

Det Kgl. Danske Videnskabernes Selskab.

Mathematisk-fysiske Meddelelser. **VI**, 9.

ON SOME RECENT INVESTI-
GATIONS CONCERNING MIXTURES
OF STRONG ELECTROLYTES

(TRANSFERENCE NUMBERS AND AMALGAM EQUILIBRIA)

BY

NIELS BJERRUM AND LUDWIG EBERT



KØBENHAVN

HOVEDKOMMISSIONÆR: ANDR. FRED. HØST & SØN, KGL. HOF-BOGHANDEL
BIANCO LUNOS BOGTRYKKERI

1925

I. Transference Numbers and Conductivity.

Last year R. F. SCHNEIDER and S. A. BRALEY published a paper¹ on transference experiments with mixtures of sodium chloride and potassium chloride. The authors arrive at the conclusion that an interpretation of their experiments is only possible on the assumption that complex ions are found in the solutions even at a salt concentration as small as 0.1 N. They characterise this as a fact speaking against the recent theories of the complete dissociation of the strong electrolytes.

As SCHNEIDER and BRALEY thus seem to consider that their experiments go to disprove the latest theories about electrolytes, we have subjected their material to a critical inspection and have come to the conclusion that their assertion is not tenable.

SCHNEIDER and BRALEY compare their experimentally determined transference numbers with calculated values. We are of opinion that the formula employed by them for the calculation is not correct, and that the correct formula gives a result more favorable to the recent theories than their own formula.

The formula employed by SCHNEIDER and BRALEY is taken from a paper by BRALEY and HALL²

¹ Journ. Amer. Chem. Soc. **45**, 1121 (1923).

² Journ. Amer. Chem. Soc. **42**, 1770 (1920).

and is as follows:

$$\frac{T_{\text{Na}}}{T_{\text{K}}} = K \cdot \frac{C_{\text{NaCl}} \cdot \Lambda_{\text{NaCl}} / \Lambda_{\theta \text{NaCl}} \cdot \Lambda_{\theta \text{Na}}}{C_{\text{KCl}} \cdot \Lambda_{\text{KCl}} / \Lambda_{\theta \text{KCl}} \cdot \Lambda_{\theta \text{K}}} \quad (1)$$

Here

$T_{\text{Na}}, T_{\text{K}}$ denote Hittorf transference numbers,
 $C_{\text{NaCl}}, C_{\text{KCl}}$ » molal concentrations,
 $\Lambda_{\text{NaCl}}, \Lambda_{\text{KCl}}$ » molal conductivities,
 $\Lambda_{\theta \text{NaCl}}, \Lambda_{\theta \text{KCl}}$ » molal conductivities at the concentration 0

and K a constant calculated to 1.17.

Let us call the specific conductivity of a solution of sodium- and potassium-chloride \varkappa , and the transference numbers in the solution $T_{\text{Na}}, T_{\text{K}}, T_{\text{Cl}}$; we may then calculate the conductivities for the sodium-, potassium-, and chlorine-ions in the solution $\Lambda_{\text{Na}}, \Lambda_{\text{K}}, \Lambda_{\text{Cl}}$ by means of the following equations:

$$C_{\text{NaCl}} (\Lambda_{\text{Na}} + \Lambda_{\text{Cl}}) + C_{\text{KCl}} (\Lambda_{\text{K}} + \Lambda_{\text{Cl}}) = 1000 \varkappa \quad (2)$$

$$\frac{C_{\text{NaCl}} \cdot \Lambda_{\text{Na}}}{1000 \varkappa} = T_{\text{Na}}; \quad \frac{C_{\text{KCl}} \cdot \Lambda_{\text{K}}}{1000 \varkappa} = T_{\text{K}}; \quad (3), (4)$$

$$\frac{(C_{\text{NaCl}} + C_{\text{KCl}}) \Lambda_{\text{Cl}}}{1000 \varkappa} = T_{\text{Cl}} \quad (5)$$

From (3) and (4) we obtain

$$\frac{T_{\text{Na}}}{T_{\text{K}}} = \frac{C_{\text{NaCl}} \cdot \Lambda_{\text{Na}}}{C_{\text{KCl}} \cdot \Lambda_{\text{K}}} \quad (6)$$

There is nothing hypothetical in the equations (2)–(6). They may be said to define the quantities $\Lambda_{\text{Na}}, \Lambda_{\text{K}}, \Lambda_{\text{Cl}}$.

¹ A similar formula is given by G. M. J. MACKAY. Journ. Amer. Chem. Soc. **33**, 308 (1911).

The hypothetical assumption only appears when, in order to try these equations we assume Λ_{Na} , Λ_{K} , Λ_{Cl} to have the same values in mixtures as they have in solutions of the pure salts with the same total salt concentration.

The recent theories on the complete dissociation of strong electrolytes involve that this assumption should be fulfilled with good approximation. It need not, however, hold good with absolute exactness as the various ions need not have exactly the same effect on the conductivity of the ion under consideration. In the main the assumption is identical with KOHLRAUSCH's old, empirically found, thesis of the additivity of the ion conductivities.

If in the formula (1) (BRALEY and HALL's formula) we introduce

$$\Lambda_{0\text{Na}} \cdot \frac{\Lambda_{\text{NaCl}}}{\Lambda_{0\text{NaCl}}} = \Lambda_{\text{Na}} \quad (7)$$

and corresponding expressions for Λ_{K} (which is permissible when the conductivities of the sodium- and chlorine-ions change proportionally with the salt concentrations), we obtain a formula

$$\frac{T_{\text{Na}}}{T_{\text{K}}} = K \cdot \frac{C_{\text{NaCl}} \cdot \Lambda_{\text{Na}}}{C_{\text{KCl}} \cdot \Lambda_{\text{K}}} \quad (8)$$

which only differs from (6) by the numerical factor $K = 1.17$. It is the presence of this numerical factor which makes (1) incorrect.

Formula (6) represents BRALEY and HALL's experiments far better than their own formula (1). This will appear from Table 1 (and Fig. 1).

The ion-conductivities necessary for the calculation after (6) were obtained in the following way: From NOYES and

Table 1.
Transference ratios in salt mixtures (NaCl:KCl = 1:1).

Total Conc.	Δ_{Na}	Δ_{K}	T_{Na}/T_{K}		
			calc. (6)	obs. (Br. a. H.)	calc. (1)
0.2 N	41.3	61.5	0.671	0.673	0.776
0.4 N	38.9	59.3	0.657	0.656	0.760
1.6 N	—	—	—	0.643	0.700

FALK's tables of salt conductivities corrected for viscosity¹ and transference numbers² were calculated the conductivities for Na⁺ and K⁺ in the chlorides at the concentrations 0.01, 0.1, and 1 N. The transference numbers designated as true by WASHBURN³ were, however, employed for 1 N.

By plotting these values against the cubic root of the concentration, the values of the transference numbers corresponding to the total salt concentrations 0.2 and 0.4 N were obtained. For the concentration 1.6 N which is also employed by BRALEY and HALL, the data necessary for the calculation are not at hand.

Table 1 shows how well the calculation after (6) agrees with the experimental result and how badly formula (1) agrees with them. It seems to us a specially striking fact that the deviations between BRALEY and HALL's experimental results and their own calculation increase with increasing dilution. According to their conception this means that the complex formation increases with increasing dilution, a result difficult to understand from the view point of the mass law.

¹ Journ. Amer. Chem. Soc. **34**, 471 (1912).

² Journ. Amer. Chem. Soc. **33**, 1449 (1911).

³ Zeitschr. physik. Chem. **66**, 552 (1907).

In the calculation given above we employed WASHBURN'S true transference numbers for the concentrated solutions. This, no doubt, is of no great importance in the results, but, in principle, seems to us more correct than using the Hittorf numbers. On electrolysis of mixtures, for instance of NaCl and KCl, we obtain transference numbers which are erroneous in about the same proportion for both cations, the concentration of both ions being changed in the same way by the transferred water, no matter whether the water is transferred by the one or the other of the ions.

We shall now compare SCHNEIDER and BRALEY'S measured values for T_{Na}/T_K with the calculated values, in the same way as we did with BRALEY and HALL'S measurements. We get the molecular conductivities of the pure salts and the values of the transference numbers of the same solutions from NOYES and FALK'S excellent tables. These values are designated "N. and F." in Table 2, while "Sch. and Br." denotes the values calculated by SCHNEIDER and BRALEY.

Table 2.

Total-Conc.	3 Na : 1 K			2 Na : 1 K			1 Na : 1 K			1 Na : 2 K			1 Na : 3 K		
	obs.	calc.		obs.	calc.		obs.	calc.		obs.	calc.		obs.	calc.	
		Sch. a. Br.	N.a.F.		Sch. a. Br.	N.a.F.		Sch. a. Br.	N.a.F.		Sch. a. Br.	N.a.F.		Sch. a. Br.	N.a.F.
0.0	—	2.40	2.05	—	1.60	1.37	—	0.799	0.685	—	0.400	0.343	—	0.266	0.228
0.1	2.12	2.35	2.03	1.46	1.57	1.35	0.749	.784	.677	0.389	.392	.339	0.235	.261	.226
0.2	1.90	2.31	2.01	1.30	1.54	1.34	.640	.770	.671	.153	.385	.336	.035	.256	.224
0.4	1.59	2.27	1.97	1.07	1.51	1.31	.510	.756	.654	.339	.378	.329	.208	.252	.219
0.8	1.81	2.22	1.95	1.18	1.48	1.30	.540	.740	.650	.343	.370	.325	.180	.247	.217
1.6	2.39	2.10	—	1.30	1.40	—	.543	.702	—	.370	.351	—	.315	.234	—

The plot in Fig. 1 will be more illustrative than Table 2. Since the value of

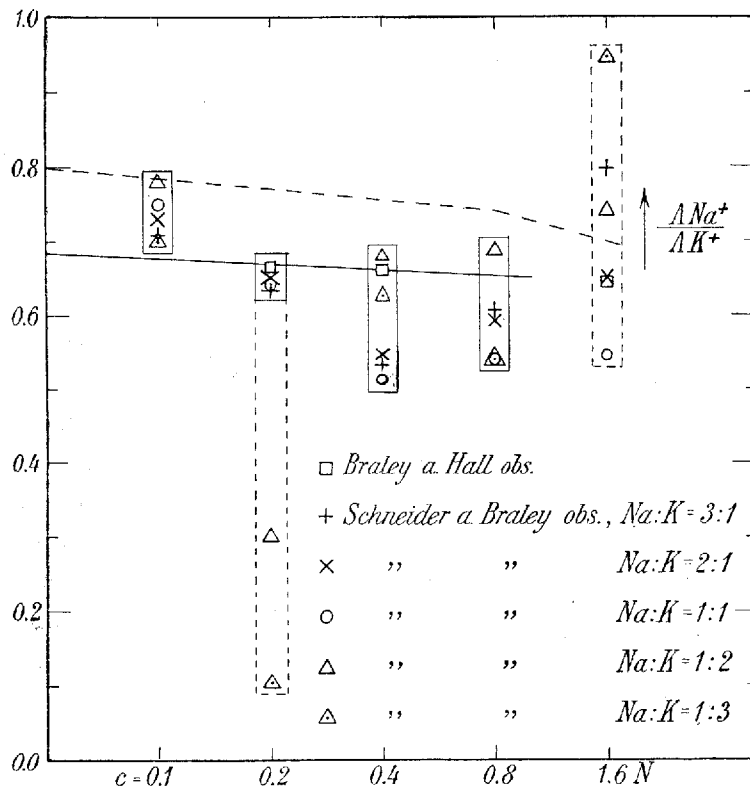


Fig. 1.

The change of mobility ratio (Λ_{Na}/Λ_K) in mixtures of NaCl and KCl with change of total salt concentration. The full line represents the values calculated by us and the dotted line the values calculated by SCHNEIDER and BRALEY.

$$\frac{\Lambda_{Na}}{\Lambda_K} = \frac{T_{Na}}{T_K} \cdot \frac{C_{KCl}}{C_{NaCl}}$$

is, according to our opinion, a constant, as long as the total salt concentration keeps constant, we plot this value against $\log C_{Total}$.

The values calculated by us are represented by a full line, the values calculated by SCHNEIDER and BRALEY by a

dotted line. All the measured values are contained within the square frames. Also the measurements of BRALEY and HALL are taken into account.

The deviations of the observed values from our theoretical curves are in many cases rather considerable, but in the average much less than those from SCHNEIDER and BRALEY'S theoretical curve. Rather striking are the two small experimental values at 0.2 N. At the same concentration, however, we have four values that show complete agreement with our calculated value. We also notice that the experimental values show great fluctuations at 1.6 N solutions. We may at any rate state that the great majority of the measurements for the concentrations 0.1, 0.2, 0.4 and 0.8 N corresponds fairly well with our theoretical values.

It is difficult to estimate how great the possible errors of analysis may be, but the rather irregular character of the deviations seems to us to render it not improbable that they are in the main caused by errors in the difficult separation of potassium from sodium. A well known fact is that the determination of transference numbers is greatly influenced even by very small errors of analysis. This view seems to be supported by two facts. Firstly: that SCHNEIDER and BRALEY'S new transference determinations do not agree very well with the earlier ones by BRALEY and HALL, a fact not discussed by SCHNEIDER and BRALEY, secondly — by the fact that the most deviating experimental values are average values from single measurements that themselves differ widely: so the striking number 0.035 for 0.2 N solution and the ratio $K:Na = 3:1$ has been calculated from the numbers 0.097, 0.021, 0.003, 0.021.

It is also of interest to consider SCHNEIDER and BRALEY'S

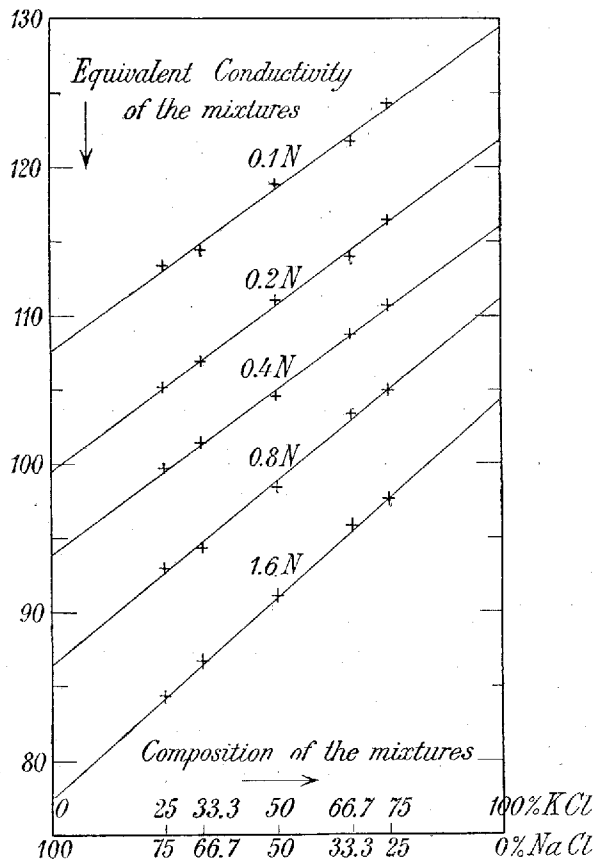


Fig. 2.

The curves obtained by plotting the equivalent conductivity of mixtures of $\frac{1}{2}$ NaCl and KCl against the mol fraction at various total salt concentrations.

conductivity measurements. If, as in Fig. 2, we plot the equivalent conductivities of the salt mixtures against the mol fraction of the mixtures, we obtain points which, for each total concentration, lie with very good approximation on a straight line.¹

¹ By using a rational concentration scale, not only do the doubly

The greatest deviations in this graphical representation amount to ± 0.4 units in Λ , i. e. about 0.4 p. c., generally they are much smaller.

A. E. STEARN'S¹ conductivity measurements in mixtures of NaCl—KCl, NaBr—KBr, NaJ—KJ show quite clearly the same simple additivity within a concentration range from 0.1 N until 0.5 N. This result affords a good corroboration of the simple additivity in the properties of these salt solutions and is thus a support of the theory of the simple, not complex, composition of such solutions.

We hope with the preceding remarks to have shown that the investigations of the transference number and conductivity in mixtures of sodium- and potassium chlorides by SCHNEIDER and BRALEY cannot be used as an argument in favor of complex formation in mixed solutions of the salts of alkali metals.

II. Amalgam Equilibria.

SCHNEIDER and BRALEY claim that their theories on complex formation in sodium chloride and potassium chloride solutions agree with papers by SMITH and WELLS. Accordingly we should like to offer a few remarks on these works. According to our view the experimental data in these papers are in good agreement with the recent theory of the complete dissociation of the strong electrolytes.

curved lines in SCHNEIDER and BRALEY'S Fig. 3 change into straight lines but, likewise, their figures 1, 5 and 6 lose much of their complicated appearance. It is, however, to be noted that the conductivity values for the pure salt solutions when extrapolated from our simple plot show rather considerable differences from the values following from NOYES and FALK'S tables.

¹ Journ. Amer. Chem. Soc. 44, 670 (1922).

In a series of papers SMITH with various co-workers has carried out a number of excellent experimental investigations on the heterogeneous equilibrium between amalgams containing two light metals (Na, K, Sr) and aqueous solutions of salts of these metals.¹

The results of these investigations are conveniently represented in tables containing the values of the following equilibrium constants:

$$K = \frac{[K_{\text{Hg}}] \cdot [\text{Na X}]}{[\text{Na}_{\text{Hg}}] \cdot [\text{K X}]}, \quad (10)$$

$$K = \frac{[\text{Sr}_{\text{Hg}}] \cdot [\text{Na X}]^2}{[\text{Na}_{\text{Hg}}]^2 \cdot [\text{Sr X}_2]}, \quad (11)$$

$$K = \frac{[\text{Sr}_{\text{Hg}}] \cdot [\text{K X}]^2}{[\text{K}_{\text{Hg}}]^2 \cdot [\text{Sr X}_2]}, \quad (12)$$

where $[K_{\text{Hg}}]$, $[\text{Na}_{\text{Hg}}]$, $[\text{Sr}_{\text{Hg}}]$ denote molal concentrations in the amalgams (mol per 1000 g mercury) and $[\text{KX}]$, $[\text{NaX}]$, $[\text{SrX}_2]$ molal salt concentrations in the aqueous phase.²

From the many experiments made by SMITH and his co-workers we are able to see how K varies with the amal-

¹ M. Mc P. SMITH, Amer. Chem. Journ. **37**, 506 (1907), Journ. Amer. Chem. Soc. **32**, 502 (1910); **35**, 39 (1913). SMITH and F. R. BALL, same Journ. **39**, 179 (1917). SMITH and S. A. BRALEY, same Journ. **39**, 1545 (1917); **40**, 197 (1918). SMITH and E. A. REES, same Journ. **40**, 1802 (1918). SMITH and L. S. WELLS, same Journ. **42**, 185 (1920).

² SMITH himself uses "mol fractions" (the total amount of salt = 1) instead of molal concentrations. This creates considerable difficulties in the case of the strontium equilibria, as the expressions need not then, according to the mass action law be constant. We have recalculated all experiments to molal concentrations. For the mixtures with strontium salts, the values tabulated by SMITH and his co-workers show far greater variations than our K -values.

Table 6.

The equilibrium constant K at 25°. K and Na possess the same normality in the solution.¹

0.15—0.20 Milliequiv. of metals per 10 g. Hg.

Ion normality	NaCl—KCl	NaCl—KBr	NaCl—KJ	NaBr—KBr	NaBr—KJ	NaJ—KJ
0.1	0.453	0.461	0.457	0.456	—	—
0.2	0.454	0.453	0.452	0.449	0.448	0.448
0.5	0.439	0.445	0.430	0.439	0.433	0.430
1.0	0.427	0.425	0.409	0.412	0.406	0.398
2.0	0.402	0.395	0.365	0.367	0.360	0.350
4.0	0.342	0.330	0.295	0.299	0.276	0.262

Table 7.

The equilibrium constant K at 25°. Sr and Na , Sr and K respectively possess the same normality

in the solution.

Ion normality	KCl—SrCl ₂	NaCl—SrCl ₂
	0.15—0.20 milliequiv. of metals per 10 g. Hg. ²	0.20—0.25 milliequiv. of metals per 10 g. Hg. ³
0.05	73.61 ⁴	—
0.1	61.7	—
0.2	53.9	10.60
0.4	56.17	8.98
0.8	63.88	8.68
1.2	—	8.89
1.6	106.6	9.90
2.4	—	12.81
3.0	222.1 ⁵	—
3.2	—	20.36

¹ WELLS and SMITH, Journ. Amer. Chem. Soc. **42**, 185 (1920).

² SMITH and REES, Journ. Amer. Chem. Soc. **40**, 1802 (1918).

³ SMITH and BRALEY, Journ. Amer. Chem. Soc. **39**, 1545 (1917).

⁴ 0.068 milliequiv. of metals pr. 10 g. Hg.

⁵ 0.35 milliequiv. of metals pr. 10 g. Hg.

gam-concentration, with the ratio between the salt concentrations, and with the total salt concentration.

The variations of K caused by the change in the amalgam-concentration, do not here concern us. The values for K given in the following tables correspond to very nearly the same amalgam-concentration. The salt concentration ratio alters K to no great extent. The values for K given in the following tables always correspond to solutions in which the two metal salts possess the same normality.

From tables 6 and 7 it follows how K changes with the total salt concentration for all the more thoroughly investigated salt-pairs. These changes in K SMITH ascribes to the existence of complexes in the salt solutions.

In the following we shall show how the changes in the K -values can be explained by the hypothesis of the complete ionisation of the strong electrolytes without assuming the existence of complexes.

The lack of constancy in K is due to the use of concentration instead of activity. In applying activity in the mass-action-expression we get a true constant, designated K_0 .

We have

$$\text{For Na — K:} \quad K_0 = K \cdot \frac{F_{\text{Na}}}{F_{\text{K}}}. \quad (13)$$

$$\text{For Na — Sr:} \quad K_0 = K \cdot \frac{F_{\text{Na}}^2}{F_{\text{Sr}}}. \quad (14)$$

$$\text{For K — Sr:} \quad K_0 = K \cdot \frac{F_{\text{K}}^2}{F_{\text{Sr}}}. \quad (15)$$

Here F_s denotes the apparent activity coefficient for the ion S , i. e. the ratio between the activity of the non-aqueous ion (a_s) and the concentration in the solution (c_s):

$$F_S = \frac{a_S}{c_S}. \quad (16)$$

If we suppose complete dissociation we can assume that the deviation of the activity coefficient from 1 is due partly to the electric forces between the electric charges of the ions and partly to the hydration of the ions. Then the following relation will hold good¹:

$$F_S = f_S \cdot \left(\frac{p_0}{p}\right)^{m_S}. \quad (17)$$

Here f_S denotes the decrease in the activity of the ion S, due to the electric forces, m_S the hydration number of the same ion, p_0 the vapor-pressure of water and p the vapor-pressure of the solution.

By introducing in (13)—(15) expressions from formula (17) and by logarithmic transformation we obtain:

For Na—K:

$$\log K_0/K = \log f_{Na} - \log f_K + (m_{Na} - m_K) \log p_0/p. \quad (18)$$

For Na—Sr:

$$\log K_0/K = 2 \log f_{Na} - \log f_{Sr} + (2m_{Na} - m_{Sr}) \log p_0/p. \quad (19)$$

For K—Sr:

$$\log K_0/K = 2 \log f_K - \log f_{Sr} + (2m_K - m_{Sr}) \log p_0/p. \quad (20)$$

In order to explain the experiments in table 6 by means of (18), we may put $f_{Na} = f_K$, since the electric forces show approximately the same effect on the activity of ions of the same valency. For K_0 we may put the value

¹ BJERRUM, Medd. fr. K. Vet. Nobelinstitut, Stockholm 5, Nr. 16 (1919)
Zeitschr. für anorg. u. allgem. Chemie 109, 275 (1920).

to which K approaches with decreasing salt concentration ($\log K_0 = -0.34$) and for $\log p_0/p$ the value from

$$\log p_0/p = 0.00421 \cdot t = 0.00421 \cdot 3.4 \cdot c_{\text{Ion}} = 0.0143 \cdot c_{\text{Ion}} \quad (21)$$

Here t denotes the lowering of the freezing point of the solution, c_{Ion} is the salt-normality of the solution, and 3.4 is a value for the molecular lowering of the freezing point which can be employed with sufficient accuracy both for the sodium- and potassium-salts within the range of concentrations here employed.

From (20) we then obtain:

$$\log K_0/K = (m_{\text{Na}} - m_{\text{K}}) \cdot 0.0143 \cdot c_{\text{Ion}} \quad (22)$$

In table 8 are given the values of $m_{\text{Na}} - m_{\text{K}}$, i. e. the difference in the sodium- and potassium-ion hydration, obtained from equation 22, for the salt pairs: KCl — NaCl and KJ — NaJ.

Table 8.

Salt-Normality	—log K	NaCl — KCl		—log K	NaJ — KJ	
		log K_0/K	$m_{\text{Na}} - m_{\text{K}}$		log K_0/K	$m_{\text{Na}} - m_{\text{K}}$
0.1 N	0.344	0.004	—	—	—	—
0.2 N	0.343	0.003	—	0.349	0.009	—
0.5 N	0.357	0.017	2.4	0.366	0.026	3.5
1.0 N	0.370	0.030	2.1	0.400	0.060	4.2
2.0 N	0.396	0.056	2.0	0.450	0.110	3.8
4.0 N	0.466	0.126	2.2	0.582	0.242	4.2
		log $K_0 = -0.34$			log $K_0 = -0.34$	

For each salt-pair the hydration-numbers found are sufficiently constant, but whilst the experiments with the chloride-pair can be explained by the fact that the sodium-ion combines with 2.2 more than the potassium-ion, the experiments demand a difference of 3.9 in the hydration

of the ions in the iodide-pair. For the other salt-pairs in table 6 the changes in $\log K$ correspond to hydration differences varying between 2.2 and 3.9. Since, according to our hypothesis the hydration difference should have been the same in all cases, the variation in the hydration numbers found for the various salt-pairs shows that the change of K with the salt concentration cannot be exclusively ascribed to hydration. In order to explain the results of the experiments, we must assume that the various anions have specific effects on the activity of the sodium- and potassium-ions.¹

From investigations on non-electrolytes we know something about the effect of such forces and hence may draw certain conclusions as to their effect on electrolytes.

Solubility experiments with non-electrolytes have shown that the activity of these substances in solution is affected by the presence of foreign substances, both ions and non-electrolytes. These effects which have been called the salting-out effects ordinarily vary linearly with the concentration of the foreign substances. They may be explained partly by the hydration and partly by the dipole and quadrupole forces between the molecules.²

Whilst the hydration-effect only depends on the depressing effect of the foreign substances on the vapor pressure of the solvent (hence mainly on the number of their molecules), the effect of the dipole and quadrupole forces is specific for the different foreign substances.

When dealing with the activity of ions we may, besides the effects of the hydration of the ion and of its gross

¹ cf. BJERRUM, *Zeitschr. physik. Chem.* **104**, 424—25 (1923). LINDERSTRØM-LANG, *Comptes Rendu des travaux du Laboratoire de Carlsberg* **15**, Nr. 4 (1923).

² cf. P. DEBYE, *Physik. Zeitschr.* **21**, 178 (1920); LINDERSTRØM-LANG *I. c.* *Vidensk. Selsk. Math.-fys. Medd.* VI, 9.

charge, also expect to find effects from possible dipole — or quadrupole forces. From the experience gained from the salting-out of non-electrolytes we may expect that these effects will be proportional to the concentration of the reacting substance. For any definite salt-pair these effects will then be proportional to the concentration like the hydration effect. If then, as above, the hydration numbers are calculated without taking into account the effect of these forces, we get constant hydration numbers for each salt-pair, but on account of the specifcness of the forces, the hydration numbers calculated for the various salt-pairs may differ. In order to explain the experimental results of SMITH and his co-workers we must assume that the dipole- and quadrupole forces between halogen-ions and alkali-metal-ions vary in such a degree with the nature of the halogen that activity-differences corresponding to a hydration of one or two molecules of water may appear. This is what might be expected from experiments of the salting-out of non-electrolytes.

To complete the discussion we may add that the typical ion-forces, i. e. the forces between the gross charge of the ions, may also lead to specific activity differences between the ions when we take into account the non-negligible dimensions of the ions.¹

As regards the salt-pairs KCl, SrCl₂, and NaCl, SrCl₂, according to table 7, K first decreases with rising salt concentration, and then afterwards rises again, slightly in the case of NaCl, SrCl₂, strongly in the case of KCl, SrCl₂. For the pair KCl, SrCl₂ the minimum value is reached at 0.2 N and for NaCl, SrCl₂ at 0.8 N. An understanding of these facts is gained from the formulas (19) and (20).

¹ P. DEBYE, l. c.; BJERRUM, Zeitschr. allg. u. anorg. Chem. **129**, 323 (1923).

In dilute solutions the influence of the terms $2 \log f_{\text{Na}}$ — $\log f_{\text{Sr}}$ predominate as these terms decrease only by the cubic root or at most the square root of the concentration, whilst the hydration terms decrease linearly with the concentration. For the divalent strontium we can according to DEBYE¹ assume $\log f_{\text{Sr}}$ 2^2 times greater than $\log f_{\text{Na}}$. For sufficiently dilute solutions, therefore, we have

$$\log K_0/K = -2 \log f_{\text{Na}}. \quad (23)$$

As $\log f_{\text{Na}}$ is negative and increases numerically with the concentration, according to (23) K must decrease in dilute solutions with increasing concentration. For great concentrations the hydration term will be the most important. Conditions will then be reversed, since the hydration of the strontium-ion, being greater than that of the sodium-ion and especially than that of the potassium-ion, will cause a marked rise of K . In accordance with the experiments the rise should be greatest and should occur earlier for the salt-pair KCl , SrCl_2 .

III. Some other properties of mixed salt solutions.

It may be of interest to summarise briefly the results of some other investigations concerning mixtures of NaCl and KCl and their bearing on the question of complex formation.

KLEIN and SVANBERG² measured the lowering of the freezing point of such solutions. Their data are as follows:—

Conc.	Freezingpoint-Lowerings
0.5 N KCl	1.686°
0.5 N NaCl	1.688°
0.25 N KCl + 0.25 N NaCl	1.716°

¹ Physik. Zeitschr. **24**, 185 (1923).

² Medd. f. Kgl. Vetenskap. Akad. Nobelinstit. Stockholm, **4**, Nr. 1, p. 9 (1920). 2*

a result in direct contradiction to any theory of complex formation. HARKINS and ROBERTS¹ seem to have observed an opposite effect, but they have not published numerical data.

A. E. STEARN's data on the viscosity of mixtures² show a good additivity in the fluidity even with 4.0 N solutions. Concerning the measurements of heats of dilution by the same author with G. M. SMITH and R. F. SCHNEIDER³ it will suffice to observe that a recalculation of these data on the basis of the later theories furnish a remarkable agreement with the observed values.

Summary.

It is shown how SCHNEIDER and BRALEY's experiments on transference-numbers in mixed solutions of NaCl and KCl might be explained on the hypothesis of the complete ionisation of the strong electrolytes. Hence these experiments cannot be used as an argument in favor of the conception that a strong complex formation takes place in such solutions.

Further it is shown how the careful experiments of SMITH and his co-workers, on equilibria between amalgams and aqueous solutions of salt mixtures, might likewise be interpreted without the necessity of assuming complex formation when taking into account the more recent views on the nature of electrolytes.

Further, a complex formation would agree badly with the freezing point measurements available and with the markedly additive properties of the alkali salts.

¹ Journ. Amer. Chem. Soc. **38**, 2678 (1916).

² Journ. Amer. Chem. Soc. **44**, 670 (1922).

³ Journ. Amer. Chem. Soc. **42**, 18, 32 (1920).