of alkali chlorides is a direct consequence of the preceding hypothesis. The range of validity of this formula is now unrestricted.

3. Other methods of interpreting transport numbers in mixtures of alkali chlorides are discussed and shown to be probably without significance.

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Transport Numbers in Mixed Aqueous Solutions of Alkali Chlorides. II. Transport Numbers of the Potassium, the Rubidium and the Cesium Ions in Concentrated Solutions of Sodium Chloride, and of the Potassium Ion in Concentrated Solutions of Lithium Chloride

BY PIERRE VAN RYSSELBERGHE AND LEE NUTTING

1. **Mixtures of Potassium and Sodium Chlorides.**—The movement of potassium in the following mixed solutions of potassium and sodium chloride

0.2 molar KCl + 1.8 molar NaCl
0.08 molar KCl + 1.92 molar NaCl
0.5 molar KCl + 4.5 molar NaCl
0.2 molar KCl + 4.8 molar NaCl

was measured by McBain and Van Rysselberghe.[1] The transport numbers were computed according to the isohydric principle and also according to the principle of independency of the two salts in the mixture. The latter set of transport numbers led to an interpretation of the results based upon unequal values of the dissociation constants of the two chlorides as in the Nernst theory of electrolytic dissociation. As shown in the first paper of this series,[2] the MacInnes formula derived from the hypothesis that *the mobilities of the various ions in the mixture are proportional to their values in solutions of the two salts alone of the same concentration as the total concentration of the mixture* affords a more straightforward interpretation of the experimental results.

Table I gives, for the five mixtures investigated by McBain and Van Rysselberghe: (1) the composition of the mixture; (2) the transport

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(1) McBain and Van Rysselberghe, THIS JOURNAL, **52**, 2336 (1930).

(2) Van Rysselberghe, *ibid.*, **55**, 990 (1933), henceforth called Paper I.