[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS.]

HETEROGENEOUS EQUILIBRIA BETWEEN AQUEOUS AND METALLIC SOLUTIONS: THE INTERACTION OF MIXED SALT SOLUTIONS AND LIQUID AMALGAMS. VI. A STUDY OF THE IONIZATION RELATIONS OF SODIUM AND POTASSIUM CHLORIDES, BROMIDES AND IODIDES IN MIXTURES.

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A. Introduction.

This investigation is a study of the equilibrium between mixed sodium and potassium salts and liquid amalgams, with free mercury present in such quantity that its active mass may be taken as constant, as represented by the equation,

$$KHg_m + NaX \rightleftarrows KX + NaHg_n,$$

in which NaX and KX represent the dissolved halides, chloride, bromide, or iodide. The investigation is the sixth of a series on this subject,[2] and its especial object is to study the influence exerted by the anions on the constitution of aqueous halide solutions.[3]

It has been shown in earlier papers of this series that in equivalent mixtures of sodium and potassium chlorides, the sodium ion fraction gains upon that of the potassium as the concentration is increased. Analogous observations have been made, to an even greater degree, in the present investigation, which, in addition to the chlorides, includes the bromides and iodides of sodium and potassium. These ion-fraction changes may be due to any or all of the following causes: the existence of intermediate ions, of hydrated ions, and of complex ions.

B. Theoretical.

Since only the free atoms and ions of the metals are supposed to take a direct part in the reaction represented by the equation,

$$K_{Hg} + Na_{H_2O} \rightleftarrows Na_{Hg} + K_{H_2O},$$

we must re-state the equilibrium in terms of the equation,

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[1] From a thesis submitted to the Graduate School of the University of Illinois by Lansing Sadler Wells in partial fulfilment of the requirements for the degree of Doctor of Philosophy in chemistry.

[2] G. McP. Smith, THIS JOURNAL, 32, 502 (1910); 35, 39 (1913); Smith and Ball, 39, 179 (1917); Smith and Braley, 39, 1545 (1917); Smith and Rees, 40, 1802 (1918).

[3] The failure of the application of the different methods of determining the degree of ionization, namely the methods involving colligative properties, and also the conductivity method of Arrhenius, may be attributed to the occurrence of complex chemical processes between the different ionic and molecular species in solution, the nature, or, at any rate, the extent of which is by no means well known (cf. Smith and Rees, *Loc. cit.*).

$$K^\circ + Na^+ \rightleftarrows Na^\circ + K^+, \qquad (1)$$

in which K° and Na° represent the free atoms of potassium and sodium in the mercurial phase, and Na^+ and K^+ the simple, free ions in the aqueous phase. And this equilibrium may be formulated into the following mass-law expression:

$$\frac{(K^\circ)(Na^+)}{(Na^\circ)(K^+)} = k, \text{ or } C_\circ,^1 \qquad (2)$$

in which (K°) and (Na°) are the mol. fractions of free, uncombined potassium and sodium in the mercurial solution, and (K^+) and (Na^+) the simple ion fractions of these metals in the aqueous solution.

A liquid alkali amalgam contains, as the solute, a compound of the general formula $MeHg_x$;[2] but, even so, the alkali metal in such an amalgam possesses a solution tension, or tendency to enter into aqueous solution in the ionic condition. The solute in these amalgams must, therefore, be very slightly dissociated, in the sense of the equation,

$$MeHg_x \rightleftarrows Me^\circ + xHg, \qquad (3)$$

for which the mass-law expression is

$$\frac{(Me^\circ)(Hg)^x}{(MeHg_x)} = const.$$

Or, in the very dilute amalgams, in which the active mass of free mercury is constant, we have

$$\frac{(Na^\circ)}{(NaHg_n)} = const., \text{ and } \frac{(K^\circ)}{(KHg_m)} = const.$$

Assuming that these expressions hold true in amalgams containing both metals, we obtain

$$\frac{(K^\circ)}{(Na^\circ)} = \frac{(KHg_m)}{(NaHg_n)} = \frac{(K^\circ) + (KHg_m)}{(Na^\circ) + (NaHg_n)} = \frac{(K_{Hg})}{(Na_{Hg})}, \qquad (4)$$

and, substituting in Equation 2, for $\frac{(K^\circ)}{(Na^\circ)}$, the value $\frac{(K_{Hg})}{(Na_{Hg})}$, we obtain the expression

$$\frac{(K_{Hg})(Na^+)}{(Na_{Hg})(K^+)} = k. \qquad (5)$$

Now, in any individual mixed salt solution, the ratio of the salt fractions must bear some numerical relationship to the ion-fraction ratio, or

$$\frac{(NaX)}{(KX)} = n\,\frac{(Na^+)}{(K^+)}, \qquad (6)$$

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[1] It is thought advisable to return to the letter *k* (or *K*), as in the original formulas, in place of the symbol $C_\circ$ which was used for a special reason in the third and fourth papers of the series (cf. Smith and Rees, *Loc. cit.*, p. 1808, footnote).

[2] Cf. G. McP. Smith, *Z. anorg. Allegem. Chem.*, **58**, 381 (1908); **88**, 161 (1914).

in which the value of n is unknown and may, of course, vary with the conditions of salt concentration. But, whatever the value of n may be at any specific composition of the aqueous mixture, it follows from the preceding equations that, in the case of any particular equilibrium mixture,

$$\frac{(K_{Hg})(NaX)}{(Na_{Hg})(KX)} = n.k = C_c{}^1. \qquad (7)$$

The values of (K_{Hg}) and (Na_{Hg}) may readily be calculated from the analytical data of the equilibrium amalgams, and (NaX) and (KX) are known concentration fractions of sodium and potassium chloride, bromide, or iodide. Thus it is possible to calculate C_c, the "equilibrium expression" at any specific salt concentration.

By definition,

$$(Na^+) + (K^+) = 1.$$

Combining this with Equation 5, and solving, we get

$$(K^+) = \frac{(K_{Hg})}{(K_{Hg}) + k(Na_{Hg})}. \qquad (8)$$

If, therefore, a means could be found of obtaining the value of k, we should be in a position to calculate the actual ion-fraction values, (Na^+) and (K^+), in the various mixed solutions.

C. Experimental Details.

1. Materials and Apparatus.—In addition to the apparatus and materials used in the preceding investigations, and there described, the following are used for the first time in this investigation:

(*a*) *Sodium Bromide, $NaBr.2H_2O$.*—The pure commercial salt was recrystallized from hot distilled water. The mother liquor was removed as completely as possible by suction, after which the remainder was thrown off in a high speed electrical centrifuge. A second crystallization was made from pure water, and the mother liquor removed as before. After this the crystals were dried for several days over calcium chloride, and the hydrated salt finally placed in tightly stoppered bottles.

(*b*) *Potassium Bromide.*—A good grade of commercial salt was recrystallized twice from hot water, as described above. The salt was then dried in a platinum dish in an electric oven at 150°. Just before use it was heated in the dish in an electric muffle furnace for at least two hours at a temperature just short of fusion. It was cooled in a desiccator over calcium chloride.

(*c*) *Sodium Iodide, $NaI.2H_2O$.*—The pure commercial salt was recrystallized three times from hot water, as described in the purification of sodium bromide. After this the crystals were dried for several days over calcium chloride, and the hydrated salt finally placed in tightly stoppered bottles.

[1] C_c, then, represents the value of $n.k$, under specific experimental conditions.

(*d*) *Potassium Iodide.*—A pure grade of commercial salt was recrystallized two or three times from hot water. The samples were then dried in an electric oven for several hours at 150°, and finally placed in tightly stoppered bottles.

2. **Method of Experimentation.** (*a*) *Solutions.*—Separate solutions of the NaX and KX (in which X represents Cl, Br, or I) were made up, each equal in concentration to the total concentration of the mixed solution desired. By mixing these solutions in the proper volume relations, solutions of any salt-concentration ratio desired, and of the given total salt concentration, were prepared.

In the case of the sodium chloride, potassium chloride, or potassium bromide, the pure dried salt was weighed out in the calculated quantity, dissolved in pure water, and the solution transferred to a calibrated volumetric flask, in which it was diluted to the mark at 25°. In the case of the potassium iodide, sodium iodide, or sodium bromide, the salt was weighed out in sufficient quantity to give a solution slightly more concentrated than desired. The normality of the solution so prepared was determined by the Volhard volumetric method, and it was then accurately diluted to the desired normality.

(*b*) *Equilibrium.*—In order that, at the start of each run, the amalgams should be as nearly as possible of the same concentration, the analyzed stock amalgams were diluted with mercury to the specific concentration desired. These amalgams were then brought into equilibrium with the solution under investigation, as described in the previous paper. The amalgam was in each case finally washed with water, and decomposed with hydrochloric acid, according to the procedure described in an earlier paper.[1]

Each run was made with 6 separate reaction mixtures, 3 of which were started with sodium amalgam and 3 with potassium amalgam; in all 6, identical mixed salt solutions were used. Equilibrium was, therefore, approached 3 times from each side.

(*c*) *Treatment of the Decomposition Products.*—The hydrochloric acid solution containing the alkali metals from the equilibrium amalgam was in each case quantitatively removed from the mercury and evaporated to dryness on the steam bath. The mercury itself was dried, and weighed to within 0.1–0.2 g. The mixed alkali chlorides were weighed and analized as described in a previous paper.[2]

D. Experimental Data.

The data obtained in this investigation are recorded in the following tables: In Table I, which is given in full to show the data in detail, as

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[1] Smith and Ball, *Loc. cit.*

[2] Smith and Ball, *Ibid.* The above procedure differs from that of Smith and Ball, in that the concentration of the equilibrium amalgams was accurately determined.

well as to afford an indication of the degree of accuracy attained,[1] the figures in the first column refer to the number of the experiment; the second column indicates the amalgam used at the start; the third, fourth and fifth columns contain the data, in grams, obtained by the analysis of the amalgam after the establishment of equilibrium between it and a solution of the composition given at the top of the table. Thus Col. 3 gives the weight of the mixed alkali chlorides; Col. 4 the weight of potassium chloroplatinate obtained in the analysis of the mixed chlorides; and Col. 5 the weight of the mercury in the equilibrium amalgam. Col. 6 shows the concentration of the equilibrium amalgam in total milli-equivalents of alkali metals per 10 g. of mercury, as calculated from the data in Cols. 3, 4 and 5; Cols. 7 and 8 give the mol. fractions of the amalgamated metals in the mercurial phase at equilibrium, as calculated from Cols. 3 and 4; and Col. 9 gives the value of the expression

$$\frac{(\mathrm{K}_{Hg})(\mathrm{NaX})}{(\mathrm{Na}_{Hg})(\mathrm{KX})} = n.k = C_c,$$

in which (K_{Hg}) and (Na_{Hg}) are the respective mol fractions in the mercurial phase, from Cols. 7 and 8, and (NaX) and (KX) are the known mol fractions of the halides in the aqueous phase.

In the light of the above description the subsequent tables, which contain the results in abbreviated form, will be self-explanatory.

1. Effect of Varying the Concentration of the Mercurial Phase at a Fixed (Equivalent) Salt-Concentration Ratio and a Fixed Normal Concentration of the Aqueous Phase.—In the sodium-potassium equilibrium, the sodium-strontium equilibrium, and the potassium-strontium equilibrium, it has previously been observed that the total concentration of the mercurial phase exerts a marked effect on the equilibrium value C_c. In the case of the sodium-strontium equilibrium the C_c value was found to be a linear function of the amalgam concentration.[2] In the potassium-strontium equilibrium it was found that the C_c value increases directly with the amalgam concentration up to about 0.3 milli-equivalent of metals per 10 g. of mercury.[3] In all 3 equilibria studied it has been observed that when highly concentrated liquid amalgams are used the values of C_c obtained are apt to be erratic.

When it was first realized that the concentration of the liquid amalgams was a factor of moment, a study was made of the question by diluting the original amalgams with varying amounts of mercury, in a series of determinations, and then bringing them to equilibrium, at 25°, with a 0.2 *N*

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[1] The most consistent values are obtained with amalgams which contain 0.15–0.20 milli-equivalents of metals per 10 g. of Hg; for this reason, beginning with Table IV, the amalgams used were all of this approximate concentration.

[2] Smith and Braley, *Loc. cit.*

[3] Smith and Rees, *Ibid.*

equivalent mixture of sodium and potassium chlorides;[1] but, owing to the incomplete nature of this first study, it has seemed desirable to investigate the question further.

TABLE I.

The Effect of Varying the Concentration of the Mercurial Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

Temperature, 25°. *NaCl : KCl.*

Expt. No.	Amalgam at start.	Analysis of the equilibrium amalgam. NaCl+KCl.	K₂PtCl₆.	Hg.	Milli-equiv. of metals per 10 g. Hg.	Mol. fractions of amalgamated metals. Na.	K.	C_c.
1	Na	0.2118	0.2353	57.3	0.586	0.713	0.287	0.403
2	Na	0.1860	0.2090	50.7	0.581	0.709	0.291	0.411
3	Na	0.2180	0.2407	57.6	0.600	0.715	0.285	0.397
4	K	0.2091	0.2300	55.2	0.601	0.715	0.285	0.398
5	K	0.2137	0.2368	56.3	0.602	0.713	0.287	0.401
6	K	0.1915	0.2111	51.0	0.596	0.715	0.285	0.398
				Mean,	0.594			0.401
7	Na	0.2018	0.2367	109.5	0.291	0.695	0.305	0.438
8	Na	0.2055	0.2403	107.7	0.301	0.696	0.303	0.435
9	Na	0.2181	0.2544	113.2	0.304	0.698	0.302	0.433
10	K	0.2148	0.2515	115.9	0.285	0.696	0.304	0.436
11	K	0.2299	0.2698	118.1	0.307	0.695	0.305	0.439
12	K	0.2133	0.2491	108.8	0.309	0.697	0.303	0.435
				Mean,	0.299			0.436
13	Na	0.1843	0.2210	198.2	0.146	0.688	0.312	0.453
14	Na	0.1990	0.2379	197.4	0.159	0.689	0.311	0.451
15	Na	0.2069	0.2476	197.4	0.165	0.689	0.311	0.451
16	K	0.2240	0.2720	199.0	0.177	0.684	0.316	0.462
17	K	0.2265	0.2715	201.0	0.177	0.688	0.312	0.453
18	K	0.2310	0.2773	199.6	0.182	0.688	0.312	0.453
				Mean,	0.168			0.454
19	Na	0.2091	0.2551	261.8	0.126	0.684	0.316	0.462
20	Na	0.1650	0.1957	256.8	0.101	0.692	0.308	0.445
21	Na	0.1575	0.1868	261.2	0.095	0.689	0.311	0.452
22	K	0.2176	0.2648	262.9	0.130	0.685	0.315	0.459
23	K	0.2311	0.2790	279.2	0.130	0.686	0.314	0.457
24	K	0.1694	0.2039	253.6	0.105	0.686	0.314	0.456
				Mean,	0.115			0.455
25	Na	0.2101	0.2546	557.1	0.0593	0.684	0.316	0.461
26	K	0.2152	0.2627	573.5	0.0586	0.683	0.317	0.463
27	K	0.2033	0.2463	554.0	0.0573	0.688	0.311	0.453
28	K	0.2171	0.2594	560.5	0.0617	0.687	0.313	0.455
				Mean,	0.0592			0.458

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[1] Smith and Ball, *Loc. cit.*

The data for this study are given in Table I. In this series of experiments, with equivalent sodium and potassium chloride mixtures at a total concentration of 0.2 *N*, the concentration of the amalgams was decreased in each successive run. It is to be noted that the mean values of the "equilibrium expression," C_c, obtained in the different runs *increase* with *decreasing* amalgam concentration. In any one run, the equilibrium amalgams of the individual mixtures were always found to differ somewhat in concentration; because, in the first place, the stock amalgams were weighed out more or less roughly for dilution, and, in the second place, evolution of hydrogen (always in evidence to a very slight extent, at best) varied somewhat in the individual experiments. However, in the case of this equilibrium, the values of C_c are not influenced enough by the slight differences of amalgam concentration in the individual experiments of a run to warrant a correction, as in the case of the sodium-strontium, or of the potassium-strontium equilibrium.

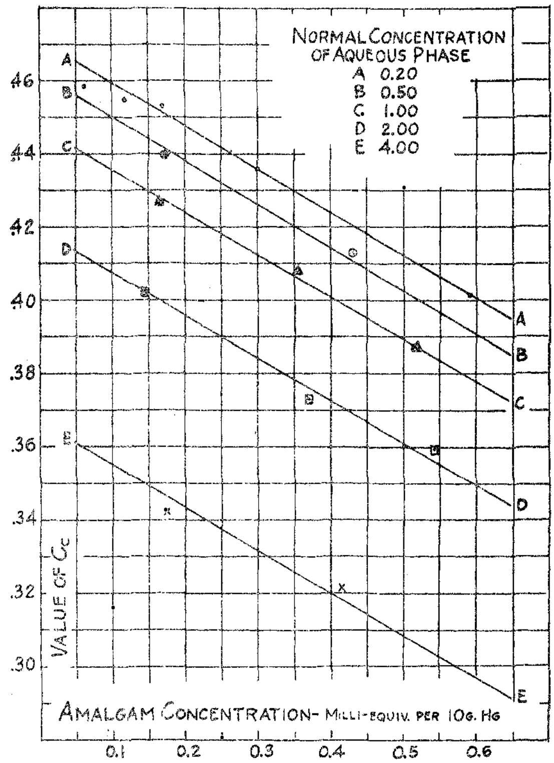

Fig. 1.—Showing the value of C_c as a function of amalgam concentration, at different salt concentrations, NaCl : KCl. Temperature, 25°.

Table II contains data showing the effect of varying the amalgam concentration, but with equivalent sodium and potassium chloride mixtures of 0.2, 0.5, 1.0, 2.0, and 4.0 *N* concentration, respectively.

In Fig. 1, the values of C_c as ordinates, are plotted against the total amalgam concentration in milli-equivalents of metals per 10 g. of mercury. Each point indicated in the plot is the average of about 6 separate determinations.

TABLE II.

The Effect of Varying the Concentration of the Mercurial Phase at Various Fixed (Equivalent) Concentrations of the Aqueous Phase.

Temperature 25°. *NaCl : KCl.*

Mean values of Expts. No.	Amalgam at start.	Milli-equivalents of metals per 10 g. Hg.	Mol. fractions of amalgamated metals. Na.	K.	C_c.
	Mixed Aqueous Phase 0.2 *N* (see Table I).				
	Mean,	0.594	0.713	0.287	0.401
	Mean,	0.299	0.696	0.314	0.436
	Mean,	0.168	0.688	0.312	0.454
	Mean,	0.115	0.687	0.313	0.455
	Mean,	0.0592	0.685	0.314	0.458
	Mixed Aqueous Phase 0.5 *N*.				
1– 3	Sodium	0.435	0.708	0.292	0.412
4– 6	Potassium	0.426	0.707	0.293	0.414
	Mean,	0.430			0.413
7– 9	Sodium	0.170	0.695	0.305	0.439
10–12	Potassium	0.174	0.694	0.305	0.440
	Mean,	0.172			0.439
	Mixed Aqueous Phase 1.0 *N*.				
13–15	Sodium	0.504	0.720	0.280	0.388
16–18	Potassium	0.527	0.722	0.278	0.386
	Mean,	0.515			0.387
19–21	Sodium	0.352	0.710	0.290	0.408
22–24	Potassium	0.357	0.710	0.289	0.408
	Mean,	0.354			0.408
25–27	Sodium	0.162	0.701	0.299	0.427
28–30	Potassium	0.166	0.700	0.300	0.427
	Mean,	0.164			0.427
	Mixed Aqueous Phase 2.0 *N*.				
31–33	Sodium	0.537	0.735	0.265	0.360
34–36	Potassium	0.541	0.735	0.265	0.360
	Mean,	0.539			0.360
37–39	Sodium	0.362	0.728	0.272	0.373
40–42	Potassium	0.374	0.729	0.271	0.372
	Mean,	0.368			0.373
43–44	Sodium	0.119	0.710	0.290	0.406
45–47	Potassium	0.159	0.715	0.285	0.398
	Mean,	0.143			0.401
	Mixed Aqueous Phase 4.0 *N*.				
48–50	Sodium	0.412	0.757	0.243	0.320
51–53	Potassium	0.420	0.756	0.244	0.322
	Mean,	0.416			0.321
54–56	Sodium	0.178	0.745	0.255	0.343
57–59	Potassium	0.173	0.746	0.254	0.341
	Mean,	0.175			0.342

2. Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio and at Various Specific Amalgam Concentrations.—Table III contains data showing the effect of increasing the total salt concentration in stages from 0.2 *N* to 4.0 *N*, the salts (sodium and potassium chlorides) being present in equivalent proportions, at various fixed amalgam concentrations. The values of C_c in this table were obtained by simply reading them from the plots in Fig. 1, at the indicated amalgam concentrations. Fig. 2 illustrates the effect upon the C_c value, at different specific amalgam concentrations, of varying the normality of the aqueous phase in the case of equivalent sodium and potassium chloride mixtures. From this series of plots it appears that a change in concentration of 0.1 milli-equivalent of metals per 10 g. of mercury produces a change of about 0.012 in the value of C_c.

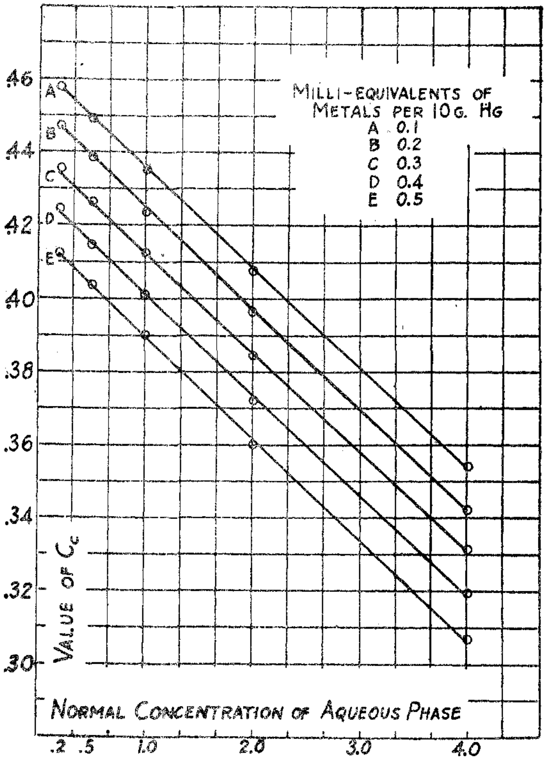

Fig. 2.—Showing the value of C_c as a function of total salt concentration, at different amalgam concentrations. NaCl : KCl. Temperature, 25°.

Table III.

The Value of C_c as a Function of Total Salt Concentration at a Fixed Equivalent Salt-Concentration Ratio and at Various Specific Amalgam Concentrations.

Temperature 25°. *NaCl:KCl.*

Normality of aqueous phase.	C_c values at x milli-equivalents of metals per 10 g. of mercury.				
	$x = 0.1$.	$x = 0.2$.	$x = 0.3$.	$x = 0.4$.	$x = 0.5$.
0.2	0.458	0.447	0.435	0.424	0.412
0.5	0.449	0.438	0.426	0.415	0.403
1.0	0.435	0.423	0.412	0.401	0.389
2.0	0.408	0.396	0.384	0.373	0.360
4.0	0.354	0.342	0.331	0.319	0.308

3. Effect of Varying the Concentration Ratio of the Salts at a Fixed Normal Concentration and a Fixed Amalgam Concentration.—If the reaction between alkali metal amalgams and alkali salt solutions is ionic, the mass-law expression,

$$\frac{(\mathrm{K}_{Hg})(\mathrm{Na}^+)}{(\mathrm{Na}_{Hg})(\mathrm{K}^+)} = k,$$

demands that the value of k should remain constant, regardless of the relative concentrations of the simple sodium and potassium ions; on the other hand, however, constancy is not necessarily demanded in the value of C_c in the equation,

$$\frac{(\mathrm{K}_{Hg})(\mathrm{NaX})}{(\mathrm{Na}_{Hg})(\mathrm{KX})} = n.k = C_c.$$

The results of previous experiments carried out in this laboratory with undiluted liquid sodium and potassium amalgams show "that if the total concentration of the solution remains constant, the value of C_c is constant even though the mol fractions of the two salts in the mixtures vary over wide limits. . . . . When diluted amalgams and more concentrated aqueous solutions were employed, a slight change in the value of C_c could be observed as the ratio of the salt concentrations was varied."[1]

TABLE IV.

The Effect of Varying the Concentration Ratio of the Salts at a Fixed Normal Concentration and a Fixed Amalgam Concentration.

Temperature 25°.

Mixed Aqueous Phase 0.2 *N*.

Mean values of Expts. No.	Amalgam at start.	Milli-equivalents of metals per 10 g. Hg.	Mol. fractions of amalgamated metals.		C_c.
			Na.	K.	
		2 NaCl:KCl.			
1– 3	Sodium	0.175	0.816	0.184	0.452
4– 6	Potassium	0.176	0.815	0.185	0.453
		Mean, 0.175			0.452
		NaCl:KCl.			
		See Table I, Expts. 13–18.			
		Mean, 0.168			0.454
		NaCl:2 KCl.			
7– 9	Sodium	0.171	0.526	0.474	0.451
10–12	Potassium	0.175	0.522	0.478	0.457
		Mean, 0.173			0.454
		Mixed Aqueous Phase 1.0 *N*.			
		2 NaCl:KCl.			
13–14	Sodium	0.178	0.823	0.177	0.431
15–17	Potassium	0.178	0.821	0.179	0.436
		Mean, 0.178			0.434
		NaCl:KCl.			
		See Table II, Expts. 25–30.			
		Mean, 0.164			0.427

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[1] Smith and Ball, *Loc. cit.*

Table IV contains the results obtained upon varying the ratio of sodium and potassium chlorides at a total concentration of 0.2 *N*, and at a total concentration of 1.0 *N*. These experiments show that within the experimental error, the value of C_c is constant when dilute amalgams and rather dilute aqueous solutions are employed. With the more concentrated aqueous solution, there appears to be a slight difference between the values of C_c obtained with a salt ratio of NaCl: KCl and those obtained with a ratio of 2 NaCl: KCl, but this difference really falls within the limit of accuracy of the latter run. These results are in accordance with, and confirmatory of, results obtained in the earlier investigations of the series.

4. Effect of Varying the Normal Concentration of Equivalent Sodium and Potassium Chloride, Bromide, or Iodide Mixtures at a Fixed Amalgam Concentration.—In a previous study of the effect of increasing the total salt concentration in sodium and potassium chloride mixtures, at a fixed salt-concentration ratio, it was found[1] that upon raising the salt concentration the value of C_c decreases. This study was later extended and now includes mixtures of sodium and potassium sulfates and chlorides,[2] sodium and strontium chlorides,[3] and potassium and strontium chlorides.[4] It has seemed desirable to further extend the investigation to include equivalent aqueous mixtures of sodium and potassium chlorides, bromides and iodides.

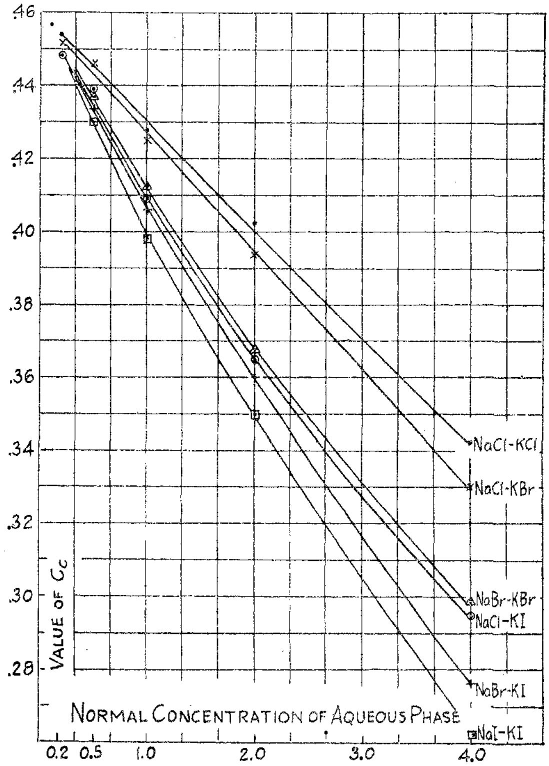

Fig. 3.—Showing the value of C_c as a function of total salt concentration, for various mixtures.
NaX : KX. Temperature, 25°.

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[1] G. McP. Smith, This Journal, 35, 39 (1913).

[2] Smith and Ball, *Loc. cit.*

[3] Smith and Braley, *Ibid.*

[4] Smith and Rees, *Ibid.*

The data for this study are given in Tables V, VI, VII, VIII, IX and X. The total concentration of the equivalent mixtures was increased from 0.1 N to 4.0 N for each salt mixture, with the exception of the sodium bromide-potassium iodide and sodium iodide-potassium iodide mixtures, with which the concentration was increased from 0.2 N to 4.0 N. In all of the individual experiments of each run, the amalgams were diluted to the same approximate concentration (about 0.2 milli-equivalent of metal per 10 g. of mercury). While the final concentration of the equilibrium amalgam was slightly less than this, the small individual differences in concentration do not warrant a correction of the C_c values. In every equilibrium studied, the value of C_c decreases with increasing concen-

TABLE V.

The Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

Temperature 25°. *NaCl:KCl.*

Mean values of Expts. No.	Amalgam at start.	Milli-equivalents of metals per 10 g. Hg.	Mol. fractions of amalgamated metals.		C_c.
			Na.	K.	
	Mixed Aqueous Phase 0.1 N.				
1– 2	Sodium	0.140	0.689	0.311	0.451
3– 5	Potassium	0.151	0.688	0.312	0.454
	Mean,	0.147			0.453
	Mixed Aqueous Phase 0.2 N. See Table I, Expts. 13–18.				
	Mean,	0.168			0.454
	Mixed Aqueous Phase 0.5 N. See Table II, Expts. 7–12.				
	Mean,	0.172			0.439
	Mixed Aqueous Phase 1.0 N. See Table II, Expts. 25–30.				
	Mean,	0.164			0.427
	Mixed Aqueous Phase 1.983 N.[a] (*0.983 NaCl:KCl*)				
6– 8	Sodium	0.166	0.710	0.290	0.401
9–11	Potassium	0.172	0.709	0.291	0.403
	Mean,	0.168			0.402
	Mixed Aqueous Phase 2.0 N. See Table II, Expts. 43–47.				
	Mean,	0.143			0.402
	Mixed Aqueous Phase 4.0 N. See Table II, Expts. 54–59.				
	Mean,	0.175			0.342

[a] The normality ratios in Expts. 6–11 of this table are 0.983 NaCl to 1.000 KCl, instead of 1.000 to 1.000 as was intended. The error in the NaCl solution was detected only after the completion of the run. The values of 0.983 N NaCl and 1.000 N KCl were used in calculating C_c. Table II, Expts. 43–47, gives the run as repeated, with NaCl:KCl, at a total concentration of 2.0 N.

tration of the mixed salt solution. The results are best studied by means of the curves in Fig. 3, in which the C_c values are plotted against the total normal salt concentrations. It will be observed that the C_c values change the more rapidly, the higher the atomic weight of the halogen.

TABLE VI

The Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

Temperature 25°. *NaCl:KBr.*

Mean values of Expts. No.	Amalgam at start.	Milli-equivalents of metals per 10 g. Hg.	Mol. fractions of amalgamated metals. Na.	K.	C_c.
		Mixed Aqueous Phase 0.1 *N*			
1– 3	Sodium	0.151	0.682	0.318	0.466
4– 6	Potassium	0.161	0.686	0.313	0.455
		Mean, 0.156			0.461
		Mixed Aqueous Phase 0.2 *N*.			
7– 9	Sodium	0.177	0.689	0.311	0.451
10–12	Potassium	0.175	0.686	0.313	0.456
		Mean, 0.176			0.453
		Mixed Aqueous Phase 0.5 *N*.			
13–15	Sodium	0.180	0.692	0.308	0.445
16–18	Potassium	0.179	0.692	0.308	0.445
		Mean, 0.180			0.445
		Mixed Aqueous Phase 1.0 *N*.			
19–21	Sodium	0.179	0.699	0.301	0.430
22–24	Potassium	0.178	0.700	0.300	0.429
25–27	Sodium	0.177	0.704	0.296	0.421
28–30	Potassium	0.179	0.704	0.296	0.421
		Mean, 0.178			0.425
		Mixed Aqueous Phase 2.0 *N*			
31–32	Sodium	0.188	0.715	0.285	0.397
33–35	Potassium	0.191	0.717	0.283	0.394
		Mean, 0.190			0.395
		Mixed Aqueous Phase 4.0 *N*.			
36–38	Sodium	0.192	0.750	0.250	0.331
39–41	Potassium	0.188	0.752	0.247	0.329
		Mean, 0.190			0.330

5. The Ion-fraction Changes which Take Place upon Increasing the Concentration of Equivalent Aqueous Mixtures of Sodium and Potassium Chlorides, Bromides, and Iodides.—In the theoretical section, it has been shown that, given the value of *k* (Equation 5), the ion fractions

TABLE VII.

The Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

Temperature 25°. *NaCl:KI.*

Mean values of Expts. No.	Amalgam at start.	Milli-equivalents of metals per 10 g. Hg.	Mol. fractions of amalgamated metals. Na.	K.	C_c.
		Mixed Aqueous Phase 0.1 *N*.			
1– 3	Sodium	0.161	0.685	0.315	0.460
4– 6	Potassium	0.164	0.688	0.312	0.453
7– 9	Sodium	0.158	0.686	0.314	0.457
10–12	Potassium	0.156	0.685	0.315	0.460
		Mean, 0.159			0.457
		Mixed Aqueous Phase 0.2 *N*.			
13–15	Sodium	0.171	0.687	0.313	0.455
16–17	Potassium	0.177	0.690	0.309	0.448
		Mean, 0.174			0.452
		Mixed Aqueous Phase 0.5 *N*.			
18–20	Sodium	0.173	0.701	0.299	0.427
21–23	Potassium	0.172	0.697	0.302	0.433
		Mean, 0.173			0.430
		Mixed Aqueous Phase 1.0 *N*.			
24–26	Sodium	0.177	0.710	0.290	0.408
27–29	Potassium	0.175	0.709	0.290	0.410
		Mean, 0.176			0.409
		Mixed Aqueous Phase 2.0 *N*.			
30–32	Sodium	0.187	0.733	0.267	0.364
33–35	Potassium	0.179	0.733	0.267	0.365
		Mean, 0.183			0.365
		Mixed Aqueous Phase 4.0 *N*.			
36–38	Sodium	0.187	0.773	0.227	0.293
39–41	Potassium	0.186	0.770	0.230	0.298
		Mean, 0.187			0.295

of the metals in the individual aqueous mixtures may be calculated by means of the expressions,

$$(\mathrm{K}^+) = \frac{(\mathrm{K}_{Hg})}{(\mathrm{K}_{Hg}) + k.(\mathrm{Na}_{Hg})},$$

and

$$(\mathrm{Na}^+) = 1 - (\mathrm{K}^+).$$

But, since we do not know either the respective degrees of dissociation of the sodium and potassium hydrargyrides in the mercurial phase, or the simple (unhydrated) ion fractions of these metals in the aqueous

TABLE VIII.

The Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

Temperature 25°. *NaBr:KBr.*

Mean values of Expts. No.	Amalgam at start.	Milli-equivalents of metals per 10 g. Hg.	Mol. fractions of amalgamated metals.		C_c.
			Na.	K.	
		Mixed Aqueous Phase 0.1 *N*.			
1– 3	Sodium	0.153	0.687	0.313	0.456
4– 6	Potassium	0.157	0.687	0.313	0.456
		Mean, 0.155			0.456
		Mixed Aqueous Phase 0.2 *N*.			
7– 9	Sodium	0.172	0.691	0.309	0.447
10–12	Potassium	0.176	0.689	0.311	0.451
		Mean, 0.174			0.449
		Mixed Aqueous Phase 0.5 *N*.			
13–15	Sodium	0.175	0.696	0.304	0.437
16–18	Potassium	0.176	0.695	0.305	0.438
		Mean, 0.176			0.437
		Mixed Aqueous Phase 1.0 *N*.			
19–21	Sodium	0.175	0.708	0.292	0.412
22–24	Potassium	0.179	0.709	0.291	0.411
		Mean, 0.177			0.412
		Mixed Aqueous Phase 2.0 *N*.			
25–27	Sodium	0.173	0.731	0.269	0.367
28–29	Potassium	0.176	0.732	0.268	0.367
		Mean, 0.175			0.367
		Mixed Aqueous Phase 4.0 *N*.			
30–32	Sodium	0.190	0.769	0.231	0.301
33–35	Potassium	0.190	0.770	0.230	0.298
		Mean, 0.190			0.299

phase, there does not seem to be any prospect for the determination of the value of *k*. We are, therefore, compelled to start with some assumption concerning the value of *k*, in order, with that as a basis, to study the *ion-fraction changes* which accompany changes in salt-concentration in the aqueous phase.

With the assumption as a starting point that in each of the equivalent sodium and potassium salt mixtures at a total concentration of 0.2 *N*, the simple sodium-ion and potassium-ion fractions are 0.500 and 0.500, we can then at least determine, by means of Equation 8, the direction and relative degree of the ion-fraction changes which accompany salt-concentration changes in the aqueous phase. On the basis of the assump-

TABLE IX.

The Effect of Varying the Normal Concentration of the Aqueous Phase as a Fixed (Equivalent) Salt-Concentration Ratio.

Temperature 25°. *NaBr:KI.*

Mean values of Expts. No.	Amalgam at start.	Milli-equivalents of metals per 10 g. Hg.	Mol. fractions of amalgamated metals.		C_c.
			Na.	K.	
		Mixed Aqueous Phase 0.2 *N*.			
1– 3	Sodium	0.170	0.691	0.309	0.447
4– 6	Potassium	0.173	0.690	0.310	0.449
		Mean, 0.172			0.448
		Mixed Aqueous Phase 0.5 *N*.			
7– 9	Sodium	0.168	0.697	0.303	0.434
10–12	Potassium	0.173	0.698	0.302	0.432
		Mean, 0.171			0.433
		Mixed Aqueous Phase 1.0 *N*.			
13–15	Sodium	0.172	0.711	0.289	0.406
16–18	Potassium	0.175	0.711	0.289	0.406
		Mean, 0.173			0.406
		Mixed Aqueous Phase 2.0 *N*.			
19–21	Sodium	0.192	0.736	0.264	0.359
22–24	Potassium	0.184	0.735	0.265	0.361
		Mean, 0.188			0.360
		Mixed Aqueous Phase 4.0 *N*.			
25–27	Sodium	0.191	0.784	0.216	0.275
28–30	Potassium	0.219	0.783	0.217	0.276
		Mean, 0.205			0.276

tion just referred to, the value of k would be equal to that of C_c at 0.2 *N* concentration.[1] If, instead of 0.2 *N*, we should select 0.1 *N* concentration as the starting point, the results would not be essentially different. The former concentration was selected because (1) the individual values (Na_{Hg}) and (K_{Hg}), calculated on the basis of the mol fractions of sodium

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[1] It should be fully realized that k is a real equilibrium constant, and that its value remains the same for all ratios and concentrations of the different mixed salt solutions of sodium and potassium.

In assuming a value for k, as a stepping stone in the ion-fraction calculations, we have preferred to assume that in each of the different salt mixtures, at an equivalent salt ratio and at 0.2 *N* concentration, the ion fractions are equal; rather than to make this assumption in the case of the chloride-chloride mixture alone, and to base all the calculations on the k value so obtained. While the former method may appear to involve a contradiction, in that several different k values are assumed, it nevertheless enables us better to compare the ion-fraction changes in the different mixtures, since in every case the calculations are started upon the same basis at 0.2 *N* concentration.

TABLE X.

The Effect of Varying the Normal Concentration of the Aqueous Phase at a Fixed (Equivalent) Salt-Concentration Ratio.

Temperature 25°. *NaI:KI.*

Mean values of Expts. No.	Amalgam at start.	Milli-equivalents of metals per 10 g. Hg.	Mol. fractions of amalgamated metals.		C_c.
			Na.	K.	
		Mixed Aqueous Phase 0.2 *N*.			
1– 3	Sodium	0.162	0.690	0.310	0.449
4– 6	Potassium	0.160	0.690	0.310	0.448
		Mean, 0.161			0.448
		Mixed Aqueous Phase 0.5 *N*.			
7– 9	Sodium	0.155	0.699	0.300	0.430
10–12	Potassium	0.174	0.699	0.301	0.431
		Mean, 0.165			0.430
		Mixed Aqueous Phase 1.0 *N*.			
13–15	Sodium	0.174	0.715	0.285	0.398
16–18	Potassium	0.176	0.715	0.285	0.399
		Mean, 0.175			0.398
		Mixed Aqueous Phase 2.0 *N*.			
19–21	Sodium	0.179	0.741	0.259	0.350
22–24	Potassium	0.181	0.741	0.259	0.350
		Mean, 0.180			0.350
		Mixed Aqueous Phase 4.0 *N*.			
25–27	Sodium	0.182	0.788	0.212	0.270
28–30	Potassium	0.183	0.797	0.203	0.254
		Mean, 0.183			0.262

and potassium in the mercurial phase, checked very closely in this case, and (2) runs for all of the salt mixtures were made at this concentration.

The data obtained show clearly that the value of C_c decreases with the increasing concentration of the amalgam, and upon plotting the values of C_c against the values of the total salt concentration (See Fig. 2) for each of 5 different specific amalgam concentrations, a series of 5 parallel curves is obtained; therefore, the statement may be made that the change in value of C_c which is due to the change in amalgam concentration is independent of the change caused by increasing the total salt concentration at a fixed (equivalent) concentration ratio. If this is true, the ion-fraction values found for mixed (equivalent) solutions of sodium and potassium chlorides at specific normal concentrations should be the same regardless of the concentration of the equilibrium amalgam. This conclusion is borne out by the figures in Table XI, which contains

TABLE XI.

The Ion-Fraction Changes which Accompany Salt-Concentration Changes in Equivalent Aqueous Mixtures of Sodium and Potassium Chlorides at 25°.

Normal concentration of mixed aqueous salt solution.	Potassium-ion fraction calculated from the C_c value at x milli-equivalents of metals per 10 g. Hg, upon the assumption that in the 0.2 N equivalent mixture $n = 1$ (Equation 6).		
	$x = 0.1$.	$x = 0.3$.	u = 0.5.
0.2	0.500	0.500	0.500
0.5	0.495	0.495	0.495
1.0	0.487	0.486	0.487
2.0	0.470	0.469	0.466
4.0	0.436	0.432	0.429

the potassium-ion fractions calculated at different amalgam concentrations for various equivalent mixtures of sodium and potassium chlorides.

Table XII shows the ion-fraction changes which accompany salt-concentration changes in equivalent aqueous mixtures of sodium and potassium chlorides, bromides, and iodides, at 25°, and in Fig. 4 these values are plotted against the total salt concentration. From these curves it is evident that the potassium-ion fraction decreases, while the sodium-ion fraction correspondingly increases, with increasing total salt concentration. These changes take place the more rapidly, the higher the atomic weight of the halogen.

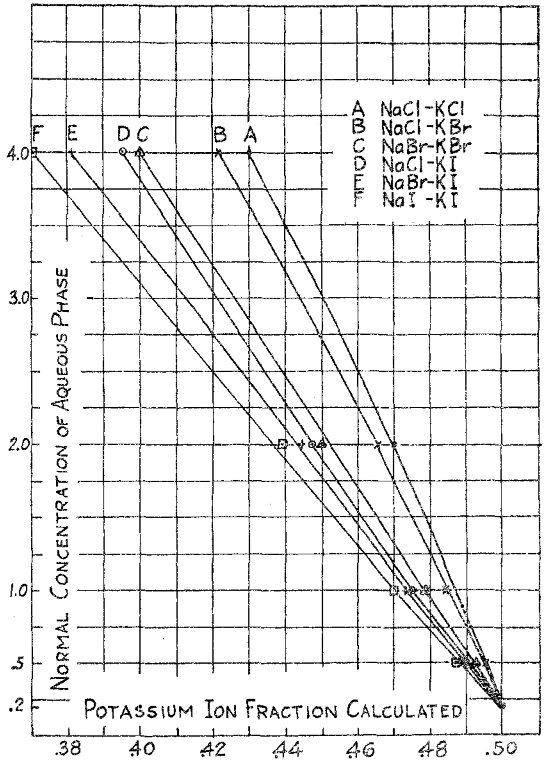

Fig. 4.—Showing the ion fractions of sodium and potassium as a function of total salt concentration, for various mixtures.
NaX: KX. Temperature, 25°.

E. Discussion.

This investigation has shown that, in equivalent, two-salt, aqueous mixtures of the halides of sodium and potassium, the simple potassium-ion fraction (K^+) decreases, while the simple sodium-ion fraction (Na^+) correspondingly increases, with the increasing total concentration of the

TABLE XII.

The Ion-Fraction Changes which Accompany Salt-Concentration Changes in Equivalent Aqueous Mixtures of Sodium and Potassium Chlorides, Bromides, and Iodides, at 25°.

		Total normal concentration of equivalent aqueous salt mixture.					
		0.1000.	0.2000.	0.5000.	1.000.	2.000.	4.000.
Potassium-ion fractions, calculated at 0.2 milli-equiv. of metals per 10 g. of mercury, upon the assumption that in the 0.2 *N* equivalent mixture $n = 1$ (Equation 6).	NaCl:KCl	0.499	0.500	0.493	0.485	0.470	0.430
	NaCl:KBr	0.504	0.500	0.495	0.484	0.466	0.421
	NaCl:KI	0.503	0.500	0.487	0.475	0.447	0.395
	NaBr:KBr	0.504	0.500	0.493	0.479	0.450	0.400
	NaBr:KI	..	0.500	0.491	0.474	0.445	0.381
	NaI:KI	..	0.500	0.490	0.470	0.439	0.370

salts. In the case of the chloride-chloride mixtures, the only halide mixtures of these metals previously investigated, these results agree with and supplement those previously obtained.[1] The results of the present investigation have brought forth the additional fact that, in the equivalent halide mixtures, these same ion-fraction changes take place the more rapidly, the higher the average atomic weight of the halogens in the mixture. The following explanation is offered to account for these phenomena.

1. The Decrease of the Potassium-ion Fraction with Increasing Total Salt Concentration in Equivalent Chloride-chloride Mixtures.—The ion-fraction changes above referred to may be due to either or both of the following causes: (*a*) the existence of hydrated ions, and (*b*) the existence of complex ions.

(*a*) It is well known, for example, that the ions of sodium and potassium are more or less hydrated in solution,[2] and very likely the non-ionized molecules that furnish these ions also are hydrated, as

$$\mathrm{MeX} + n\mathrm{H_2O} \rightleftarrows \mathrm{Me(H_2O)}_n\mathrm{X}.$$

It has been pointed out in previous papers of this series[3] that such hydrated compounds may also yield intermediate and complex ions, in varying quantities or degrees of stability. There is good evidence that many complexes, not sufficiently stable or insoluble to be isolated, exist in solution. Kendall[4] has quite recently emphasized the ideas of Werner in regard to the mechanism of the ionization process: "Ionization is preceded by combination between solvent and solute, and is, indeed, a consequence of such combination, and the two phenomena proceed in parallel." Such ideas are in particular harmony with Werner's very

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[1] G. McP. Smith, THIS JOURNAL, 35, 39 (1913); Smith and Ball, *loc. cit.*

[2] E. W. Washburn, *Tech. Quart.*, 21, 360 (1908); G. McP. Smith, THIS JOURNAL, 37, 722 (1915); Arrhenius, "Theories of Solutions," pp. 184–195.

[3] Cf. Smith and Rees, *Loc. cit.*

[4] THIS JOURNAL, 39, 2323 (1917).

plausible theory of bases[1] and acids, and with his theory of the formation of higher-order compounds.[2] Hydration is evidently a case of complex-formation.

(*b*) Complexes may be formed in other ways than through the agency of water. The alkali halides are capable of forming addition compounds with one another, as well as with other substances, and these may ionize to give complex ions.[3] Furthermore, the alkali halides show a tendency to polymerize.[4] In recent years, evidence (based upon absorption-spectra data) has been adduced which tends to show that the alkali metals, through the agency of secondary valence unions, are capable of effecting closed-ring structures, with the formation of inner-complex salts.[5] Through conductance studies of the alkali salts of certain organic acids, Lifschitz[6] has arrived at a similar conclusion.

Evidently, then, since we may have hydrated ions and molecules, addition and polymerized compounds, and many complexes capable of furnishing ions of various species, speculation as to just what specific complexes do exist in these solutions is more or less futile. If, however, as we should expect, potassium has a greater tendency to form complex ions than sodium, then, upon increasing the total concentration of the equivalent aqueous chloride mixtures, the concentration of the simple potassium ion would naturally be decreased more rapidly by mass action than that of the simple sodium ion.

2. The Further Decrease of the Potassium-ion Fraction with Increasing Atomic Weight of the Halogen in the Mixed Salt Solutions.— In the case of chlorine, bromine and iodine, it is well known that the tendency towards complex formation increases with the atomic weight of the halogen. Thus we find iodine forming a great many compounds in which it functions as the central nucleus.[7]

In short, owing to the greater tendency of potassium than of sodium, and of iodine and bromine than of chlorine to form complexes, we should expect the simple potassium-ion fraction to decrease with increasing

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[1] *Ber.*, 40, 4133 (1907).

[2] A. Werner, *Neuere Anschauungen a. d. Gebiete d. anorgan. Chemie*, Braunschweig, 1913.

[3] Cf. Werner, *Neuere Anschauungen*, etc., p. 28; Joannis, *Compt. rend.*, 112, 338 (1891); Abegg and Riesenfeld, *Z. physik. Chem.*, 40, 84 (1902).

[4] Zannovich-Tessarin, *Z. physik. Chem.*, 19, 251 (1896); Andrews and Ende, *Ibid.*, 17, 136 (1895); E. W. Washburn, *Trans. Am. Electrochem. Soc.*, 21, 137 (1912).

[5] Hantzsch, *Ber.*, 43, 3049 (1910); Hantzsch and Voigt, *Ibid.*, 45, 85 (1912).

[6] *Z. physik. Chem.*, 87, 567 (1914).

[7] A. Werner, *Neuere Anschauungen*, etc., L. Gattermann, "The Practical Methods of Organic Chemistry," Macmillan, 1914, p. 244; C. Willgerodt, *Die organischen Verbindungen mit mehrwertigem Jod*, F. Enke, 1914. See also Hantzsch, *Ann.*, 349, 1 (1906); D. McIntosh, *J. Chem. Soc.*, 87, 784 (1905); and K. Hellwig, *Z. anorg. Chem.*, 25, 157 (1900).

total salt concentration; and, also, that this decrease should take place the more rapidly, the higher the average atomic weight of the halogens present.

In conclusion, we may again point out that ionization is most often discussed as if it were a simple dissociation alone, *e. g.*, of the type: $KCl \rightleftharpoons K^+ + Cl^-$, and great emphasis is laid upon the supposition that the mass-law (a law which applies even to the disintegration of radium) is non-applicable to the dissociation of strong electrolytes. Perhaps the mass-law is less at fault than we ourselves, in our inability to determine just what molecular species are present in such solutions, and their individual concentrations.

F. Summary.

1. At a fixed total salt concentration, the value of the equilibrium expression, C_c, decreases with the increasing concentration of the amalgam.

2. At fixed amalgam and total-salt concentrations, but with varying salt ratio, the value of the equilibrium expression, C_c, is constant.

3. At a fixed amalgam concentration, the value of the equilibrium expression, C_c, decreases with the increasing concentration of the mixed (equivalent) salt solution.

4. Ion-fraction calculations are offered for aqueous two-salt mixtures containing the salts in equivalent proportions. It is found that the simple potassium-ion fraction decreases, while the sodium-ion fraction correspondingly increases, with the increasing total salt concentration. These changes take place the more rapidly, the higher the average atomic weight of the halogens in the mixture.

These results are not in harmony with the general conception which prevails in some quarters that, at equivalent concentrations, salts of the same type (*e. g.*, potassium chloride, bromide, iodide, sodium chloride, etc.) are ionized to the same degree.

5. The results of the investigation, insofar as the aqueous salt mixtures are concerned, are readily explainable in terms of A. Werner's theories concerning the formation and dissociation of higher-order compounds.

SEATTLE, WASH.