G. Same solution and experiment as E except that the aluminium hydroxide was removed after about 5 cc. of hydrogen had been collected, the anode replaced and the process continued until another 5 cc. had been collected, and so on until the end of the experiment.

In every case the precipitated aluminium hydroxide possessed at first the appearance of a colloidal gel, changing to the crystallin modification as the experiment proceeded. It has already been pointed out that it was impossible to entirely prevent the solution of the precipitate in the base which was unavoidably present in the anode section. In spite of this fact there was obtained, in experiments 7, 15 and 17, a ratio of aluminium oxide to oxygen that would be impossible for any formula that has been suggested for sodium aluminate. With further refinements in methods of carrying out electrolytic decomposition, we may expect to obtain still larger ratios.

Summary.

Known properties of aluminium have indicated a doubt as to whether aluminium hydroxide is amphoteric. An examination of previous cryoscopic investigations has strengthened this doubt. Measurements of the heat of solution of aluminium hydroxide in sodium hydroxide, of the quantitative relations between ammonium nitrate and sodium aluminate and observations made upon the electrolysis of sodium aluminate indicate that the *colloidal* properties of aluminium hydroxide play a far more important part in conditioning its solubility in bases and there is at least room for doubt as to whether "aluminates," as definit salts, exist at all.

The work is being continued and solutions of "zincates" will also be investigated.

Chemical Laboratory of Purdue University,
Lafayette, Ind., June, 1912.

[Contribution from the Chemical Laboratory of the University of Illinois.]

HETEROGENEOUS EQUILIBRIA BETWEEN AQUEOUS AND METALLIC SOLUTIONS.

[SECOND PAPER.]

THE INTERACTION OF MIXED SALT SOLUTIONS AND LIQUID AMALGAMS.

By George McPhail Smith.

Received November 5, 1912.

The Ionization Relations of Sodium and Potassium Salts in Mixtures. I.

Contents: 1. Purpose of the Investigation. 2. Principles relating to the Ionization of Salts in Mixtures. 3. The Experimental Method. 4. The Experimental Data. 5. Method of Calculation and Results. 6. Discussion of the Results.

1. *Purpose of the Investigation.*—The general purpose of the investigation was to study, by means of an independent method,[1] the ionization

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[1] Cf. This Journal, 32, 502 (1910); *Z. physik. Chem.*, 73, 424 (1910).

relations which exist in mixtures of salts, and to compare the results with those previously obtained by other methods.

2. *Principles Relating to the Ionization of Salts in Mixtures.*—Previous studies of the ionization of salts have led to the conclusion that at any definit concentration salts of the same ionic type have approximately the same degree of ionization. Moreover, it has been shown that the conductance of a mixture of salts with a common ion corresponds to the value calculated on the assumption that the degree of ionization of each salt is equal to that which it has when alone present in a solution in which its positive or negative ions have a concentration equivalent to that of the common ion in the mixture.[1]

In a recent paper by Miles S. Sherrill,[2] a study was made of the ionization relations which exist in mixed salt solutions with no common ion. Sherrill, who studied this question by means of conductance measurements, investigated various mixtures of potassium sulfate and sodium chloride and of potassium chloride and sodium sulfate, at 18°, the total salt concentration being 0.2 *N* in one series of experiments, and 0.1 *N* in a second series. From his results, Sherrill concludes that: '*When the concentrations of the separate ions of the salts in the mixtures are calculated by the principle expressed by the equation*[3] $(A)(B)/(A_xB_y) = K(\Sigma i)^{2-n}$ *the sum of the ion concentrations is obtained with an accuracy of about* $^1/_2\%$ *at* 0.2 *N and of about* $^1/_4\%$ *at* 0.1 *N*." Sherrill goes on to say that "The possibility must, of course, be recognized that a compensation takes place owing to the un-ionized tri-ionic salts being present in a larger or smaller proportion and the un-ionized di-ionic salts being present in a correspondingly smaller or larger proportion than that calculated. This might be the case, for example, if the ionization relations of the di-ionic and tri-ionic salts were determined by a different principle instead of by the same principle as has been assumed. All that can be said is that there are at present no facts known that make necessary this more complicated assumption."

Very recently, another paper, by G. M. J. Mackay,[4] has appeared, in which transference experiments made at 18° with a solution 0.2009 *N* with respect both to potassium chloride and to potassium sulfate, are described. Under the assumption that the transference number of

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[1] Cf. summary by A. A. Noyes, *Science*, **20**, 577–87 (1904); *Z. physik. Chem.*, **52**, 634–36 (1905).

[2] THIS JOURNAL, **32**, 741 (1910).

[3] In this equation A_xB_y represents the non-ionized salt, *A* and *B* are the ions, Σi = the total equivalent ion concentration, and *n* is an empirical constant, the values of which, though varying somewhat with the nature of the salt, all fall within the limits of 1.40 to 1.55 (cf. A. A. Noyes and others, THIS JOURNAL, **30**, 343 (1908); **31**, 1000 (1909)).

[4] THIS JOURNAL, **33**, 308 (1911).

the chlorine in the potassium chloride in this mixture is the same as it is in dilute potassium chloride solutions, the proportion of the current carried by its ions was found to be 0.573, and the proportion carried by the ions of the potassium sulfate to be 0.427. By multiplying these values by the measured specific conductance of the mixture, the partial specific conductances of the two salts in the mixture were obtained. The partial specific conductance of the potassium chloride so obtained was found to be 2.0% larger, and that of the potassium sulfate 5.2% smaller, than the values calculated by the principle, previously tested only by conductance measurements, that each salt in the mixture has an ionization equal to that which it has when present alone in a solution in which its positive or negative ions have a concentration equivalent to that of the common ion in the mixture. Mackay concludes that *the principle of ionization in mixtures is subject to serious inaccuracy*, especially with respect to the effect upon the unibivalent salt, in the case of the mixture investigated, which involves salts of two different types and a moderately high concentration (0.4 normal). He emphasizes the fact that, though the ratio of the actual partial conductances of the two salts is 7.5% larger than that required by the principle, yet the observed conductance of the mixture differs from the sum of the calculated partial conductances by only about 1%, a result which is in accord with the previous tests of the principle which have been based upon conductance measurements alone.

3. The Experimental Method.—The general method employed was as follows: The liquid amalgams, which were prepared by electrolysis as described in a previous paper,[1] and which were preserved in small sealing bottles, whose necks were drawn into capillaries, were poured in suitable quantities from the opened capillaries into 50–100 cc. portions of the mixed solutions. The reaction mixtures were then agitated for a given time in a thermostat, after which the aqueous solutions were quickly decanted, to be replaced by fresh portions; the mixtures were again agitated in the thermostat, and this process was repeated several times. Finally the amalgams were washed, as described in the first paper, and analyzed.

By thus agitating a dilute amalgam with successive portions of a solution, especially if at the start the amalgam approximates in composition that existing at equilibrium, a mixture is soon obtained in which at equilibrium the concentrations of the salts in the mixed solution are identical with those in the untreated mixed salt solution. It is then necessary to analyze only the amalgams.

4. The Experimental Data.[2]—The experimental data will be found in

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[1] THIS JOURNAL, 31, 799 (1909).

[2] The mercury used in the preparation of the amalgams was purified as described

Table I. The amalgams used in the first 5 experiments were prepared by mixing 0.33% potassium amalgam and 0.26% sodium amalgam in calculated proportions, the mixtures being preserved in sealing bottles. In the remaining experiments, pure 0.33% potassium amalgam was started with. The solutions used in the first two experiments were made by first preparing 0.2 *N* solutions of the separate salts, and then mixing these in the proper proportions. The remaining solutions were prepared by weighing out the requisit quantity of each salt, dissolving both in water, and diluting to the mark in a measuring flask.

In experiment 1, about 100 grams of amalgam were treated, during 15 minute periods, with four successive portions of the mixed solution. In experiment 2, the amalgam was treated, during 15 minute periods, with three separate portions of the mixed solution, and then for 30 minutes with a fourth portion. In experiments 3–5, there were four 15 minute treatments, followed by a 30 minute treatment, and in experiments 6–11 there were four 15 minute treatments.

It will be noted, on comparing Tables I and IV, that in experiments 1 and 2, for example (**K** = 0.476 and 0.465, respectively), $NaHg_n$ was in excess at the start, while in experiment 5 (**K** = 0.479) KHg_m was in excess at the start; *i. e.*, that the equilibrium is approachable from either direction,—a fact which, in the case of the mixed chloride solutions, was demonstrated in the first paper.

TABLE I.[1]—EXPERIMENTAL DATA AT 18°.

	Atomic fractions of alkali metals in amalgam at start.		Normal concentration of salts in mixed solutions.				Total volume used of salt solution.	The amalgam gave on analysis in grams.		It therefore contained in grams.	
No.	K.	Na.	NaCl.	Na_2SO_4.	KCl.	K_2SO_4.	Cc.	KCl+ NaCl.	K_2PtCl_6.	K.	Na.
1	0.2490	0.7510	0.1000	....	....	0.1000	200	0.6542	0.8062	0.1293	0.1597
2	0.2490	0.7510	....	0.1000	0.1000	....	400	0.5752	0.7004	0.1123	0.1421
3	0.5726	0.4274	....	0.7500	....	0.7500	500	0.5598	0.6360	0.1020	0.1437
4	0.2490	0.7510	0.1000	....	0.1000	....	500	0.6385	0.7756	0.1244	0.1580
5	0.5726	0.4274	....	0.1000	....	0.1000	500	0.5365	0.6657	0.1068	0.1310
6	1.0000	....	0.1000	....	0.1000	....	500	0.2568	0.3158	0.0506	0.0631
7	1.0000	....	0.2000	....	0.2000	....	500	0.4002	0.4716	0.0756	0.1008
8	1.0000	....	0.3000	....	0.3000	....	500	0.3772	0.4294	0.0689	0.0968
9	1.0000	....	0.4000	....	0.4000	....	500	0.4279	0.4877	0.0782	0.1097
10	1.0000	....	0.5000	....	0.5000	....	500	0.3220	0.3731	0.0598	0.0818
11	1.0000	....	1.0000	....	1.0000	....	500	0.3668	0.4019	0.0645	0.0960

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in the first paper, and the water used in the investigation was very pure, ammonia-free, distilled water. The sodium chloride was purified by precipitation with gaseous hydrogen chloride, and the dried salt was ignited in a large platinum dish. Each of the remaining salts, which were of Kahlbaum's best grade, was ignited in a large platinum dish and preserved in bottles, sealed with paraffin. They were carefully tested and were found to be exceptionally pure.

[1] The equilibrium data given in Tables III and IV are calculated from the experimental data in this table.

5. Method of Calculation and Results.—Starting with the assumption that the interaction between the amalgam and the salt solution is, in so far as the latter is concerned, wholly ionic, we arrive at the equation:

$$\mathrm{KHg}_m + \mathrm{Na}^+ \rightleftarrows \mathrm{K}^+ + \mathrm{NaHg}_n + (m-n)\mathrm{Hg};$$

and, since in these experiments free mercury was present in such excess that its concentration may be taken as constant, the law of mass action requires that, at equilibrium,

$$\frac{(\mathrm{KHg}_m)(\mathrm{Na}^+)}{(\mathrm{NaHg}_n)(\mathrm{K}^+)} = \mathbf{K},$$

in which (KHg_m) and (NaHg_n) represent the mol fractions of these compounds in the amalgam, (Na^+) and (K^+) are the ion fractions of sodium and potassium in the mixed salt solution, and **K** is the equilibrium constant.

We have:

$$\frac{(\mathrm{KHg}_m)(\mathrm{Na}^+)}{(\mathrm{NaHg}_n)(\mathrm{K}^+)} = \mathbf{K}$$

and, by definition,

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

Solving, we get

$$(\mathrm{K}^+) = \frac{(\mathrm{KHg}_m)}{(\mathrm{KHg}_m) + \mathbf{K}(\mathrm{NaHg}_n)}, \text{ and } (\mathrm{Na}^+) = 1 - (\mathrm{K}^+).$$

The values of (KHg_m) and (NaHg_n) may readily be calculated from the experimental data; if, therefore, a means can be found of obtaining the value of **K**, we shall be able to calculate the values of the ion fractions of sodium and potassium in the mixed solutions.

Before entering upon a discussion of the results obtained in the present investigation, it is desirable in this connection to consider the equilibrium

TABLE II.[1]—EQUILIBRIUM DATA AT 24°.

No.	Total normal concentration of salts.	Equivalent fractions of salts in the mixed solution. (NaCl).	(KCl).	Mol. fractions of compounds in the amalgam. (KHg_m).	(NaHg_n).	$\frac{(\mathrm{KHg}_m)(\mathrm{NaCl})}{(\mathrm{NaHg}_n)(\mathrm{KCl})}$.
(1)	1.50	0.6345	0.3655	0.1564	0.8436	0.322
(2)	1.50	0.6722	0.3278	0.1312	0.8683	0.311
(3)	1.50	0.3116	0.6884	0.4108	0.5892	0.316
(4)	1.50	0.3485	0.6515	0.3600	0.6400	0.315
(5)	1.25	0.7600	0.2400	0.0903	0.9097	0.314
(6)	1.25	0.8037	0.1963	0.0722	0.9278	0.318
(7)	1.25	0.1835	0.8165	0.5942	0.4058	0.329
(8)	1.25	0.2257	0.7743	0.5149	0.4851	0.309
					Mean =	0.317

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[1] The numbers correspond with those in the first paper; they are enclosed in parenthesis in order to distinguish them from the numbers referring to experiments performed in the present investigation.

data previously obtained in the case of mixed sodium and potassium chloride solutions in which the total salt concentration did not vary very much; only the data for solutions between 1.25–1.50 N will be considered. These data, in slightly different form, were given in the first paper, but their bearing upon the present investigation is so significant that it is thought necessary to reconsider them at this point. They are given in Table II.

The results given in the last column of Table II show conclusively that, in the case of the mixed solutions investigated, in which the individual salt concentrations varied between wide limits, though the total salt concentrations varied only between the limits 1.25–1.50 N,

$$n\,\frac{(\mathrm{NaCl})}{(\mathrm{KCl})} = \frac{(\mathrm{Na}^+)}{(\mathrm{K}^+)},$$

the values of n being identical for all the mixed solutions in question.

If $n = 1$, it follows that

$$\frac{(\mathrm{KHg}_m)(\mathrm{NaCl})}{(\mathrm{NaHg}_n)(\mathrm{KCl})} = \frac{(\mathrm{KHg}_m)(\mathrm{Na}^+)}{(\mathrm{NaHg}_n)(\mathrm{K}^+)} = 0.317 \text{ (at } 24^\circ).$$

Of course the possibility exists that this may not be true, and it was with this in mind that experiments 6–11 were performed. It will be noted that, in these experiments, the magnitude of the expression, $\frac{(\mathrm{KHg}_m)(\mathrm{Na\ salt})}{(\mathrm{NaHg}_n)(\mathrm{K\ salt})}$, decreases with the increasing total salt concentration of the mixed solutions (Table III). This fact, taken in connection with that deduced from the data in Table II, shows that the value of n in the above expression slowly increases with increasing total salt concentration, *i. e.*, that the concentration of Na^+ ion gains on that of K^+ ion. This will be referred to later in connection with Table V.

TABLE III.[1]—EQUILIBRIUM DATA AT 18°.

No.	Total normal concentration of salts in mixed solution.	Equivalent fractions of salts.		Mol. fractions of compounds in amalgam.		$\frac{(\mathrm{KHg}_m)(\mathrm{Na\ salt})}{(\mathrm{NaHg}_n)(\mathrm{K\ salt})}$.
		(NaCl).	(KCl).	(KHg_m).	(NaHg_n).	
5	0.2	0.5000[2]	0.5000[2]	0.3241	0.6759	0.479
6	0.2	0.5000	0.5000	0.3208	0.6792	0.472
7	0.4	0.5000	0.5000	0.3062	0.6937	0.442
8	0.6	0.5000	0.5000	0.2950	0.7049	0.418
9	0.8	0.5000	0.5000	0.2954	0.7046	0.419
10	1.0	0.5000	0.5000	0.3007	0.6993	[0.430]
3	1.5	0.5000[2]	0.5000[2]	0.2945	0.7055	0.417
11	2.0	0.5000	0.5000	0.2831	0.7169	0.395

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[1] It will be noted that the values in the last column of the table are much higher than those obtained at 24° in the earlier experiments. That this is due to the lower temperature at which the work was carried out in this investigation was shown by the following experiments: 2–3 cc. portions of 0.26% sodium amalgam, and of 0.33% potassium amalgam, both under water to prevent oxidation, and 2 cc. portions of

[2] These equivalent fractions were not chlorides, but sulfates.

In dilute solutions containing only one salt, sodium and potassium chlorides have, at any given concentration, approximately the same degree of ionization. Moreover, since the conductance of a mixture of salts with a common ion corresponds to the value calculated on the assumption that the degree of ionization of each salt is equal to that which it has when alone present in a solution in which its positive or negative ions have a concentration equivalent to that of the common ion in the mixture,[1] and since in this case both salts are uni-univalent and very similar, there would seem in the case of the 0.2 N chloride mixtures to be no reason for any other assumption than that the two salts are ionized approximately to the same extent. Making this assumption, it follows that

$$\frac{(\mathrm{Na}^+)}{(\mathrm{K}^+)} = \frac{(\mathrm{NaCl})}{(\mathrm{KCl})};$$

so that in 0.2 N mixed chloride solutions, the expression,

$$\frac{(\mathrm{KHg}_m)(\mathrm{NaCl})}{(\mathrm{NaHg}_n)(\mathrm{KCl})} = \mathbf{K},$$

gives us a means of arriving at a value for **K** which is possibly very nearly correct. This value, calculated from the data of the experiments in Table IV, will be seen to lie between the limits 0.463 and 0.479, at 18°; the mean of all the values is $\mathbf{K} = 0.471$.

In the case of a dilute mixture containing equivalent quantities of the sulfates of sodium and potassium, since the salts are of the same ionic type, and therefore equally ionized, we should expect to find in the same way an identical value for **K**. The value actually obtained is 0.479 (Experiment 5, Table IV).

In the case of a dilute solution made by mixing equal volumes of 0.2 N sodium chloride (or sulfate), and 0.2 N potassium sulfate (or chloride) solution, two other salts are formed by metathesis, and since the two chlorides are equally ionized, and also the two sulfates, we should expect the ion fractions (though not the actual ion concentrations)

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saturated sodium chloride, and of saturated potassium chloride solution, all in separate test tubes, were kept in the thermostat for 20 minutes, after which the water was absorbed from the surface of the amalgams with filter paper. The sodium amalgam and potassium chloride solution were then removed from the thermostat and mixed, the mixture being gently stirred with a thermometer, which had stood during the whole time in the test tube containing the amalgam; the temperature at once rose about 1°. The potassium amalgam and sodium chloride solution were mixed in the same way, and the temperature fell about 1°. Since the ionization is about the same at 18° as at 24°, it follows from the van't Hoff-LeChatellier principle that the equilibrium should be displaced in the direction observed.

[1] Experiments which confirm this principle up to a concentration of 0.5 N, within the small experimental error, have been made with 8 pairs of salts with 2 univalent ions (cf. Summary by A. A. Noyes, *loc. cit.*).

to be identical with those which exist in a 0.2 N chloride solution containing equivalent quantities of the sodium and potassium salts. That this is the case is shown in experiments 1 and 2 (Table IV), in which the values found for **K** are 0.476 and 0.465, respectively,—values practically identical with those obtained in experiments 4, 5 and 6.

Table IV.—Equilibrium Data at 18°.

No.	Total normal concentration of salts.	Equivalent fractions of salts in the mixed solution.				Mol. fractions of the compounds in the amalgam.		$\frac{(KHg_m)(\text{Na salt})}{(NaHg_n)(\text{K salt})}$
		(NaCl).	(Na_2SO_4).	(KCl).	(K_2SO_4).	(KHg_m).	($NaHg_n$).	
1	0.2	0.5	...	...	0.5	0.3227	0.6773	0.476
2	0.2	...	0.5	0.5	...	0.3174	0.6826	0.465
4	0.2	0.5	...	0.5	...	0.3166	0.6834	0.463
5	0.2	...	0.5	...	0.5	0.3241	0.6759	0.479
6	0.2	0.5	...	0.5	...	0.3208	0.6792	0.472

Mean value: **K** = 0.471

Finally, in the case of chloride and sulfate mixtures which do not contain equivalent quantities of the two salts, we should expect again to find the same value for **K**, provided that the ionization relations of the di-ionic and tri-ionic salts were determined by the same principle as has been assumed in the conductance experiments already referred to.[1] If, however, the ionization relations of the two salts are determined by different principles, then the fraction $\frac{(\text{Na salt})}{(\text{K salt})}$ is, in this case, no longer equal to the fraction $\frac{(Na^+)}{(K^+)}$, and we can no longer obtain the value of **K** by substituting the former fraction for the latter in the formula $\frac{(KHg_m)(Na^+)}{(NaHg_n)(K+)}$ = **K**. That the ionization relations of the di-ionic and tri-ionic salts are actually determined by different principles would seem to follow from the different values of the expression, $\frac{(KHg_m)(\text{Na salt})}{(NaHg_n)(\text{K salt})}$, which have been obtained in the experiments carried out to test this case. The results, however, seem so peculiar that it is desired to repeat the work before attempting to ascribe to them any definit theoretical significance. An analogous study of mixed solutions containing common ion salts of the types MeX and MeX_2 will be carried out also in this connection, and both sets of results will be published together in a later paper.

6. Discussion of the Results.—Starting with the assumptions that the reaction takes place in exact accordance with the equation,

$$KHg_m + Na^+ \rightleftarrows NaHg_n + K^+ + (m - n)Hg,$$

and that, in the solutions containing a common ion, and in which the total salt concentration was 0.2 N, the relation,

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[1] Sherrill, *loc. cit.*

$$\frac{(\text{Na salt})}{(\text{K salt})} = \frac{(\text{Na}^+)}{(\text{K}^+)},$$

holds approximately (whence **K** = 0.471), the ion fractions of sodium and potassium, in the cases of the experiments in which the sodium and potassium salts were present in equivalent quantities, have been calculated as described in the preceding section. The results are given in Table V.

TABLE V.[1]

No.	Total normal concentration of salts.	In equivalent fractions.				Mol. fractions of compounds in amalgam.		Calculated ion fractions.	
		ΣNa.	ΣK.	ΣCl.	ΣSO_4.	(KHg_m).	($NaHg_n$).	(Na^+).	(K^+).
1	0.2	0.5	0.5	0.5	0.5	0.3227	0.6773	0.4971	0.5029
2	0.2	0.5	0.5	0.5	0.5	0.3174	0.6826	0.5032	0.4968
4	0.2	0.5	0.5	1.0	...	0.3166	0.6834	0.5041	0.4959
5	0.2	0.5	0.5	...	1.0	0.3241	0.6759	0.4955	0.5045
6	0.2	0.5	0.5	1.0	...	0.3208	0.6792	0.4993	0.5007
7	0.4	0.5	0.5	1.0	...	0.3062	0.6937	0.5162	0.4838
8	0.6	0.5	0.5	1.0	...	0.2950	0.7049	0.5295	0.4705
9	0.8	0.5	0.5	1.0	...	0.2954	0.7046	0.5291	0.4709
10	1.0	0.5	0.5	1.0	...	0.3007	0.6993	0.5227	0.4772
3	1.5	0.5	0.5	...	1.0	0.2945	0.7055	0.5302	0.4698
11	2.0	0.5	0.5	1.0	...	0.2831	0.7169	0.5440	0.4560

It will be seen that, whether 0.471 is the correct value of **K** or not, the sodium ion fraction increases with the total salt concentration of the solution. This fact is especially striking, since, owing to the more electropositive nature of the metal, we should expect the potassium salts in such mixtures to be somewhat more readily ionized than the sodium salts.[2] The following explanation, which has an important bearing on the ionization relations of salts in general, is offered to account for this apparent anomaly.

It is well known, for example, that the ions of sodium and potassium are more or less hydrated in solution. But, in the hydration reactions, $MeCl + nH_2O \rightleftarrows [Me(OH_2)_n]Cl$,[3] water was present in such excess in the above experiments that its concentration should probably be taken as constant, just as was done in the case of mercury. On the other hand, however, substances which form hydrates often also form addition compounds.

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[1] The ion fractions in the last column were calculated from the equations $(K^+) = \frac{(KHg_m)}{(KHg_m) + (\mathbf{K}NaHg_n)}$, in which **K** = 0.471 (Table IV), and $(Na^+) = 1 - (K^+)$. These equations should give correct values if **K** really equals 0.471, for in every case $\mathbf{K} = \frac{(KHg_m)(Na^+)}{(NaHg_n)(K^+)}$.

[2] The following are the degrees of ionization calculated from the conductance measurements for 0.2 *N* solutions of the single salts: KCl = 83.0%, NaCl = 80.5%, K_2SO_4 = 66.1%, Na_2SO_4 = 63.4%.

[3] Cf. Werner, "Zur Theorie der Basen," *Ber.*, **40**, 4133–45 (1907).

with ammonia, halides, cyanides, etc. As an example may be cited the silver complexes, $[Ag(OH_2)_2]^+$, $[Ag(NH_3)_2]^+$, $[AgCl_2]^-$, $[Ag(CN)_2]^-$, etc.[1] That alkali chlorides are capable of forming addition compounds with ammonia has been shown by Joannis,[2] and Berthelot has shown that they tend to unite also with halogen acids.[3] Again, hydrofluoric acid has a strong tendency to associate, or form complexes, in aqueous solution, and this behavior would seem to account for its not being a strong acid, and for the existence of acid fluorides. Werner[4] assigns to the acid the constitutional formula, H(F.H.F), and to acid potassium fluoride the formula, K (F.H.F). That hydrochloric acid also has a tendency to associate, or form complexes, is indicated by the fact that in glacial formic or acetic acid solution, instead of dissociating, it gives only half the normal molecular depression of the freezing point, as if it formed double molecules.[5] In glacial formic acid, lithium chloride is highly dissociated, but in glacial acetic acid solution even it behaves as if it were largely associated into double molecules, though sodium bromide appears to be almost normally dissociated in glacial acetic acid.[1] It would appear that, on the basis of Werner's formula for hydrofluoric acid, the structural formulas of the double molecules in question are H(Cl.H.Cl), Li(Cl.Li.Cl), and Na(Cl.Na.Cl).[6]

While sodium and potassium chlorides in unmixed aqueous solutions apparently give no evidence of polymerization, they do in mixed aqueous solutions nevertheless form complexes, whereby it results that the sodium ion fraction increases in value, as is clearly indicated by the data in Tables III and V. This cannot result altogether from the formation of Na(Cl.Na.Cl) and K (Cl.K.Cl), unless we assume that the latter is more readily formed than the former, which is questionable in the light of the data just given in regard to the lithium and sodium complexes in glacial acetic

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Of these complexes, only the second and fourth are known to be correctly represented by the above formulas. However, the ion $[Ag(NH_3)_2]^+$ has the same electrolytic mobility as the silver ion in silver nitrate solution, and, since water and ammonia have many properties in common and approximately equal molecular weights, it is concluded that the silver ion is hydrated in aqueous solution to the extent indicated. The formula of the third complex is assigned solely on the ground of analogy.

[2] *Compt. rend.*, 112, 338 (1891).

[3] *Ann. chim. phys.*, [5] 23, 94 (1881).

[4] "Neuere Anschaunngen auf dem Gebiete der anorganischen Chemie," p. 103 (1909). Werner emphasizes that in the case of hydrofluoric acid the hydrogen must play the principle role in the formation of polymeric molecules, since, if it is replaced by alkyls, polymerization does not take place; the alkyl fluorides are monomolecular.

[5] Zanninovich-Tessarin, *Z. physik. Chem.*, 19, 251 (1896).

[6] Werner (Neuere Anschaunngen, etc., p. 26) calls attention to the fact that all binary compounds, with the single exception of the saturated hydrocarbons, have the property of forming addition products with other similar compounds. As examples may be cited the well known complex and double salts: K_2PtCl_6, K_2HgI_4, K_2CdI_4, $KCl.MgCl_2.6H_2O$ (carnallite), $CaCl_2.2MgCl_2.12H_2O$ (tachhydrite), etc.

acid. The formation of K(Cl.Na.Cl) would lower the value of the sodium ion fraction; so it would seem, as the only conclusion in harmony with the facts, that the preponderating complex formed is Na(Cl.K.Cl), and that this ionizes somewhat to give Na^+ and $(\text{Cl.K.Cl})^-$ ions.[1]

It might be objected that this explanation is not in harmony with the data in Table II, in which, though the total salt concentration of the mixed solutions varied only between the limits 1.25–1.50 *N*, the equivalent fractions, (NaCl) : (KCl), varied between the limits 0.1835 : 0.8165 and 0.8037 : 0.1963; and yet in which the values of the expression, $\frac{(\text{KHg}_m)(\text{NaCl})}{(\text{NaHg}_n)(\text{KCl})}$, are constant within the experimental error. This difficulty is removed, however, if we assume that the complex formation takes place only through the direct union of the non-ionized molecules,[2] according to the equation,

$$\text{NaCl} + \text{KCl} \rightleftarrows \text{Na(Cl.K.Cl)} \rightleftarrows \text{Na}^+ + (\text{Cl.K.Cl})^-.$$

The law of mass action would then require a constant value for the expression,[3] $\frac{[\text{NaCl}][\text{KCl}]}{[\text{Na(Cl.K.Cl)}]}$, and, so long as the total salt concentration remained approximately constant, a finite preponderance of either salt in the solution would lead to the same result.

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METHODS FOR THE PREPARATION OF NEUTRAL SOLUTIONS OF AMMONIUM CITRATE.

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The method at present approved by the Association of Official Agricultural Chemists[4] for the preparation of neutral solutions of ammonium

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[1] Other salts which would appear to form such complexes, in much more stable form, are the iodide of cadmium, $\text{Cd(CdI}_4)$ [cf. W. Hittorf, *Pogg. Ann.*, **106**, 545f (1859)], and mercuric chloride and cyanide, all of which, as is well known, are much less ionized than most other salts of the same type. Again, the fact that the pink color of aqueous solutions of CoCl_2 changes to a deep blue upon the addition of concentrated hydrochloric acid may be ascribed to the formation of complexes, such as $[\text{CoCl}_6]^{---}$ [cf. also Berthelot, *Ann. chim. phys.*, [5] **23**, 85–93 (1881)].

[2] Cf. Werner, "Zur Theorie der Basen," *loc. cit.;* cf. also in this connection the notable address on "Theories of Solution," by J. Walker; *Science*, **34**, 622–31 (1911). For example, after having pointed out strong evidence that in the case of the abnormal electrolyte, ammonium cyanate, the abnormality of the ionization equilibrium is to be attributed entirely to the non-ionized portion, he goes on to say (p. 629): "But ammonium cyanate differs in no respect, with regard to its electrolytic conductivity, from hundreds of other abnormal binary electrolytes with univalent ions; and I am therefore disposed to conclude that it is to the non-ionized portion in general of these electrolytes that the abnormality is to be attributed."

[3] The expressions inclosed in the brackets refer to the concentrations of the non-ionized portions of the substances in question.

[4] Bureau of Chemistry, *Bull.* **107** (revised), 1.