## 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

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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 1.

number of the potassium ion calculated according to the MacInnes formula (see paper I, formula (22), in which $\alpha$ and $\beta$ are equal)

$$T_A = \frac{x \dfrac{T^\circ_A}{T^\circ_{Cl,A}}}{x\left(1 + \dfrac{T^\circ_A}{T^\circ_{Cl,A}}\right) + (1 - x)\left(1 + \dfrac{T^\circ_B}{T^\circ_{Cl,B}}\right)} \qquad (1)$$

(3) the experimental transport number; (4) the ratio $\alpha/\beta$ of the degrees of dissociation of potassium and sodium chlorides in the mixture, calculated according to the formula (see Paper I, formula (23))

$$\frac{\alpha}{\beta} = \frac{1 - x}{x} \times \frac{T_A}{T^\circ_A - T_A} \times \frac{T^\circ_{Cl,A}}{T^\circ_{Cl,B}} \qquad (2)$$

The numerical values of the transport numbers $T^\circ_K$, $T^\circ_{Na}$, etc., were taken from the Landolt–Börnstein–Roth tables and from the recent paper of MacInnes and Dole.[3]

TABLE I

| Concentration of mixture, moles per liter | $T_K$ MacInnes | $T_K$ Measured | $\alpha/\beta$ |
|---|---|---|---|
| 0.2 KCl + 1.8 NaCl | 0.060 | 0.057 | 0.96 |
| 0.08 KCl + 1.92 NaCl | .024 | .019 | .78 |
| 0.04 KCl + 1.96 NaCl | .012 | .010 | .82 |
| 0.5 KCl + 4.5 NaCl | .061 | .052 | .84 |
| 0.2 KCl + 4.8 NaCl | .025 | .025 | 1.00 |

McBain and Van Rysselberghe[4] expressed the values of $T_K$ in terms of one faraday of current carried by potassium chloride. In Table I, $T_K$ is expressed in terms of one faraday carried by the mixture. By examining Table III of McBain and Van Rysselberghe's paper, one will notice that the discrepancy between the two sets of values of $T_K$ reported in Table I is of the same order as the experimental error. It might seem that the fact that most of the experimental values of $T_K$ are smaller than the calculated ones indicates a systematic discrepancy. This is certainly not the case as the new data obtained with a total concentration of 4 $N$ exhibit a departure in the other direction from the values calculated by means of the MacInnes formula.

These data are reported in Table II. They were obtained by exactly the same method as those of McBain and Van Rysselberghe.[1]

**Apparatus.**—Three U-tubes with ground joints, three middle portions; precipitation of potassium as potassium sodium cobaltinitrite; temperature, ±25°; current strength, ±40 milliamperes; length of each run, four to four and one-half hours.

In Table III the experimental values of $T_K$ are compared with those deduced from the MacInnes formula and the values of $\alpha/\beta$ calculated according to formula (2) are given.

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(3) MacInnes and Dole, THIS JOURNAL, **53**, 1357 (1931).

(4) Ref. 1, p. 2341.

TABLE II

MIGRATION DATA FOR MIXTURES OF POTASSIUM AND SODIUM CHLORIDES. TOTAL CONCENTRATION 4 $N$

| Concn. of mixture, moles per liter | Ratio $\frac{\text{NaCl}}{\text{KCl}}$ | Ag in coulometer, g. | Change in K content Middle, % | Anode, mg. | Cathode, mg. | $T_K$ |
|---|---|---|---|---|---|---|
| 0.2 KCl + 3.8 NaCl | 19 | 0.6809 | 0.6 | −11.7 | +7.0 | 0.038 |
| | | | | −7.7 | +11.3 | |
| 0.1 KCl + 3.9 NaCl | 39 | .8385 | 0.6 | −3.5 | +6.5 | .018 |
| | | | | −3.8 | +4.9 | |
| | | | | −5.7 | +8.4 | |
| 0.1 KCl + 3.9 NaCl | 39 | .6717 | 1.3 | −3.9 | +2.8 | .015 |
| | | | | −4.4 | +3.7 | |

TABLE III

| Concn. of mixture, moles per liter | $T_K$ MacInnes | $T_K$ measured | $\alpha/\beta$ |
|---|---|---|---|
| 0.2 KCl + 3.8 NaCl | 0.030 | 0.038 | 1.05 |
| 0.1 KCl + 3.9 NaCl | .015 | .016 (av.) | 0.98 |

Considering together the data of Table I and of Table III and noting that the values of $\alpha/\beta$ are probably accurate to ±0.2, it seems that the MacInnes formula holds for these mixtures and that the two chlorides are dissociated to the same extent, within the limits of experimental error. The average value of $\alpha/\beta$ for the seven mixtures is 0.92.

2. **Mixtures of Rubidium and Sodium Chlorides.**—The movement of the rubidium ion was measured in various mixtures of rubidium and sodium chloride of total concentration 2 and 4 $N$, the ratio between the total concentration and that of rubidium chloride being 20 and 40.

The experimental method was the same as that of McBain and Van Rysselberghe. The rubidium chloride used was obtained from C. P. Kahlbaum rubidium iodide which was treated with an excess of chlorine. The iodine was evaporated off, the rubidium chloride was purified by several successive recrystallizations and thoroughly dried. C. P. General Chemicals sodium chloride was used. Rubidium was precipitated as rubidium chloroplatinate. On account of the small solubility of sodium chloride in alcohol the usual procedure had to be slightly modified. The samples were treated by the same excess of 10% solution of C. P. General Chemicals chloroplatinic acid and the precipitates were allowed to settle for at least twelve hours. The liquid was then decanted on weighed filters. Alcohol was added to the residues and filtration was carried out. The precipitates were washed several times with alcohol. The filters were dried at 120° and weighed. Nine weighed samples of about 10 cc. were analyzed for each experiment, namely, two samples of the original solution, two of the cathode portion, two of the anode portion, one of each, the central, anode and cathode middle portions: temperature, ±25°; current strength, ±40 milliamperes; length of each run, four to four and one-half hours. The results are given in Table IV.

TABLE IV

MIGRATION DATA FOR MIXTURES OF RUBIDIUM AND SODIUM CHLORIDES

| Concn. of mixture, moles per liter | Ratio $\frac{NaCl}{RbCl}$ | Ag in coulometer, g. | Change in Rb content Middle, % | Anode, mg. | Cathode, mg. | $T_{Rb}$ |
|---|---|---|---|---|---|---|
| 0.1 RbCl + 1.9 NaCl | 19 | 0.7408 | 0.1 | −20.0 | ... | 0.035 |
| | | | | −20.8 | | |
| 0.1 RbCl + 1.9 NaCl | 19 | .6689 | 1.2 | −23.9 | +11.7 | .033 |
| | | | | −19.2 | +15.2 | |
| 0.05 RbCl + 1.95 NaCl | 39 | .6469 | 0.2 | − 9.9 | + 9.1 | .017 |
| | | | | − 9.2 | + 6.7 | |
| 0.2 RbCl + 3.8 NaCl | 19 | .8320 | 1.0 | −30.1 | +12.0 | .031 |
| | | | | −20.5 | +18.1 | |
| 0.1 RbCl + 3.9 NaCl | 39 | .8257 | 1.1 | −10.8 | +10.7 | .015 |
| | | | | − 6.0 | +10.8 | |

In Table V the experimental values of $T_{Rb}$ are compared with those deduced from the MacInnes formula and the values of $\alpha/\beta$ calculated according to formula (2) are given. The values of $T^{\circ}_{Rb}$ were taken equal to those of $T^{\circ}_{K}$ at the same concentrations.

TABLE V

| Concn. of mixture, moles per liter | $T_{Rb}$ MacInnes | $T_{Rb}$ measured | $\alpha/\beta$ |
|---|---|---|---|
| 0.1 RbCl + 1.9 NaCl | 0.030 | 0.034 | 1.18 |
| 0.05 RbCl + 1.95 NaCl | .015 | .017 | 1.13 |
| 0.2 RbCl + 3.8 NaCl | .030 | .031 | 1.05 |
| 0.1 RbCl + 3.9 NaCl | .015 | .015 | 1.00 |

One sees again that the two sets of transport numbers agree within the limits of experimental error. If, moreover, one notes that there is a certain element of uncertainty in the values of $T^{\circ}_{Rb}$, it seems safe to conclude that the probable value of $\alpha/\beta$ is unity. The average $\alpha/\beta$ for the four mixtures is 1.09.

3. **Mixtures of Cesium and Sodium Chlorides.**—The movement of the cesium ion was measured in four mixtures of cesium and sodium chlorides analogous to the four mixtures of rubidium and sodium chlorides of the foregoing section of this paper. The method was identical with the one described in this section. C. P. Kahlbaum cesium chloride and C. P. General Chemicals sodium chloride were used.

The experimental results are reported in Table VI. In Table VII the experimental values of $T_{Cs}$ are compared with those deduced from the MacInnes formula and the values of $\alpha/\beta$ calculated according to formula (2) are given. The values of $T^{\circ}_{Cs}$ were taken equal to those of $T^{\circ}_{K}$ at the same concentrations.

The values of $\alpha/\beta$ are rather smaller than 1. If this is significant it might simply mean that $T^{\circ}_{Cs}$ is smaller than $T^{\circ}_{K}$ at these high concentrations, but since for all the mixtures investigated here $\alpha/\beta$ is probably ac-

TABLE VI

MIGRATION DATA FOR MIXTURES OF CESIUM AND SODIUM CHLORIDES

| Concn. of mixture, moles per liter | Ratio $\frac{\text{NaCl}}{\text{CsCl}}$ | Ag in coulometer, g. | Change in Cs content Middle, % | Anode, mg. | Cathode, mg. | $T_{\text{Cs}}$ |
|---|---|---|---|---|---|---|
| 0.1 CsCl + 1.9 NaCl | 19 | 0.7464 | 0.2 | −23.5 | +24.8 | 0.026 |
| | | | | −22.7 | +24.0 | |
| 0.05 CsCl + 1.95 NaCl | 39 | 1.1270 | .2 | +19.2 | −19.0 | .014 |
| | | | | +19.1 | −19.0 | |
| 0.2 CsCl + 3.8 NaCl | 19 | 1.1536 | .2 | +40.6 | −32.8 | .026 |
| | | | | +40.7 | ... | |
| 0.1 CsCl + 3.9 NaCl | 39 | 1.0385 | .2 | +12.6 | −21.2 | .013 |
| | | | | +16.8 | −15.2 | |

TABLE VII

| Concn. of mixture, moles per liter | $T_{\text{Cs}}$ MacInnes | $T_{\text{Cs}}$ measured | $\alpha/\beta$ |
|---|---|---|---|
| 0.1 CsCl + 1.9 NaCl | 0.030 | 0.026 | 0.86 |
| 0.05 CsCl + 1.95 NaCl | .015 | .014 | .92 |
| 0.2 CsCl + 3.8 NaCl | .030 | .026 | .85 |
| 0.1 CsCl + 3.9 NaCl | .015 | .013 | .84 |

curate to only ±0.2, it seems that cesium and sodium chlorides are dissociated to the same extent, within the limits of experimental error.

The average value of $\alpha/\beta$ for the four mixtures is 0.87 and the average $\alpha/\beta$ for all the mixtures studied so far is 0.95.

4. **Mixtures of Potassium and Lithium Chlorides.**—The movement of the potassium ion in mixed aqueous solutions of potassium and lithium chlorides of total concentration 2 and 4 *N*, the ratio between the total concentration and that of potassium chloride being 20 and 40, was measured. The experimental method was the same as that used for the other mixtures studied in this paper. C. P. Kahlbaum lithium chloride and C. P. General Chemicals potassium chloride were used. Potassium was precipitated and weighed as potassium sodium cobaltinitrite, according to the method previously used for the mixtures of potassium and sodium chlorides.[5,1] The accuracy of the analyses was of the order of 1%.

The results are reported in Table VIII.

In Table IX the measured transport numbers are compared with those calculated by means of the MacInnes formula and the values of $\alpha/\beta$ calculated by means of formula (2) are given. The values of $T^{\circ}_{\text{Li}}$ were taken from the Landolt–Börnstein–Roth tables.

The agreement between the measured and the calculated values of $T_{\text{K}}$ is again within the limits of experimental error. The departure from 1 of the ratio $\alpha/\beta$ is probably not significant.

The average $\alpha/\beta$ for these four mixtures is 1.08.

The average $\alpha/\beta$ for all the mixtures studied in this paper is 0.99.

(5) Van Rysselberghe, *Ind. Eng. Chem., Anal. Ed.*, **3**, 3 (1931).

TABLE VIII

MIGRATION DATA FOR MIXTURES OF POTASSIUM AND LITHIUM CHLORIDES

| Concn. of mixture, moles per liter | Ratio $\frac{LiCl}{KCl}$ | Ag in coulometer, g. | Change in K content Middle, % | Anode, mg. | Cathode, mg. | $T_K$ |
|---|---|---|---|---|---|---|
| 0.1 KCl + 1.9 LiCl | 19 | 0.5805 | 0.3 | −8.0 | +7.2 | 0.037 |
| | | | | −9.1 | +6.7 | |
| 0.1 KCl + 1.9 LiCl | 19 | .6905 | 1.7 | −8.2 | +10.3 | .036 |
| | | | | −8.2 | +8.9 | |
| 0.05 KCl + 1.95 LiCl | 39 | .7515 | 0.2 | −4.9 | +4.1 | .019 |
| | | | | −5.8 | +4.8 | |
| | | | | −6.2 | +6.2 | |
| 0.2 KCl + 3.8 LiCl | 19 | .6678 | 0.5 | −9.3 | +6.6 | .036 |
| | | | | −9.0 | +10.0 | |
| 0.1 KCl + 3.9 LiCl | 39 | .6522 | 0.1 | −5.8 | +2.9 | .022 |
| | | | | ... | +6.5 | |
| | | | | −4.9 | +5.3 | |

TABLE IX

| Concn. of mixture, moles per liter | $T_K$ MacInnes | $T_K$ measured | $\alpha/\beta$ |
|---|---|---|---|
| 0.1 KCl + 1.9 LiCl | 0.034 | 0.036 | 1.05 |
| 0.05 KCl + 1.95 LiCl | .017 | .019 | 1.09 |
| 0.2 KCl + 3.8 LiCl | .034 | .036 | 1.07 |
| 0.1 KCl + 3.9 LiCl | .017 | .022 | 1.11 |

## Summary

1. The MacInnes formula for the transport number of one of the two metallic ions in a mixture of alkali chlorides, as derived from the fundamental hypothesis developed in Paper I of this series, accounts for the transport numbers of the potassium, the rubidium and the cesium ions in mixtures of their chlorides with large amounts of sodium chloride and for the transport numbers of the potassium ion in mixtures of its chloride with large amounts of lithium chloride.

2. It seems then likely that, within the limits of experimental error: (A) the mobilities of the various ions in these mixtures are proportional to their values in solutions of the chlorides alone of the same concentration as the total concentration of the mixture; (B) the alkali chlorides are dissociated to the same extent in all the mixtures investigated.

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