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HETEROGENEOUS EQUILIBRIA BETWEEN AQUEOUS AND METALLIC SOLUTIONS.

[THIRD PAPER.]

THE INTERACTION OF MIXED SALT SOLUTIONS AND LIQUID AMALGAMS. A STUDY OF THE IONIZATION RELATIONS OF SODIUM AND POTASSIUM CHLORIDES AND SULFATES IN MIXTURES.

BY G. McP. SMITH AND T. R. BALL.[1]

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A. Introduction.

1. Purpose of the Investigation.—This investigation is one of a number that are being carried out in this laboratory, having for their object

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[1] Thesis submitted to the Graduate School of the University of Illinois by T. R. Ball in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1916.

the study of the ionic relationships which exist in mixed salt solutions. The present work comprises a study of the chlorides and sulfates of sodium and potassium in total concentrations ranging from 0.20 N to 4.0 N, the object being to throw light upon the ionic relationships which exist in mixtures of sodium and potassium salts, whether with or without a common ion. The method used is one which has recently been developed in this laboratory,[1] and which is based upon an equilibrium which has been found to exist between mixed sodium and potassium salts and liquid amalgams.

2. Principles Relating to the Ionization of Salts in Mixtures. (*a*) *Salts with a Common Ion.*—Studies of the ionization of salts by conductance methods have led to the conclusion that, as a rule, salts of the same ionic type are ionized to the same extent.[2] 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 in the mixture is the same as 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."[3] This principle has been further tested by conductance methods by MacGregor, Archibald, McIntosh, and McKay,[4] and found to be valid "not only for uni-univalent salts but also for those of higher types, even in cases where the mass law would require a very different effect."[5] G. J. M. Mackay[6] has studied this principle by means of transference experiments on a mixed solution of KCl and K_2SO_4 which was 0.2009 N with respect to each salt. Assuming that the transference number of the chlorine in KCl in this mixture is the same (0.504) as it is in dilute KCl solutions, the portion of the current carried by the ions from the KCl is 0.573 and that carried by the ions from the K_2SO_4 is 0.427. Multiplying these values by the measured specific conductance of the mixture, the partial specific conductance of each salt in the mixture was obtained. That of the KCl was found to be 2.0% larger and that of the K_2SO_4 5.2% smaller than that required by the principle. Therefore Mackay says that "The principle of ionization in mixtures is subject to serious inaccuracy." It is significant that the ratio of the partial conductances of the two salts is 7.5% larger than the principle requires, yet the observed conductance of the mixture differs from the sum of the calculated partial conductances by only about 1.0%. In the light of the conductance data alone, therefore, the above mentioned principle

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[1] G. McP. Smith, This Journal, 32, 502 (1910); 35, 39 (1913).

[2] See A. A. Noyes and K. G. Falk, *Ibid.*, 34, 479 (1912).

[3] See A. A. Noyes, *Science*, 20, 577 (1904).

[4] *Trans. Nova Scotia Inst. Sci.*, 9–10 (1895–99).

[5] See A. A. Noyes, *Loc. cit.*

[6] This Journal, 33, 308 (1911).

would seem to be valid; but when the transference data also are taken into account, they point to the conclusion that the agreement of the conductance data with the principle referred to may be due only to an accidental compensation of errors and that the principle itself is open to serious question.

This principle has also been tested in this laboratory with solutions as concentrated as 1.25 and 1.50 N. In the first paper of this series,[1] from calculations based upon equilibrium data of the reaction

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

the conclusion is drawn that " * * * * in mixed sodium and potassium chloride solutions, the ratios which exist between the relative ion concentrations of sodium and potassium in the different solutions are identical with those which exist between the relative molal concentrations of the two salts in the respective solutions." That is to say:

$$\frac{(Na^+)_1}{(K^+)_1} : \frac{(Na^+)_2}{(K^+)_2} = \frac{(\text{Total NaCl})_1}{(\text{Total KCl})_1} : \frac{(\text{Total NaCl})_2}{(\text{Total KCl})_2}$$

where the subscripts 1 and 2 refer to Solutions 1 and 2, respectively. The isohydric principle of Arrhenius is then stated and the addition made that "The present investigation offers, through an independent method, a striking confirmation of the above conclusions, and moreover, it shows that they hold good even in very concentrated solutions." However, in a later paper[2] much more data covering a wider range of concentration are given. It is shown that in equivalent mixtures of sodium and potassium chlorides and sulfates, in which the total concentration ranges from 0.20 N to 2.0 N, the ion fraction of the potassium decreases with increasing salt concentration. At 2.0 N the ion fraction of the potassium is only 0.456. This is about 9.0% lower than the isohydric principle would require.

(*b*) *Salts without a Common Ion.*—Miles S. Sherrill[3] has studied the ionization of salts without a common ion by conductance methods. Working with various mixtures of KCl and Na_2SO_4, at total concentrations of 0.10 N and 0.20 N at 18°, he developed a series of equations which enabled him to calculate the ion and also the total undissociated salt concentrations in the mixtures. His calculations are based upon the assumption that for each salt in the mixture, the ratio of the product of the ion concentrations, (A) (B), to the undissociated salt concentration, (A_xB_y), is a function of the total ion concentration of the mixture. This function he shows to be

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[1] G. McP. Smith, THIS JOURNAL, 32, 502 (1910).

[2] G. McP. Smith, *Ibid.*, 35, 39 (1913).

[3] THIS JOURNAL, 32, 741 (1910).

$$\frac{(A)(B)}{(A_xB_y)} = K(\Sigma i)^n,$$

where K and n are constants. The value of n is empirical and lies between 1.4 and 1.55 depending upon the salt.[1] From the ion concentrations, thus calculated, Sherrill calculated the equivalent conductances of the mixtures and found them to agree with the observed values within 0.50% in 0.20 N solutions and within 0.25% in 0.10 N solutions. But he says: "The possibility must of course be recognized, that a compensation takes place, owing to the un-ionized tri-ionic salt being present in larger or smaller proportions 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 and not 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."

B. Theoretical.

When a liquid potassium amalgam is placed in a sodium salt solution, the potassium, because of its solution pressure, tends to pass into the ionic state, and there results a difference of potential between the amalgam and the solution. The amalgam becomes negatively charged and attracts the positive ions of the solution. Theoretically one of two things will happen: either the potassium will continue to pass into the solution until the attractive force between the potassium ions and the amalgam, due to the electrostatic charges, becomes equal to the solution pressure of the potassium in the amalgam, or some other positive ions will be forced out of the solution before the above equilibrium can be reached. In the case under consideration, assuming that there is no reaction between the water and the amalgam, sodium ions will be forced into the amalgam until the solution pressure of the sodium becomes great enough to prevent the entrance into the amalgam of any more sodium from the solution. At this point an equilibrium will exist between the sodium and potassium in the amalgam and the sodium and potassium ions in the solution. On the other hand, upon starting with a sodium amalgam and a potassium salt solution, the sodium will pass into the ionic condition and in so doing displace potassium in equivalent quantity from the solution, until the reaction is stopped by the attainment of the same equilibrium. The reaction may, therefore, be written reversibly, as follows:

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

If mercury is present in large excess, so that its concentration may be regarded as constant, the reaction is one of the second order and, for equilibrium, the mass law expression may be written as follows:

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[1] See A. A. Noyes and J. Johnston, This Journal, 31, 1009 (1909).

$$\frac{(\mathrm{KHg}_m)(\mathrm{Na}^+)}{(\mathrm{NaHg}_n)(\mathrm{K}^+)} = \mathrm{C}_o \qquad (1)$$

It is not possible at present to tell the actual ion concentrations of a solution of this kind. But in any solution of a mixture of sodium and potassium salts the ion concentrations must be some function of the respective salt concentration. That is to say

$$\frac{(\mathrm{Na}^+)}{(\mathrm{K}^+)} = n \cdot \frac{(\mathrm{Na\ salt})}{(\mathrm{K\ salt})}, \qquad (2)$$

in which at the start we assume nothing as to the value of n. For aught we know this value may be constant for all solutions or it may vary with the total concentration of the mixtures, or with the ratio of the salts in the mixtures. But in the case of such highly ionized salts as those under consideration, and at such low concentrations that the salts are almost completely ionized, the value of n must necessarily approach unity; at infinite dilution it must be equal to unity. In that event Equation 1 may be written

$$\frac{(\mathrm{KHg}_m)(\mathrm{Na\ salt})_o}{(\mathrm{NaHg}_n)(\mathrm{K\ salt})_o} = \mathrm{C}_o \qquad (3)$$

in which the subscript "o" indicates that the solution of the mixed salts is infinitely dilute.

Now for any given solution of mixed salts at a concentration "c" we may write

$$\frac{(\mathrm{KHg}_m)(\mathrm{Na\ salt})_c}{(\mathrm{NaHg}_n)(\mathrm{K\ salt})_c} = \mathrm{C}_c, \qquad (4)$$

but C_c does not equal C_o unless n is equal to unity under the conditions.

Since the reaction under consideration is undoubtedly ionic, we could derive the value of C_o from the expression

$$\frac{(\mathrm{KHg}_m)(\mathrm{Na}^+)_c}{(\mathrm{NaHg}_n)(\mathrm{K}^+)_c} = \mathrm{C}_o \qquad (5)$$

if we but knew the values of the ion concentrations.

By dividing Equation 5 by Equation 4 we get

$$\frac{(\mathrm{Na}^+)_c}{(\mathrm{K}^+)_c} \cdot \frac{(\mathrm{K\ salt})_c}{(\mathrm{Na\ salt})_c} = \frac{\mathrm{C}_o}{\mathrm{C}_c}$$

or,

$$\frac{(\mathrm{Na}^+)_c}{(\mathrm{K}^+)_c} = \frac{\mathrm{C}_o}{\mathrm{C}_c} \cdot \frac{(\mathrm{Na\ salt})_c}{(\mathrm{K\ salt})_c}. \qquad (6)$$

If the concentrations are expressed in terms of ion fractions, then

$$(\mathrm{Na}^+)_c + (\mathrm{K}^+)_c = 1. \qquad (7)$$

From Equations 6 and 7, if we knew the values of C_c and C_o, we could calculate the ion fractions of sodium and potassium in solutions of any salt concentration c. While the value of C_o cannot be determined directly, the value of C_c can in any given case be readily calculated from the experimental data by means of Equation 4, and, by determining the values of C_c for a number of different total salt concentrations and by plotting these values against the total concentrations, it is possible to obtain a curve which will enable us, by extrapolation to zero concentration, to arrive at the value of C_o, since C_o is but the limiting value of C_c as the solution becomes more and more dilute.

Unless it should prove that the values of C_c are independent of the ratios in which the salts are present to give the total concentration c, all of the plotted values of C_c would have to be determined with the use of solutions containing the two salts always in the same ratio. Having established a value of C_o for salts mixed in a definite ratio, and knowing the value of C_c, we are then in a position to calculate the ion fractions of sodium and potassium in the solution of total salt concentration c.

By solving Equations 6 and 7 we get

$$\frac{(K^+)_c \cdot C_o \cdot (\text{Na salt})_c}{C_c \cdot (\text{K salt})_c} = 1 - (K^+)_c$$

from which it follows that

$$(K^+)_c = \frac{C_c\,(\text{K salt})_c}{C_o(\text{Na salt})_c + C_c(\text{K salt})_c}. \qquad (8)$$

And, for those cases in which, at equilibrium, the salts are present in equivalent quantities, the formula reduces to the simple expression[1]

$$(K^+)_c = \frac{C_c}{C_o + C_c}. \qquad (9)$$

Throughout this investigation the agreement which exists among the values of C_c which have been obtained under any given experimental conditions has been used as a check upon the accuracy of the work. These values are in all cases readily accessible in the tables which follow.

C. Materials, Apparatus and Method of Experimentation.

1. Materials.—It is necessary that the water, salts and mercury used in this work be exceptionally pure, since heavy metals even when present in slight traces catalyze the decomposition of alkali metal amalgams by the water.[2]

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[1] G. McP. Smith (*loc. cit.*) has developed a formula in terms of the concentrations of the alkali metals in the amalgams, by means of which the ion fractions of the sodium and potassium in the solution may be calculated. The equation is

$$(K^+)_c = \frac{(\text{KHg}_m)}{(\text{KHg}_m) + C_o(\text{NaHg}_n)}$$

in which the symbol C_o has been substituted for the letter K in the original formula, in order to avoid confusion with the symbol for potassium. In this case, however, Formula 9 above has the advantage of being expressed in terms of C_o and C_c alone.

[2] Abegg, *Handb. d. anorg. Chem.*, Vol. II, ii, p. 581; G. McP. Smith and H. C. Bennett, THIS JOURNAL, 31, 802 (1909).

Water.—The water used in these determinations was prepared by distilling the laboratory distilled water successively from alkaline potassium permanganate and dilute sulfuric acid. The distilling flasks were fitted with safety distilling bulbs to prevent spray being carried over, and glass condensers were used; it was feared that if tin condensers were used colloidal tin might be present in the water and catalyze the decomposition of the amalgams.

Salts.—All of the salts used were very carefully purified by recrystallization or precipitation. The mother liquor was removed as completely as possible by suction at the water pump, after which the remainder was thrown off in a high speed electrical centrifuge. In all cases the crystallizations were carried out in vessels of Jena glass, and with the exception of the final one, which was made from the special water, the crystallizations were made from the distilled water of the laboratory.

Sodium Chloride.—Commercial salt was dissolved in distilled water and the saturated solution filtered through paper in a Büchner funnel. The salt was then precipitated with gaseous HCl and treated as described in the preceding paragraph. Two precipitations were made, after which the salt was placed in an open dish and heated on the electric hot plate until the odor of HCl was removed. Just before use the salt was either fused in a platinum dish or it was kept in the dish in an electric muffle furnace for at least an hour at a temperature just short of fusion. It was cooled in a desiccator over calcium chloride.

Potassium Chloride.—The purest commercial grades of the salt were recrystallized from two to three times from hot water. The samples were dried in an electric oven at 150°, but before use they were finally heated in the same manner as the sodium chloride.

Sodium Sulfate.—The best grade of the commercial salt was recrystallized twice from hot water. The crystal water was removed by heating the salt in a large platinum dish in an electric drying oven, the temperature being raised gradually to prevent creeping. When the salt appeared to be dry it was bottled. It was finally dried in the electric muffle furnace at 500° for at least 12 hours.[1]

Potassium Sulfate.—The pure commercial salt was recrystallized three times from hot water. Before use the salt was ground to a fine powder in an agate mortar and dried for at least four hours in the electric muffle at 500°.

Chloroplatinic Acid.—Platinum black, prepared in this laboratory, was dissolved in aqua regia and the resulting solution evaporated alternately with hydrochloric acid and with water until the diphenylamine test for nitric acid gave a negative result. The acid was then dissolved in water, the solution was saturated with chlorine gas, and the excess of the latter

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[1] Cf. T. W. Richards, THIS JOURNAL, 36, 3 (1914).

was completely removed by passing a stream of well washed air through the solution at room temperature. The solution was then diluted so that each cubic centimeter contained 0.05 g. of platinum.

The factor to be used with acid prepared in this way was found (*a*) by converting a known weight of pure fused KCl (mixed with a small known weight of NaCl) into the chloroplatinate, and (*b*) by preparing a sample of potassium chloroplatinate from the acid, reducing it in a current of illuminating gas, and weighing the KCl after reduction. The factors obtained by the two methods were 0.3048 and 0.3052, respectively. The commonly accepted factor is 0.3056,[1] but since 0.3050 differs from 0.3056 by only about 0.2%, and since we were not able with certainty to check determinations of the value of C_c within less than 1.0%, it evidently makes no difference which value is used. Owing to the fact that 0.3056 is the factor commonly recommended, we have preferred to use it (rather than 0.3050) in all of our calculations.

Mercury.—Commercial mercury was freed as completely as possible from dregs by passing it through a pin hole filter. It was then shaken in a heavy separatory funnel with a dilute solution of sulfuric acid and potassium dichromate.[2] The mercury was drawn off from the oxide formed, shaken with a fresh portion of the solution and again drawn off. A good deal of oxide came off with the mercury but this was removed by shaking with dilute nitric acid. The mercury was then poured into a funnel with a capillary outlet, from which it was allowed to run in a very fine spray through a long cylinder filled with a saturated solution of mercurous nitrate in dilute nitric acid. Adhering moisture was absorbed from the mercury with a filter paper and the metal was then distilled from a 200 cc. Claisen bulb in a slow current of air. The bulb was attached to an air condenser which extended into a vacuum vessel such as is used for collecting fractions of organic distillates, and which was attached to the water pump. The capillary tube through which the air was drawn, extended nearly to the bottom of the bulb, the air current being regulated by means of a screw pinch cock and rubber tube which were fitted upon the upper end of the tube. The air served the double purpose of preventing bumping and of oxidizing any base metals which might have escaped removal in the preceding operations. The metallic distillate contained some oxide of mercury, and to remove this it was again run through the nitric acid-mercurous nitrate column. After being washed with water, this mercury was used in the preparation of the amalgams.

Amalgams.—The amalgams were prepared by electrolysis, as described by G. McP. Smith and H. C. Bennett.[3] About 2.5 kilos of mercury

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[1] Treadwell-Hall, "Analytical Chemistry," Vol. 2, p. 45.

[2] Cf. J. W. Brühl, *Ber.*, **12**, 204 (1879).

[3] THIS JOURNAL, **31**, 799 (1909).

were placed in a heavy Jena beaker of about 400 cc. capacity and 50 cc. of saturated sodium or potassium chloride solution were added. Then enough of the solid salt was added to furnish sufficient alkali metal for an amalgam of the desired concentration. In this way the solution was still saturated with salt at the end of the electrolysis.

The amalgams were preserved in sealing bottles holding from 500 to 800 g., the neck of each bottle being drawn to a capillary and sealed.

The amalgams were analyzed, either by decomposing 30 to 40 g. (weighed to the closest centigram) with an excess of 0.10 *N* HCl and titrating the excess with 0.10 *N* Na_2CO_3, with methyl orange as an indicator, or they were decomposed with HCl, the acid solution evaporated to dryness and the chloride weighed. The concentration which was found most convenient was 0.23% Na and 0.39% K by weight. This concentration, which is one milligram equivalent of alkali metal per 10 g. of mercury, was sought in each case, and most of the amalgams were approximately of this concentration.

2. Apparatus. *Thermostat.*—A large Freas thermostat, holding about 350 l. of water, was used. It was adjusted at 25° and was constant within about 0.02 of a degree and accurate within about the same limits.

Thermometer. — The thermometer was standardized by comparison with a U. S. Bureau of Standards thermometer which was kindly loaned to us by Dr. E. W. Washburn. It was kept in the thermostat all of the time, with the bulb very near the center.

Shaking Device.—The amalgams were agitated in the flasks on the platform of the shaker shown in the accompanying photograph (Fig. 1). The platform of the apparatus was immersed in the thermostat to such a depth that the surface of the

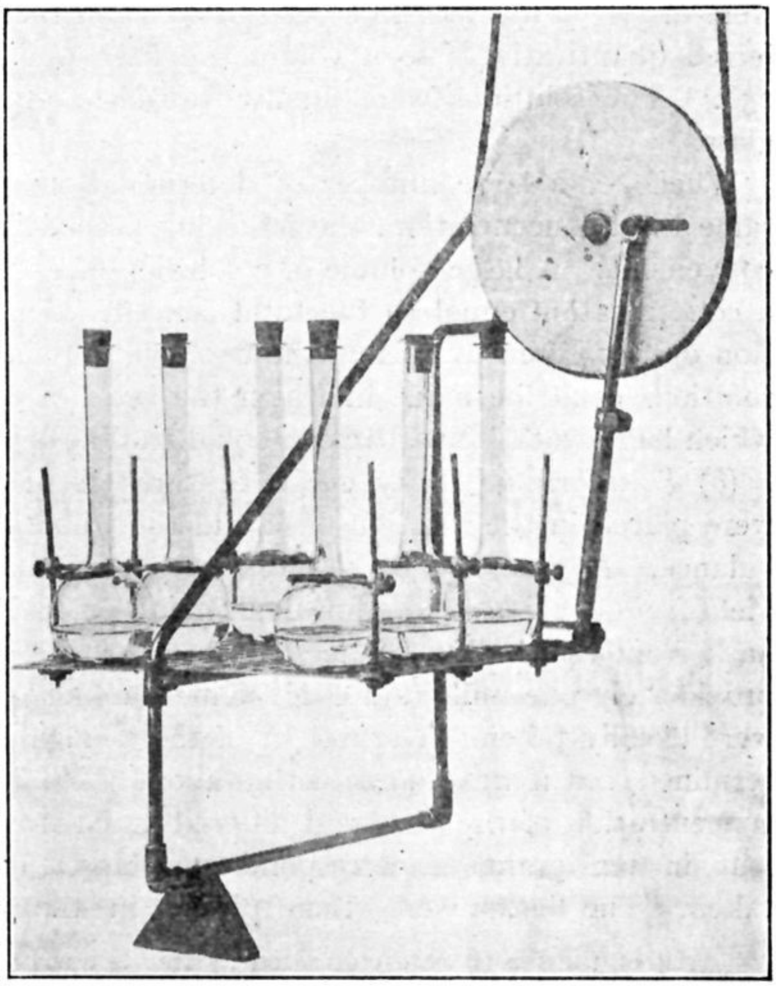

Fig. 1.

water came within about an inch and a half of the mouths of the flasks when the latter were at their lowest level. The upper end of the apparatus was screwed to the board which supported the lid of the thermostat, while the lower end rested upon a triangular piece of wood which was secured, by means of a copper wire, to the horizontal screen above the stirring paddles. The shaker was propelled by an independent motor placed on a shelf above the thermostat. The platform made one complete oscillation per second. By moving the propelling arm in or out in the slot in the wheel the magnitude of the oscillation could be varied. The whole apparatus was made of brass, as was also a table for holding the stock solutions in the thermostat.

Drying Oven and Furnace.—A Freas drying oven with automatic control was used. The temperature was read on a thermometer inserted through an opening in the wall. A small Hoskins muffle furnace, calibrated to an accuracy of perhaps 5°, was used for drying the salts preparatory to making the standard solutions.

3. **Method of Experimentation.** (*a*) *Solutions.*—The pure salts, dried as already stated, were weighed out in the calculated quantities. They were dissolved in water in a Jena beaker and the solution was then transferred quantitatively to a volumetric flask and diluted to the mark at 25°.[1] The solutions were finally transferred to bottles of "Resistenz" glass.

Whenever a large number of determinations were to be made at the same total concentration, the following procedure was found to be more convenient: A large volume of a solution of each salt was made up with a concentration equal to the total concentration of the mixed salt solution desired; then by mixing the two solutions in the proper proportions, solutions could be made in which the ratio of the salts might vary, but which had a total concentration equal to that of each pure solution alone.

(*b*) *Equilibrium.*—Fifty cubic centimeters of the mixed salt solution were placed in the reaction flask and the whole balanced on a small trip balance. A quantity of sodium or potassium amalgam, sufficient to yield from 0.25 to 0.30 g. of alkali metal chlorides, was weighed into the flask from the sealing bottle. Since all of the amalgams contained approximately one milligram equivalent of alkali metal in ten grams, 60 g. were usually taken. The weight of the amalgam was not accurately determined, but it was known within about 1.0% in each case. Where the concentration of the amalgam differed much from one milligram equivalent in ten grams a correspondingly larger or smaller quantity was taken. The flasks were then placed in the thermostat and shaken

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[1] All of the flasks were calibrated at this temperature in the usual manner by weighing into them the calculated amount of freshly distilled water and bringing them to 25° in the thermostat.

for twenty minutes, after which the solutions were decanted from the amalgams and quickly replaced by fresh portions. (The stock solution was of course kept in the thermostat all of the time except when a change of solution was actually being made.) The reaction flask was again placed on the shaking apparatus and agitated for twenty minutes. This process was repeated at least five times with 50 cc. portions of solution if the total concentration of the solution was less than normal. For solutions that were normal or above, one 50 cc. and three 25 cc. portions were found to be sufficient to produce the desired equilibrium.[1]

About eight minutes were required to change the solutions on the six amalgams held at one time upon the shaking apparatus. The shaking was not stopped during all of this time however. The five flasks left on the rack were agitated while the change of solution was being made on the sixth. Finally the solutions were decanted and the amalgams washed.

(*c*) *Washing the Amalgams.*—Five 150 cc. beakers, each containing about 100 cc. of distilled water, were placed in a row; the reaction flask was removed from the thermostat, the aqueous solution decanted and the amalgam poured into beaker number one. The water was then quickly decanted and the amalgam poured into beaker number two. After passing successively through all five beakers the amalgam was placed in a 50 cc. flask containing about 20 cc. of very dilute HCl, where decomposition took place rapidly. After its removal from the thermostat, it took about one minute to wash an amalgam and get it into the decomposition flask. The washing of the amalgams in this way is very efficient, *e. g.*, in one case a 0.60 N solution of the chlorides was decanted from the reaction flask, and the wash water from the third beaker gave no precipitate with silver nitrate.

(*d*) *Drying of the Mixed Chlorides.*—The HCl solution containing the alkali metals was drawn off from the mercury in the decomposition flask and evaporated to dryness in a weighed platinum or porcelain dish. At this point it is well to call attention to the fact that, since it is the ratio between the alkali metals which is sought and not the total amount of each, no attempt was made to remove the solution from the mercury quantitatively. As much as possible was removed with a pipet, but the mercury was not washed. Therefore, in the tables which will follow, the weight of "mixed chlorides" is only an approximate measure of the actual concentrations of the metals in the amalgams.

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[1] That the action of the water upon the amalgams is negligible is shown by the following: The first portions of an equivalent mixture of K_2SO_4 and Na_2SO_4, at a total concentration of 0.20 N were decanted from the amalgams after twenty minutes' agitation in the thermostat, and 100 cc. of this solution required only 1.66 cc. of 0.10 N HCl for neutralization. This corresponds to an alkalinity of 0.00166 N, or to the liberation by each amalgam of 0.09 cc. of gaseous hydrogen in the course of the first treatment. In the later treatments the evolution of hydrogen ceased almost entirely.

In most cases in which sodium and potassium are to be separated it is necessary first to expel ammonium salts, and for that reason the alkali metal chlorides have to be heated nearly to their melting point. In this work, however, the mixed chlorides were simply dried in the electric oven at 160° for at least two hours. That this procedure is adequate for our purpose was shown by the following experiment: 0.1094 g. of fused NaCl and 0.2236 g. of fused KCl (approximately the ratio in which the salts occur in most of the amalgams at equilibrium) were dissolved in water in a weighed platinum dish, and about 1.0 cc. of dilute HCl was added. The solution was then evaporated on the water bath and the residue dried at 160° for two hours. After this treatment, its weight indicated the presence of 1.2 mg. of water. After twelve hours' further heating in the oven at 160° the salts apparently still contained 1.0 mg. of water. Since in the calculations the sodium is gotten by difference, this retained water would all fall on the sodium; a recalculation of an actual experiment, in which equilibrium was brought about with a solution containing five equivalents of potassium to one of sodium, showed that the error due to the presence of 1.2 mg. of water in this case would be about 1.0% of the actual value of C_c, and in cases in which equilibrium was brought about with equivalent mixtures of alkali salts the error would be less than 0.50%. Since we were not able with certainty to check values of the equilibrium constant within limits of less than 1.0%, when all experiments and analyses were made under the same conditions and were therefore subject to corresponding errors of the same magnitude, and since drying at a higher temperature would have introduced the possibility of errors due to decrepitation, it was not considered advisable to dry the salts at the higher temperatures.

(*e*) *Separation of Sodium from Potassium.*—The weighed mixed chlorides were converted into chloroplatinates by solution in water and the addition of chloroplatinic acid. About 0.50 cc. was added in excess of the quantity required to convert the chlorides into chloroplatinate on the assumption that they consisted entirely of sodium chloride. The solution was evaporated on a slow water bath (the dish being protected from direct contact with steam by a sheet of paper) until the odor of HCl was not perceptible upon stirring the residue with a blunt glass rod. Methyl alcohol[1] was then added and the residue thoroughly broken up with a glass rod, and after allowing the residue to settle, the alcoholic solution was decanted through a filter paper previously moistened with alcohol.

The great tendency of the alcoholic solution to "creep" led to annoying difficulties, but these were overcome in the following manner: Three glass rods were fused together at one end in such a way that they met at angles of about 120°, but extended slightly upwards as well as out-

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[1] Cf. Treadwell-Hall, "Analytical Chemistry," Vol. 2, p. 44.

wards; so that when placed upon a funnel, the concentric ends would fall below the rim of the funnel. The dish was placed upon the rods and a thin stream of alcohol, from the constricted end of a separatory funnel was directed upon the edge of the dish in such a way that most of the alcohol went inside of the dish while some went outside; the latter portion followed the rods to the center and then dripped into the paper filter. In this way the dish could be washed inside and out with very little alcohol and without danger of loss of precipitate.

The K_2PtCl_6 in the dish was washed in this manner until the washings were almost colorless, after which the dish was placed under the funnel and the small quantity of potassium salt upon the paper was washed back into the dish by means of boiling water. Ten or twelve drops of chloroplatinic acid, together with a few drops of HCl, to prevent hydrolysis, were added, and the solution evaporated.[1] The residue was extracted with alcohol and washed by decantation until the alcohol came off colorless. Any potassium salt that had decanted onto the filter paper was washed back into the dish and the solution evaporated to dryness.

The K_2PtCl_6 was dried in the oven at 160° for at least 45 minutes.[2] The weight of KCl was found by using the conversion factor 0.3056.

D. Experimental Data.

The following tables contain the experimental data which have been obtained in this investigation. Unless otherwise stated, the figures in the first column of each table refer to the number of the experiment; the second and third columns give the concentration of potassium and of sodium salt, respectively, the total concentration of the solution being equal to the sum of these; Cols. four and five show the mol fractions of KHg_m and $NaHg_n$ in the amalgam at the start; Col. six gives the weight of mixed alkali chlorides obtained from the amalgam after the establishment of equilibrium between it and a solution of the composition represented in the second and third columns; and in the seventh column is given the weight of K_2PtCl_6 which was obtained in the analysis of the mixed chlorides. From the data contained in Cols. six and seven the mol fractions of KHg_m and $NaHg_n$ in the amalgam at equilibrium may be calculated, and these are given in Cols. eight and nine. The last column contains the value of the expression

$$\frac{(KHg_m)(\text{Na salt})_c}{(NaHg_n)(\text{K salt})_c} = C_c$$

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[1] By making this second evaporation with a few drops of chloroplatinic acid the K_2PtCl_6 finally obtained was always of a pure golden yellow color; otherwise it had the appearance of being contaminated with the sodium salt.

[2] Five samples dried in this way did not change in weight upon two hours' further heating at the same temperature.

TABLE I.

KCl-NaCl. Total Concentration 0.20. Temperature 25°.

No.	Normal conc. of salts. KCl.	NaCl.	Mol fract. in amalg. at start. K.	Na.	Wt. NaCl plus KCl.	Wt. K_2PtCl_6.	Mol fract. in amalg. at equilib. K.	Na.	C_c.
1.........	0.1600	0.0400	0.53	0.47	0.2888	0.6197	0.5990	0.4010	0.373
2.........	0.1600	0.0400	0.75	0.25	0.2840	0.6173	0.6080	0.3920	0.387
3.........	0.1333	0.0666	0.43	0.57	0.3195	0.5165	0.4336	0.5664	0.382
4.........	0.1333	0.0666	0.75	0.25	0.2792	0.4502	0.4324	0.5676	0.381
5.........	0.1000	0.1000	1.0	....	0.2550	0.2722	0.2752	0.7248	0.379
6.........	0.1000	0.1000	....	1.0	0.2700	0.2902	0.2771	0.7229	0.383
7.........	0.0666	0.1333	0.13	0.87	0.2804	0.1829	0.1633	0.8367	0.389
8.........	0.0666	0.1333	0.27	0.73	0.2970	0.1907	0.1607	0.8393	0.383
9.........	0.0400	0.1600	1.0	....	0.2585	0.0910	0.0939	0.9061	0.390
10.........	0.0400	0.1600	0.43	0.57	0.2366	0.0837	0.0868	0.9132	0.380
									Mean, 0.383

The Na amalgam used contained 0.234% Na.
The K amalgam used contained 0.293% K.
The total wt. of amalgam used was in each case about 60 g.

TABLE II.

K_2SO_4-Na_2SO_4. Total Concentration 0.60 *N*. Temperature 25°.

No.	Normal conc. of salts. K_2SO_4.	Na_2SO_4.	Mol fract. in amalg. at start. K.	Na.	Wt. NaCl plus KCl.	Wt. K_2PtCl_6.	Mol fract. in amalg. at equilib. K.	Na.	C_c.
1.........	0.500	0.100	0.57	0.43	0.2687	0.6259	0.6593	0.3407	0.387
2.........	0.500	0.100	0.57	0.43	0.3161	0.7376	0.6612	0.3388	0.390
3.........	0.500	0.100	1.0	....	0.2776	0.6469	0.6599	0.3401	0.388
4.........	0.500	0.100	1.0	....	0.2775	0.6494	0.6632	0.3368	0.394
5.........	0.400	0.200	0.40	0.60	0.2368	0.3905	0.4434	0.5566	0.398
6.........	0.400	0.200	0.40	0.60	0.2400	0.3918	0.4384	0.5616	0.390
7.........	0.400	0.200	1.0	....	0.2488	0.4050	0.4370	0.5630	0.388
8.........	0.400	0.200	1.0	....	0.2775	0.4481	0.4330	0.5670	0.382
9.........	0.300	0.300	0.20	0.80	0.2434	0.2650	0.2811	0.7189	0.391
10.........	0.300	0.300	0.20	0.80	0.2867	0.3093	0.2784	0.7216	0.385
11.........	0.300	0.300	1.0	....	0.2595	0.2772	0.2753	0.7247	0.380
12.........	0.300	0.300	1.0	....	0.2555	0.2727	0.2752	0.7248	0.380
13.........	0.200	0.400	....	1.0	0.2397	0.1594	0.1666	0.8333	0.400
14.........	0.200	0.400	....	1.0	0.1722	0.1115	0.1620	0.8380	0.387
15.........	0.200	0.400	1.0	....	0.2563	0.1632	0.1594	0.8406	0.379
16.........	0.200	0.400	1.0	....	0.2795	0.1778	0.1589	0.8411	0.379
17.........	0.100	0.500	....	1.0	0.2185	0.0640	0.0715	0.9285	0.385
18.........	0.100	0.500	....	1.0	0.2263	0.0660	0.0716	0.9284	0.385
19.........	0.100	0.500	1.0	....	0.2657	0.0764	0.0701	0.9299	0.378
20.........	0.100	0.500	1.0	....	0.2583	0.0769	0.0726	0.9274	0.392
									Mean, 0.387

The amalgam used contained 0.157% Na.
The K amalgam used contained 0.349% K.
The total wt. of amalgam used was in each case about 60 g.

which is calculated from the data of the second, third, eighth and ninth columns.

There are three studies which can be based upon these equilibria: first, the effect of varying the ratio of the salt concentrations at a fixed total salt concentration; second, the effect of varying the total concentration at a fixed salt-concentration ratio; and third, the effect of changing the temperature. From the data obtained at different temperatures the heat of the reaction may be calculated by means of the van't Hoff equation.

1. The Effect of Varying the Ratio of the Salt Concentrations at a Fixed Total Salt Concentration.—In Table I will be found the data for sodium and potassium chlorides in varying ratios, with a total concentration of 0.20 *N*. An examination of the last column shows very conclusively that under the conditions, the equilibrium is in accordance with the mass law expression even over widely varying ratios.

TABLE III.

K_2SO_4-NaCl. Total Concentration 0.60 *N*. Temperature 25 °.

No.	Normal conc. of salts.		Mol fract. in amalg. at start.		Wt. NaCl plus KCl.	Wt. K_2PtCl_6.	Mol fract. in amalg. at equilib.		C_c
	K_2SO_4.	NaCl.	K.	Na.			K.	Na.	
1	0.500	0.100	....	1.0	0.2255	0.5257	0.6595	0.3404	0.388
2	0.500	0.100	....	1.0	0.2527	0.5824	0.6514	0.3486	0.374
3	0.500	0.100	1.0	....	0.2040	0.4788	0.6653	0.3347	0.397
4	0.500	0.100	1.0	....	0.2230	0.5187	0.6583	0.3417	0.385
5	0.500	0.100	1.0	....	0.2273	0.5296	0.6600	0.3400	0.388
6	0.400	0.200	....	1.0	0.1461	0.2419	0.4452	0.5584	0.401
7	0.400	0.200	....	1.0	0.2575	0.4151	0.4321	0.5679	0.380
8	0.400	0.200	1.0	....	0.2095	0.3428	0.4402	0.5598	0.393
9	0.400	0.200	1.0	....	0.1644	0.2730	0.4467	0.5533	0.404
10	0.300	0.300	....	1.0	0.2170	0.2405	0.2868	0.7138	0.401
11	0.300	0.300	....	1.0	0.1711	0.1875	0.2827	0.7173	0.394
12	0.300	0.300	1.0	....	0.1887	0.2072	0.2795	0.7205	0.388
13	0.300	0.300	1.0	....	0.2284	0.2478	0.2798	0.7202	0.389
14	0.300	0.300	....	1.0	0.2755	0.2711	0.2520	0.7480	(0.337)
15	0.300	0.300	1.0	....	0.2165	0.2267	0.2690	0.7310	(0.368)
16	0.200	0.400	....	1.0	0.2763	0.1747	0.1581	0.8419	0.376
17	0.200	0.400	....	1.0	0.2520	0.1590	0.1578	0.8422	0.376
18	0.200	0.400	1.0	....	0.1942	0.1256	0.1611	0.8389	0.384
19	0.200	0.400	1.0	....	0.2038	0.1300	0.1596	0.8404	0.380
20	0.100	0.500	....	1.0	0.2526	0.0764	0.0738	0.9262	0.399
21	0.100	0.500	....	1.0	0.2484	0.0782	0.0770	0.9230	(0.416)
22	0.100	0.500	1.0	....	0.2815	0.0782	0.0678	0.9322	(0.363)
23	0.100	0.500	....	1.0	0.2560	0.0713	0.0678	0.9322	(0.364)
									Mean, 0.388

The Na amalgam used contained 0.234% Na.
The K amalgam used contained 0.386% K.
The total weight of amalgam used was in each case about 60 g.

Table II contains similar data for mixtures of sodium and potassium sulfates at a total concentration of 0.60 *N*. In this series the higher total concentration made it possible to vary the ratios between still wider limits than was feasible in the previous case. Here again the value of C_c remains constant over the range studied.

In Tables III and IV the same is seen to hold, even in the case of mixtures made from salts of different ionic types and with no common ion.

TABLE IV.

KCl-Na_2SO_4. Total Concentration 0.60 *N*. Temperature 25°.

	Normal conc. of salts.		Mol fract. in amalg. at start.				Mol fract. in amalg. at equilib.		
No.	KCl.	Na_2SO_4.	K.	Na.	Wt. NaCl plus KCl.	Wt. K_2PtCl_6.	K.	Na.	C_c.
1	0.500	0.100	0.50	0.50	0.2525	0.5847	0.6546	0.3454	0.379
2	0.500	0.100	0.25	0.75	0.2650	0.6190	0.6618	0.3382	0.391
3	0.500	0.100	0.63	0.37	0.3257	0.7629	0.6638	0.3362	0.395
4	0.500	0.100	1.0	....	0.2566	0.5990	0.6610	0.3390	0.390
5	0.400	0.200	0.25	0.75	0.3083	0.5040	0.4394	0.5609	0.391
6	0.400	0.200	1.0	....	0.3181	0.5260	0.4446	0.5554	0.400
7	0.400	0.200	1.0	....	0.2127	0.3475	0.4328	0.5672	0.381
8	0.400	0.200	0.50	0.50	0.1870[1]	0.3058	0.4390	0.5610	0.391
9	0.300	0.300	....	1.0	0.2320	0.2485	0.2762	0.7238	0.381
10	0.300	0.300	1.0	....	0.1635[1]	0.1791	0.2828	0.7172	0.394
11	0.300	0.300	0.25	0.75	0.2649	0.2886	0.2812	0.7188	0.391
12	0.300	0.300	1.0	....	0.3137	0.3422	0.2818	0.7182	0.392
13	0.200	0.400	0.85	0.15	0.2833	0.1845	0.1630	0.8370	0.390
14	0.200	0.400	1.0	....	0.2876	0.1886	0.1669	0.8331	0.400
15	0.200	0.400	....	1.0	0.2330	0.1482	0.1591	0.8409	0.379
16	0.200	0.400	0.50	0.50	0.2006	0.1293	0.1613	0.8387	0.384
17	0.100	0.500	1.0	....	0.1785[1]	0.0533	0.0728	0.9272	0.393
18	0.100	0.500	....	1.0	0.3206	0.0918	0.0698	0.9302	0.376
19	0.100	0.500	1.0	....	0.2931	0.0873	0.0729	0.9271	0.393
								Mean,	0.389
20	0.400	0.200	0.75	0.25	0.0858[2]	0.1474	0.4640	0.5360	0.433
21	0.300	0.300	0.25	0.75	0.1708[1]	0.1972	0.2990	0.7010	0.427
22	0.300	0.300	0.50	0.50	0.1672[1]	0.1917	0.2975	0.7025	0.423
23	0.100	0.500	....	1.0	0.2434	0.0788	0.0792	0.0208	0.430
24	0.100	0.500	0.50	0.50	0.2388	0.0778	0.0799	0.9201	0.434

The Na amalgam contained 0.157% of Na.

The K amalgam contained 0.296% of K.

The total weight of amalgam used in each experiment was 75 g.

Expts. No. 20–24 were performed in a single run. Upon repeating the determinations, however, the values given in the main table were obtained.

It is interesting to note that the values of C_c are in all four tables practically identical, the mean value ranging from 0.383 to 0.389. In view

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[1] Slight evolution of hydrogen.

[2] This amalgam evolved hydrogen quite vigorously.

of the fact that additional data for more concentrated solutions will be given in the latter part of this paper, it seems advisable to postpone the discussion of this case.

2. The Effect of Varying the Concentration of Alkali Metal in the Liquid Amalgams.—Table V contains the data obtained in a first attempt to study the effect of changing the total salt concentration of the mixed solution while keeping the salt-concentration ratio constant. The results are far from satisfactory. In the first seven experiments in which identical solutions and amalgams were used, values of C_c were found which vary all the way from 3.48 to 0.417; and we are positive that this variation did not arise from faulty analytical work.[1]

TABLE V.

K_2SO_4-Na_2SO_4. Total Concentration 0.20 to 2.00 *N*. Temperature 25°.

No.	Normal conc. of salts.		Mol fract. in amalg. at start.		Wt. NaCl plus KCl.	Wt. K_2PtCl_6.	Mol fract. in amalg. at equilib.		C_c.
	K_2SO_4.	Na_2SO_4.	K.	Na.			K.	Na.	
1	0.10	0.10	0.25	0.75	0.1803[2]	0.1963	0.2818	0.7182	0.392
2	0.10	0.10	0.25	0.75	0.1916[2]	0.2168	0.2945	0.7055	0.417
3	0.10	0.10	0.25	0.75	0.3582	0.3528	0.2608	0.7392	0.353
4	0.10	0.10	1.00	....	0.2222	0.2406	0.2792	0.7208	0.388
5	0.10	0.10	1.00	....	0.3514	0.3606	0.2638	0.7362	0.358
6	0.10	0.10	0.25	0.75	0.3673	0.3694	0.2581	0.7410	0.348
7	0.10	0.10	1.00	....	0.3546	0.3610	0.2615	0.7385	0.354
8	0.25	0.25	0.80	0.20	0.2009[2]	0.2179	0.2798	0.7202	0.389
9	0.25	0.25	0.80	0.20	0.3912	0.3919	0.2570	0.7430	0.346
10	0.25	0.25	1.00	....	0.2828	0.2981	0.2714	0.7286	0.373
11	0.25	0.25	1.00	....	0.3409	0.3496	0.2635	0.7365	0.358
12	0.25	0.25	1.00	....	0.2597	0.2682	0.2658	0.7342	0.362
13	0.25	0.25	1.00	....	0.3654	0.3688	0.2592	0.7408	0.350
14	0.50	0.50	0.20	0.80	0.2028[2]	0.2191	0.2787	0.7213	0.381
15	0.50	0.50	0.20	0.80	0.2047[2]	0.2238	0.2821	0.7179	0.393
16	0.50	0.50	0.20	0.80	0.3596	0.3600	0.2569	0.7431	0.346
17	0.50	0.50	1.00	....	0.2828	0.2981	0.2714	0.7286	0.373
18	0.50	0.50	1.00	....	0.3771	0.3660	0.2302	0.7698	0.329
19	0.50	0.50	1.00	....	0.3393	0.3385	0.2559	0.7441	0.344
20	1.00	1.00	0.20	0.80	0.3497	0.3580	0.2629	0.7371	0.357
21	1.00	1.00	0.20	0.80	0.3470	0.3531	0.2613	0.7387	0.354
22	1.00	1.00	0.20	0.80	0.3673	0.3694	0.2581	0.7419	0.348
23	1.00	1.00	0.20	0.80	0.3546	0.3610	0.2615	0.7385	0.354
24	1.00	1.00	1.00	....	0.2703	0.2880	0.2745	0.7255	0.378
25	1.00	1.00	1.00	....	0.2795	0.2987	0.2756	0.7244	0.380

The Na amalgam used contained 0.272% Na.

The K amalgam used contained 0.355% K.

The total amount of amalgam used was in each case 60 g.

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[1] It should be noted at this point that the data in Tables I–IV were obtained before it became known that the concentration of the liquid amalgams was a matter to be considered.

[2] Hydrogen was evolved freely at first, but towards the end of the experiment this action had ceased.

In Expts. 1 and 2 hydrogen was evolved freely at first, but towards the end the liberation of gas had almost entirely ceased. This action, which takes place at localized spots on the surface of the amalgams, is a rather common phenomenon and is possibly attributable to the catalytic influence of dust particles[1] which finally become disengaged before the last change of solution is made; it is not considered directly responsible for the variation in question. Upon studying the mixed chloride column in connection with the value of C_c in the first seven experiments, it will be noted that the latter decreases with increasing weight of the mixed chlorides; and it has already been pointed out that, although the weight of the mixed chlorides does not give an exact measure of the weight of the alkali metals in the amalgams, nevertheless it does represent it very closely. At least the relative amounts in two separate analyses can be judged by a comparison of these values. The approximate percentages of sodium and potassium in the amalgams calculated from the weight of the mixed chlorides and of K_2PtCl_6, are given in Table V*a*. The values represent the minimum percentage concentrations and they are certainly very nearly correct.

TABLE V*a*.

No.	Approximate percentage of K.	Approximate percentage of Na.	C_c.
1	0.052	0.078	0.392
2	0.058	0.082	0.417
3	0.064	0.097	0.388
4	0.094	0.164	0.353
5	0.096	0.158	0.358
6	0.096	0.160	0.354
7	0.098	0.165	0.348

The figures in the column headed "No." refer to the number of the experiments in Table V. The data given in the first three and in the last four lines in Table V*a* would seem to show that the values of C_c are in some way dependent upon the concentration of the amalgam—an observation which is now made for the first time. Furthermore, a similar study of the results within any one of the four sets of data compiled in Table V will lead to the same conclusion.

A sample of potassium amalgam which had stood in a sealed bottle for three years, and which had a thick layer of bright crystals at the surface, was analyzed by pouring a portion of the liquid through the capillary tube of the sealing bottle into standard hydrochloric acid and titrating the excess of acid with sodium carbonate, using methyl orange as an indicator. The mean of two determinations showed the amalgam to contain only 0.0965% of potassium. This was peculiar in view of the fact that

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[1] Impurities of heavy metals in the salts hasten the decomposition of the amalgams, but in that case the reaction does not cease until the whole of the amalgam has been decomposed.

the literature is very concordant concerning the concentration of saturated potassium amalgams. Kerp and Böttger[1] found 0.47% K at 20° and 0.53% at 25°, while Smith and Bennett[2] found 0.46% at 20°. Another portion of the liquid amalgam referred to was analyzed by decomposing it with hydrochloric acid and weighing the potassium chloride; it was found to contain 0.0963% of potassium. The chloride was converted into the chloroplatinate, and of this it gave the theoretical quantity. The salt gave the characteristic potassium flame, and it is clear that the bottle was not mislabeled.

A sodium amalgam which had stood for six years in a sealed bottle was analyzed and found to contain 0.204% of sodium, but a careful examination showed that no crystals were present. Therefore no final conclusion can be drawn as to the solubility of the sodium. It is, however, very unlikely that the amalgam was supersaturated after this long period. An investigation of the solubilities of the alkali and alkali-earth amalgams in mercury will be taken up at once in this laboratory. The fact that the solubility of potassium in mercury at 20° has been found to be about one-fifth of the previously published values makes it seem worth while to reinvestigate all of the solubility data.[3]

In Table V*a*, it will be noted that when the percentage of potassium has reached 0.09 a very decided lowering effect is produced upon the value of C_c. This cannot be attributed to a separation of solid KHg_m, for that would cause C_c to increase in value, since KHg_m appears in the numerator of the mass law expression. If the amalgam is in a metastable condition, there is no way of predicting what the effect of this might be.

When it became known that the concentration of the liquid amalgams was probably a matter to be considered, a series of determinations was carried out in which the original amalgams were diluted with varying amounts of mercury and then brought to equilibrium at 25°, with an equivalent mixture of sodium and potassium chlorides at a total concentration of 0.20 *N*. This study appears in Table VI. Column one contains numbers for reference; Cols. two and three, the number of grams of the respective amalgams used; Col. four shows the weight of pure mercury that was added to the amalgam; and Cols. five and six show the weight of the mixed alkali chlorides from the amalgam and of the K_2PtCl_6 obtained from them. In the seventh and eighth columns are given the number of milligram equivalents of potassium and of sodium

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[1] *Z. physik. Chem.*, **25**, 22 (1900).

[2] *Loc, cit.* Owing to a typographical error, in the paper of Smith and Bennett, the values 0.47 and 0.46 appear in the rubidium column instead of in the potassium column.

[3] The investigation has already advanced far enough to indicate the existence of a solid potassium amalgam in two crystalline modifications of widely differing degrees of solubility in mercury.

per gram of mercury in the amalgam at equilibrium, the total weight of the mercury being assumed as being equal to the sum of the weights of the pure mercury and of the amalgam to which it was added. Columns nine and ten show the percentages of the alkali metals in the amalgam at equilibrium. The values of C_c are given in the last column.

TABLE VI.

Showing the effect of diluting the amalgams with pure mercury. The aqueous solution used was an equivalent mixture of KCl and NaCl.

KCl-NaCl. Total concentration 0.20 *N*. Temperature 25° C.

No.	Grams of amalgam used. K.	Grams of amalgam used. Na.	Grams of Hg added.	Wt. KCl plus NaCl.	Wt. K_2PtCl_6.	Milligram equivalents per gm. of Hg at equilib. K.	Milligram equivalents per gm. of Hg at equilib. Na.	Per cent. of alk. metals at equilibrium. K.	Per cent. of alk. metals at equilibrium. Na.	C_c.
1	19	41[1]	none	0.3669	0.3777	0.0258	0.0725	0.101	0.167	0.355
2	19	41[1]	none	0.3716	0.3800	0.0260	0.0726	0.102	0.167	0.356
3	19	41[1]	none	0.3620	0.3706	0.0253	0.0710	0.100	0.163	0.357
4	22	38[1]	none	0.3395	0.3529	0.0241	0.0660	0.095	0.151	0.365
5	22	38[1]	none	0.3451	0.3546	0.0242	0.0675	0.095	0.155	0.359
6	22	38[1]	none	0.3475	0.3581	0.0245	0.0680	0.096	0.156	0.360
7	15	45	none	0.2184	0.2399	0.0164	0.0414	0.065	0.095	0.396
8	22	38	none	0.2567	0.2796	0.0191	0.0490	0.075	0.112	0.391
9	..	60	100	0.2504	0.2963	0.0076	0.0171	0.029	0.039	0.444
10	..	60	100	0.2601	0.3086	0.0079	0.0177	0.031	0.041	0.446
11	..	60	100	0.2638	0.3076	0.0079	0.0182	0.031	0.042	0.433
12	..	60	100	0.2589	0.3030	0.0078	0.0178	0.030	0.041	0.437
13	60	..	100	0.2977	0.3514	0.0090	0.0203	0.035	0.047	0.442
14	60	..	100	0.2781	0.3298	0.0084	0.0190	0.033	0.043	0.445
15	60	..	100	0.2399	0.2830	0.0073	0.0164	0.028	0.038	0.442
16	..	60	150	0.2474	0.2860	0.0056	0.0130	0.022	0.030	0.428
17	..	60	150	0.2740	0.3133	0.0061	0.0141	0.023	0.033	0.421
18	..	60	150	0.2447	0.2802	0.0055	0.0130	0.021	0.030	0.422
19	60	..	150	0.2687	0.3089	0.0060	0.0142	0.023	0.032	0.425
20	60	..	150	0.2380	0.2796	0.0055	0.0124	0.021	0.029	0.439
21	60	..	150	0.2354	0.2768	0.0054	0.0123	0.021	0.028	0.440
22	..	60	200	0.2376	0.2710	0.0043	0.0102	0.017	0.023	0.420
23	60	..	200	0.2658	0.3046	0.0048	0.0113	0.019	0.026	0.422

Throughout the series the concentration of the amalgam was diminished in stages until it reached about one-fifth the original value. With increasing dilution the value of C_c was found to increase and then to decrease. The maximum value was obtained upon diluting 60 g. of the amalgam with 100 g. of pure mercury. While further dilution caused a slight decrease, this did not exceed about 2.5% on the average, and some of the values obtained upon dilution with 150 g. of mercury are slightly

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[1] The sodium amalgam used here contained 0.272% Na. In all other cases the sodium amalgam contained 0.191% Na. The potassium amalgam used contained in all cases 0.355% K.

higher than some of those obtained upon dilution with 100 g.[1] Owing to these facts, it was decided in all future determinations to use amalgams prepared by adding 100 g. of pure mercury to 60 g. of the stock amalgam. The results which have been obtained seem to fully justify this procedure. At this dilution no trouble was experienced in duplicating results, even though the concentration of the amalgams at equilibrium often varied considerably, owing to a temporary evolution of hydrogen in some cases. With the undiluted amalgams, difficulty was often experienced in getting check results; upon looking over some of the earlier data, which it is not considered worth while to publish, it is found that some of the inconsistent results can be explained from the standpoint of concentration while some of them cannot. This tends to show that the behavior of the amalgams, when too concentrated, is more or less erratic. The dependable behavior of the diluted amalgams is evidenced by the fact that out of 144 determinations which were made with them only seven had to be thrown out for unknown causes. Six of these, which were made at one time with the same aqueous solution, agreed among themselves, and, although the solutions were no longer at hand to be tested, it is considered almost certain that an error was made in their preparation; this is especially likely in view of the fact that upon repeating the work with a fresh solution of the intended salt-concentration ratio normal values of C_c were obtained.

3. The Effect of Changing the Temperature: Heat of Reaction.—In the case of this reaction, determinations have previously been made[2] of the equilibrium constant at 18° and at 24°, but the data obtained cannot be used to calculate the heat of the reaction because the solutions used at the two different temperatures were not identical; it was shown, however, that the reaction,

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

is endothermic. But if identical solutions are used at the different temperatures, and if the temperature range is not too great, the heat of the reaction may be calculated from the equilibrium constants by means of the van't Hoff equation,

$$2.303 \log_{10} \frac{C_2}{C_1} = \frac{\Delta U}{R} \left[\frac{1}{T_1} - \frac{1}{T_2}\right],$$

where C_1 and C_2 are the values of the equilibrium constants at the absolute temperatures T_1 and T_2, respectively; R is the gas constant expressed in calories and has the value 1.9852; ΔU is the heat evolved when the sub-

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[1] The effect of dilution is much more marked and regular in the case of the equilibrium $2NaHg_n + Sr^{++} \rightleftarrows 2Na^+ + SrHg_m + (2n - m)Hg$, which is at present under investigation in this laboratory by Mr. S. A. Braley.

[2] G. McP. Smith, This Journal, **32**, 502 (1910); **35**, 39 (1913).

stances in the numerator of the mass law expression react to form the substances in the denominator, *i. e.*, when the above reaction proceeds from left to right.

The equilibrium constant has been determined at four different temperatures for which the data are given in Tables VII–X. In each case, sixty grams of amalgam were diluted with 100 g. of pure mercury and the aqueous solution used was an equivalent mixture of sodium and potassium chlorides at a total concentration of 0.20 *N*. The mean values of the equilibrium constants are as follows:

Temperature.....	15°	20°	25°	30°
C_c..............	0.520	0.473	0.440	0.397

TABLE VII.

KCl-NaCl. Total Normality 0.200. Temperature 15°.

	Normal conc. of salts.		Mol fract. in amalg. at start.				Mol fract. in amalg. at equilib.		
No.	KCl.	NaCl.	K.	Na.	Wt. NaCl plus KCl.	Wt. K_2PtCl_6.	K.	Na.	C_c.
1...........	0.100	0.100	....	1.00[1]	0.1600	0.2113	0.3425	0.6575	0.521
2...........	0.100	0.100	....	1.00	0.3014	0.3924	0.3413	0.6587	0.518
3...........	0.100	0.100	....	1.00	0.2957	0.3854	0.3417	0.6583	0.519
4...........	0.100	0.100	....	1.00	0.2798	0.3672	0.3443	0.6557	0.525
5...........	0.100	0.100	1.00[1]	....	0.1877	0.2439	0.3405	0.6595	0.516
6...........	0.100	0.100	1.00	....	0.2844	0.3729	0.3430	0.6560	0.524
7...........	0.100	0.100	1.00	....	0.3002	0.3922	0.3425	0.6575	0.521
8...........	0.100	0.100	1.00	....	0.3045	0.3940	0.3391	0.6609	0.513
								Mean,	0.520

The Na amalgam contained 0.191% Na. 60 g. used.
The K amalgam contained 0.355% K. 60 g. used.

TABLE VIII.

KCl-NaCl. Total Normality 0.200. Temperature 20°.

	Normal conc. of salts.		Mol fract. in amalg. at start.				Mol fract. in amalg. at equilib.		
No.	KCl.	NaCl.	K.	Na.	Wt. NaCl plus KCl.	Wt. K_2PtCl_6.	K.	Na.	C_c.
1...........	0.100	0.100	....	1.00	0.2595	0.3188	0.3204	0.6796	0.471
2...........	0.100	0.100	....	1.00	0.2882	0.3552	0.3214	0.6786	0.474
3...........	0.100	0.100	....	1.00	0.2798	0.3449	0.3214	0.6786	0.474
4...........	0.100	0.100	1.00	....	0.2833	0.3472	0.3195	0.6805	0.469
5...........	0.100	0.100	1.00	....	0.2894	0.3569	0.3217	0.6783	0.474
6...........	0.100	0.100	1.00	....	0.3073	0.3805	0.3231	0.6769	0.477
								Mean,	0.473

The Na amalgam contained 0.191% Na. 60 g. used.
The K amalgam contained 0.355% K. 60 g. used.
100 g. of mercury were added to the amalgam in each case.

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[1] 60 grams of mercury were added in Nos. 1 and 5; in all other cases 100 g. were added to the amalgam.

TABLE IX.

KCl-NaCl. Total Normality 0.200. Temperature 25°.

	Normal conc. of salts.		Mol fract. in amalg. at start.				Mol fract. in amalg. at equilib.		
No.	KCl.	NaCl.	K.	Na.	Wt. NaCl plus KCl.	Wt. K_2PtCl_6.	K.	Na.	C_c.
1	0.100	0.100	...	1.0	0.2504	0.2963	0.3073	0.6926	0.444
2	0.100	0.100	...	1.0	0.2601	0.3086	0.3084	0.6916	0.446
3	0.100	0.100	...	1.0	0.2464	0.2919	0.3077	0.6923	0.446
4	0.100	0.100	...	1.0	0.2271	0.2655	0.3034	0.6966	0.434
5	0.100	0.100	...	1.0	0.2638	0.3076	0.3026	0.6974	0.433
6	0.100	0.100	...	1.0	0.2589	0.3030	0.3040	0.6960	0.437
7	0.100	0.100	1.0	...	0.2380	0.2796	0.3050	0.6950	0.439
8	0.100	0.100	1.0	...	0.2354	0.2768	0.3054	0.6946	0.440
9	0.100	0.100	1.0	...	0.2399	0.2830	0.3065	0.6935	0.442
10	0.100	0.100	1.0[1]	...	0.1737	0.2083	0.3120	0.6880	(0.454)
11	0.100	0.100	1.0	...	0.2977	0.3514	0.3067	0.6933	0.442
12	0.100	0.100	1.0	...	0.2781	0.3298	0.3082	0.6918	0.445

Mean, 0.440

The Na amalgam contained 0.191% Na. 60 g. used.
The K amalgam contained 0.355% K. 60 g. used.
100 g. mercury were added to the amalgam in each case.

TABLE X.

KCl-NaCl. Total Normality 0.200. Temperature 30°.

	Normal conc. of salts.		Mol fract. in amalg. at start.				Mol fract. in amalg. at equilib.		
No.	KCl.	NaCl.	K.	Na.	Wt. NaCl plus KCl.	Wt. K_2PtCl_6.	K.	Na.	C_c.
1	0.100	0.100	...	1.0	0.2551	0.2773	0.2807	0.7193	0.390
2	0.100	0.100	...	1.0	0.2766	0.3036	0.2835	0.7165	0.396
3	0.100	0.100	...	1.0	0.2432	0.2685	0.2853	0.7147	0.399
4	0.100	0.100	1.0	...	0.2651	0.2914	0.2838	0.7162	0.396
5	0.100	0.100	1.0	...	0.2855	0.3157	0.2859	0.7141	0.400
6	0.100	0.100	1.0	...	0.2811	0.3109	0.2858	0.7142	0.400

Mean, 0.397

The amalgams used were the same as in the table above. 100 g. of mercury were added to the amalgam in each case.

By substituting these values in the van't Hoff equation and solving for ΔU, the heat of reaction is found to be equal to —3200 calories between 15° and 20°; to —2500 calories between 20° and 25°; and to —3700 calories between 25° and 30° C. The mean of these values is —3100 calories. The results are not as concordant as might be expected, but it should be noted that a change of 1% in the numerical value of the fraction C_2/C_1 gives rise to a 10% change in the magnitude of its logarithm,

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[1] This amalgam was the last of a bottle that had stood for several weeks. The air in the bottle had partially removed the K by oxidation; hence the low weight of mixed salts.

and that in case each of the two values of C_c were in error by as much as 1.0% in opposite directions, the error made in computing the heat of the reaction would amount to 20% of the true value. At present, all that can be said with certainty is that the heat of the reaction is in the neighborhood of —3000 calories, between 15° and 30°.

Berthelot[1] has made the only existing study of the heats of formation of liquid amalgams, but unfortunately the least concentrated of his amalgams contained 0.32% of potassium and 0.45% of sodium, respectively. On the other hand, the potassium amalgam used in the present study contained at the start, after dilution, approximately 0.13% of potassium, and in the sodium amalgam sodium was present at an equivalent concentration. A calculation based upon the data of Berthelot's most dilute amalgams, together with the necessary data fron Landolt and Börnstein's tables gives —6400 calories as the heat of the reaction in question. But in view of the fact that the difference in concentration of the two amalgams is great, such a calculation is meaningless except as regards the order of magnitude. Even if a 0.32% potassium amalgam could have been started with in this work, Berthelot's data could not be used in strict comparison, since they do not include the heat of formation of a sodium amalgam of equivalent concentration.

4. The Effect of Increasing the Total Salt Concentration at a Fixed Salt-Concentration Ratio. (*a*) *Salts with a Common Ion,* (α) *KCl-NaCl.*—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[2] that upon raising the concentration from 0.20 N to 2.0 N the value of the equilibrium constant, C_c, decreased from 0.472 to 0.395, at 18°. Upon calculating the ion fractions of the sodium and potassium by means of the equations

$$(K^+)_c = \frac{(KHg_m)}{(KHg_m) + (NaHg_n)C_o} \text{ and } (Na^+)_c = 1 - (K^+)_c,$$

it was found that "The concentration of the sodium ion gains on that of the potassium ion" with increasing total salt concentration. Since, however, these experiments were carried out by starting with amalgams containing 0.26% sodium and 0.33% potassium, respectively, and since it has been found that liquid potassium amalgams at concentrations greater than 0.09% probably contain potassium in a somewhat metastable condition, it has seemed advisable to repeat the work with more dilute amalgams. This has been done at 25°. The data will be found in Table XI.

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[1] *Ann. chim.*, [5] **18**, 433 (1879).

[2] G. McP. Smith, THIS JOURNAL, **35**, 39 (1913).

TABLE XI.

KCl·NaCl. Total Concentration 0.20 *N* to 4.0 *N*. Temperature 25°.

No.	Normal conc. of salts.		Mol fract. in amalg. at start.		Wt. NaCl plus KCl.	Wt. K_2PtCl_6.	Mol fract. in amalg. at equilib.		C_c.
	KCl.	NaCl.	K.	Na.			K.	Na.	
	0.10	0.10	See Table IX.					Mean,	0.440
1	0.25	0.25	....	1.0	0.2649	0.3080	0.3019	0.6981	0.432
2	0.25	0.25	....	1.0	0.2698	0.3129	0.3009	0.6991	0.430
3	0.25	0.25	1.0	....	0.2366	0.2768	0.3038	0.6962	0.436
4	0.25	0.25	1.0	....	0.2616	0.3064	0.3042	0.6958	0.437
								Mean,	0.434
5	0.50	0.50	....	1.0	0.2848	0.3253	0.2959	0.7041	0.421
6	0.50	0.50	....	1.0	0.2957	0.3379	0.2962	0.7038	0.421
7	0.50	0.50	1.0	....	0.2591	0.2955	0.2953	0.7047	0.419
8	0.50	0.50	1.0	....	0.3087	0.3490	0.2927	0.7073	0.414
								Mean,	0.419
9	1.0	1.0	....	1.0	0.3204	0.3427	0.2757	0.7243	0.381
10	1.0	1.0	....	1.0	0.3195	0.3444	0.2781	0.7219	0.385
11	1.0	1.0	1.0	....	0.3075	0.3290	0.2757	0.7243	0.381
12	1.0	1.0	1.0	....	0.2845	0.3024	0.2740	0.7260	0.377
								Mean,	0.381
13	1.66	0.33	0.62	0.38	0.3764	0.8678	0.6515	0.3448	0.374
14	1.66	0.33	0.62	0.38	0.3791	0.8793	0.6561	0.3439	0.382
15	1.66	0.33	1.0	....	0.3291	0.7607	0.6536	0.3464	0.377
16	1.66	0.33	1.0	....	0.3313	0.7652	0.6532	0.3468	0.377
17	1.66	0.33	....	1.0	0.3294	0.7688	0.6612	0.3388	0.390
18	1.66	0.33	....	1.0	0.3473	0.8119	0.6623	0.3377	0.392
19	1.66	0.33	1.0	....	0.3694	0.8630	0.6614	0.3386	0.391
20	1.66	0.33	0.33	0.67	0.3660	0.8275	0.6368	0.3632	(0.351)
								Mean,	0.383
21	0.33	1.66	....	1.0	0.2607	0.0750	0.0689	0.9311	0.371
22	0.33	1.66	....	1.0	0.2853	0.0808	0.0692	0.9308	0.372
23	0.33	1.66	....	1.0	0.2739	0.0779	0.0694	0.9306	0.373
24	0.33	1.66	1.0	....	0.2161	0.0628	0.0708	0.9292	0.382
25	0.33	1.66	1.0	....	0.2194	0.0626	0.0695	0.9305	0.374
26	0.33	1.66	1.0	....	0.2126	0.0616	0.0706	0.9294	0.381
27	0.33	1.66	1.0	....	0.2727	0.0789	0.0705	0.9295	0.381
								Mean,	0.376
28	2.00	2.00	....	1.0	0.3018	0.2886	0.2446	0.7554	0.324
29	2.00	2.00	....	1.0	0.3088	0.2919	0.2424	0.7576	0.320
30	2.00	2.00	1.0	....	0.2985	0.2832	0.2424	0.7576	0.320
31	2.00	2.00	1.0	....	0.2971	0.2856	0.2460	0.7540	0.326
								Mean,	0.322

The Na amalgam contained 0.191% Na and 60 g. were used.
The K amalgam contained 0.355% K and 60 g. were used.
100 grams of Hg were added in each case.

TABLE XII.

K_2SO_4-Na_2SO_4. Total Concentration 0.20 to 2.0 *N*. Temperature 25°.

	Normal conc. of salts.		Mol fract. in amalg. at start.				Mol fract. in amalg. at equilib.		
No.	K_2SO_4.	Na_2SO_4.	K.	Na.	Wt. NaCl plus KCl.	Wt. K_2PtCl_6.	K.	Na.	C_c.
1	0.10	0.10	...	1.0	0.2439	0.2831	0.3010	0.6990	0.431
2	0.10	0.10	...	1.0	0.2923	0.3379	0.2999	0.7001	0.428
3	0.10	0.10	...	1.0	0.2816	0.3257	0.3000	0.7000	0.428
4	0.10	0.10	...	1.0	0.2939	0.3394	0.2996	0.7004	0.428
5	0.10	0.10	1.0	...	0.2811	0.3318	0.3067	0.6933	0.442
6	0.10	0.10	1.0	...	0.2822	0.3305	0.3041	0.6959	0.437
7	0.10	0.10	1.0	...	0.2600	0.3073	0.3073	0.6927	0.443
8	0.10	0.10	1.0	...	0.2354	0.2746	0.3026	0.6974	0.434
								Mean,	0.434
9	0.50	0.50	...	1.0	0.2828	0.3280	0.3010	0.6990	0.431
10	0.50	0.50	...	1.0	0.2810	0.3281	0.3030	0.6970	0.435
11	0.50	0.50	...	1.0	0.2999	0.3496	0.3025	0.6975	0.434
12	0.50	0.50	...	1.0	0.3223	0.3743	0.3013	0.6987	0.431
13	0.50	0.50	1.0	...	0.2800	0.3264	0.3029	0.6971	0.434
14	0.50	0.50	1.0	...	0.2810	0.3275	0.3024	0.6976	0.434
15	0.50	0.50	1.0	...	0.2907	0.3372	0.2983	0.7017	0.425
16	0.50	0.50	1.0	...	0.2616	0.3040	0.3016	0.6984	0.432
								Mean,	0.432
17	0.833	0.166	...	1.0	0.3246	0.7814	0.6858	0.3142	0.436
18	0.833	0.166	...	1.0	0.3833	0.9221	0.6836	0.3164	0.432
19	0.833	0.166	...	1.0	0.3670	0.8811	0.6854	0.3146	0.435
20	0.833	0.166	1.0	...	0.3107	0.7476	0.6854	0.3146	0.435
21	0.833	0.166	1.0	...	0.2940	0.7086	0.6866	0.3134	0.438
22	0.833	0.166	1.0	...	0.3155	0.7572	0.6840	0.3160	0.431
								Mean,	0.434
23	0.166	0.833	...	1.0	0.2920	0.0927	0.0778	0.9222	0.421
24	0.166	0.833	...	1.0	0.3004	0.0958	0.0781	0.9219	0.423
25	0.166	0.833	...	1.0	0.2825	0.0896	0.0776	0.9224	0.420
26	0.166	0.833	...	1.0	0.3160	0.1003	0.0780	0.9220	0.422
27	0.166	0.833	1.0	...	0.2626	0.0858	0.0788	0.9212	0.427
28	0.166	0.833	1.0	...	0.2913	0.0944	0.0800	0.9200	0.431
29	0.166	0.833	1.0	...	0.2740	0.0862	0.0769	0.9231	0.417
30	0.166	0.833	1.0	...	0.2872	0.0908	0.0773	0.9227	0.419
								Mean,	0.423
31	1.0	1.0	...	1.0	0.3400	0.3895	0.2968	0.7032	0.422
32	1.0	1.0	...	1.0	0.2822	0.3266	0.3001	0.6999	0.429
33	1.0	1.0	...	1.0	0.3071	0.3558	0.3005	0.6995	0.429
34	1.0	1.0	...	1.0	0.3270	0.3766	0.2988	0.7012	0.426
35	1.0	1.0	1.0	...	0.3040	0.3534	0.3018	0.6982	0.432
36	1.0	1.0	1.0	...	0.2938	0.3409	0.3010	0.6990	0.431
37	1.0	1.0	1.0	...	0.2481	0.2885	0.3017	0.6983	0.432
38	1.0	1.0	1.0	...	0.3031	0.3516	0.3010	0.6990	0.430
								Mean,	0.430

The Na amalgam contained 0.288% Na; the K amalgam, 0.328% K.

Used 40 g. Na amalgam with 120 g. of Hg.

Used 60 g. K amalgam with 100 g. of Hg.

TABLE XIII.

MeCl-Me'$_2$SO$_4$. Total Concentration 0.20 to 3.0 *N*. Temperature 25°.

	Normal conc. of salts.		Mol fract. in amalg. at start.				Mol fract. in amalg. at equilib.		
No.	KCl.	Na$_2$SO$_4$.	K	Na.	Wt. NaCl plus KCl.	Wt. K$_2$PtCl$_6$.	K.	Na.	C_c.
1	0.10	0.10	...	1.0	0.2576	0.3011	0.3033	0.6967	0.435
2	0.10	0.10	...	1.0	0.2688	0.3145	0.3038	0.6962	0.436
3	0.10	0.10	...	1.0	0.2712	0.3192	0.3056	0.6944	0.440
4	0.10	0.10	1.0	...	0.2681	0.3182	0.3079	0.6921	0.445
5	0.10	0.10	1.0	...	0.2879	0.3419	0.3087	0.6913	0.446
6	0.10	0.10	1.0	...	0.3161	0.3750	0.3084	0.6916	0.446
								Mean,	0.441
7	0.50	0.50	...	1.0	0.3169	0.3617	0.2957	0.7043	0.420
8	0.50	0.50	...	1.0	0.3413	0.3886	0.2950	0.7050	0.418
9	0.50	0.50	...	1.0	0.2930	0.3353	0.2964	0.7036	0.421
10	0.50	0.50	1.0	...	0.2870	0.3283	0.2966	0.7034	0.421
11	0.50	0.50	1.0	...	0.3318	0.3791	0.2962	0.7038	0.421
12	0.50	0.50	1.0	...	0.3162	Lost	....	....	.....
								Mean,	0.420
	NaCl.	K$_2$SO$_4$.							
13	0.50	0.50	...	1.0	0.2983	0.3397	0.2949	0.7051	0.418
14	0.50	0.50	...	1.0	0.2964	0.3388	0.2962	0.7038	0.421
15	0.50	0.50	...	1.0	0.3202	0.3658	0.2960	0.7040	0.420
16	0.50	0.50	1.0	...	0.2913	0.3334	0.2966	0.7034	0.422
17	0.50	0.50	1.0	...	0.2929	0.3380	0.2992	0.7008	0.427
18	0.50	0.50	1.0	...	0.2979	0.3395	0.2952	0.7048	0.419
								Mean,	0.421
	KCl.	Na$_2$SO$_4$.							
19	1.0	1.0	...	1.0	0.2935	0.3280	0.2889	0.7111	0.406
20	1.0	1.0	...	1.0	0.3121	0.3482	0.2884	0.7116	0.406
21	1.0	1.0	...	1.0	0.3015	0.3372	0.2894	0.7106	0.407
22	1.0	1.0	1.0	...	0.2885	0.3223	0.2890	0.7110	0.407
23	1.0	1.0	1.0	...	0.2955	0.3303	0.2890	0.7110	0.407
24	1.0	1.0	1.0	...	0.2872	0.3229	0.2899	0.7101	0.408
								Mean,	0.407
25	1.5	1.5	...	1.0	0.2935	0.3269	0.2881	0.7119	0.404
26	1.5	1.5	...	1.0	0.2865	0.3179	0.2873	0.7127	0.403
27	1.5	1.5	...	1.0	0.3121	0.3439	0.2848	0.7152	0.398
28	1.5	1.5	1.0	...	0.2974	0.3287	0.2854	0.7146	0.400
29	1.5	1.5	1.0	...	0.2969	0.3071	0.2660	0.7340	(0.362)
30	1.5	1.5	1.0	...	0.2824	0.3150	0.2884	0.7116	0.405
								Mean,	0.402

40 g. of 0.288% Na amalgam were used with 120 g. of mercury.

60 g. of 0.328% K amalgam were used with 100 g. of mercury.

Expts. 13–27, which were carried out with solutions containing the salts in other than equivalent proportions, will be discussed later. The total concentration of the equivalent mixtures was increased from 0.20 normal to 4.0 *N*, and the value of C_c was found to decrease from 0.440 to 0.322. The complete data for the 0.20 *N* solutions have already been given in Table IX, and for that reason only the mean value is shown here. The effect of increasing the total salt concentration is best studied by reference to the KCl-NaCl curve in Fig. 2, where the values of C_c have been plotted against those of the total salt concentration (Table XI). The dots mark the points determined experimentally with chloride-chloride mixtures. A straight line connecting the highest and lowest values of C_c passes very close to all of the other points determined; at 1.0 *N* the observed value of C_c is slightly above the line and at 2.0 *N* it is slightly below it, but in neither case is the deviation as great as 1.0% of the absolute value of C_c at that particular concentration. This is within the limits of experimental error, as can be seen from the data of Table XI; so we may conclude that in the case of equivalent mixtures of sodium and potassium chlorides at 25° the value of the equilibrium constant, C_c, is a linear function of the total salt concentration.

(β) K_2SO_4-Na_2SO_4.—Table XII contains the data obtained upon increasing the total concentration of equivalent mixtures of sodium and potassium sulfates. Expts. 17–30 will be discussed later, together with Expts. 13–27 of Table XI. In the case of the sulfate-sulfate mixtures, the value of C_c obtained at 0.20 *N* is 0.434, and at 2.0 *N* it is 0.429—a decrease of only 1.1%; in the case of the mixed chlorides a similar increase in concentration was found to lower the value of C_c by 13.4%.

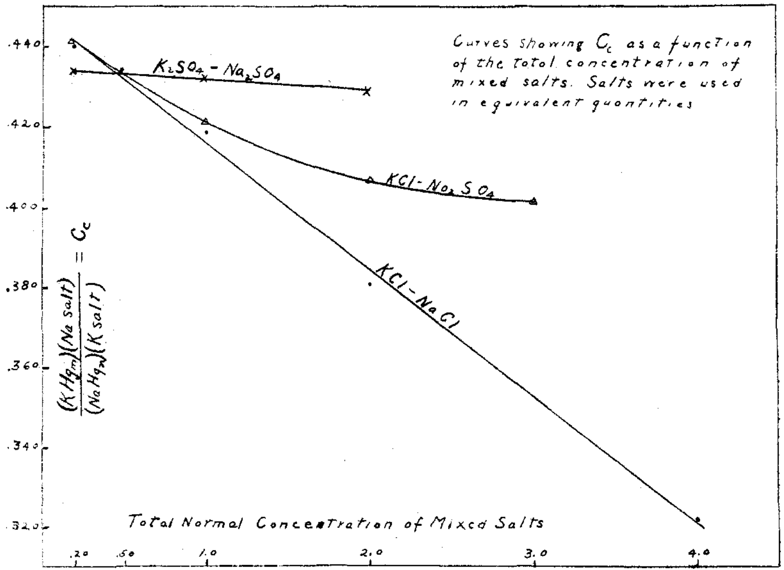

Fig. 2.

The sulfate-sulfate data are also plotted in Fig. 2, in which it will be noted that the value of C_c is a linear function of the salt concentration, if it depends upon it at all. The slight decrease of 1.1% in the value of C_c between 0.20 and 2.0 *N* is, however, of but little significance—owing to the fact that several of the values obtained at the higher concentration are higher than some of those obtained at the lower concentration. (Compare Nos. 35, 36, 37 and 38 with Nos. 2, 3 and 4, in Table XII.)

(*b*) *Salts without a Common Ion, KCl-Na_2SO_4.*—The effect of increasing the total concentration of equivalent mixtures of salts of two different types and with no common ion (KCl and Na_2SO_4) has been studied, and the results are given in Table XIII. As a check upon the accuracy of the work, the solutions for Expts. 7–12 were prepared by mixing equivalent quantities of KCl and Na_2SO_4 and for Expts. 13–18 by mixing equivalent quantities of $NaCl$ and K_2SO_4. As was expected, both combinations of salts gave substantially identical values for C_c. In this series an increase in the salt concentration produces a decrease in the value of C_c; since on mixing KCl and K_2SO_4 there would result, by metathesis, two other salts, $NaCl$ and Na_2SO_4, a curve falling between the chloride-chloride and the sulfate-sulfate curves was to be expected. If the metathesis,

$$KCl + {}^1/_2Na_2SO_4 \rightleftarrows NaCl + {}^1/_2K_2SO_4,$$

were all that took place, then the form of the curve should be the same as that of the other two, *i. e.*, the curve should be a straight line. The chloride-sulfate data also are plotted in Fig. 2. In this case the value of C_c is not a linear function of the concentration, but decreases at a constantly diminishing rate, until between 2.0 normal and 3.0 normal the effect of changing the concentration becomes almost negligible.

(*c*) *Calculation of the Ion Fractions in Cases a and b.*—In the theoretical discussion, an equation,

$$(K^+)_c = \frac{C_c(\text{K salt})}{C_0(\text{Na salt}) + C_c(\text{K salt})},$$

is developed, by means of which it is possible to calculate, from data such as those included in Tables XI, XII and XIII, the ion fractions in which sodium and potassium are present at any particular concentration. Since in all of the cases now under consideration the salts were present in the mixtures in equivalent quantities, the equation reduces to the simple form

$$(K^+)_c = \frac{C_c}{C_o + C_c}.$$

By extrapolating to zero concentration on the curves of Fig. 2, it is possible to obtain the value of C_0 in the equilibrium expression,

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

i. e., to find the true equilibrium constant at 25° for the reversible ionic reaction,

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

Extrapolation on the chloride-chloride, or on the chloride-sulfate curve gives a value of 0.448 for C_o, and by substituting this value, together with the values of C_c from the tables, in the above simple equation, the values of the ion fractions which exist in the various mixtures may readily be calculated. The data for the three different types of mixtures are given in Table XIV.

TABLE XIV.

Calculation of the Ion Fractions at 25°.

Normality of salts in sol.		Total normality.	C_o.	C_c.	Calculated ion fractions.	
KCl.	NaCl.				K^+.	Na^+.
0.00	0.00	0.00	0.448	(0.448)	*0.500*	*0.500*
0.10	0.10	0.20	0.448	0.440	0.495	0.505
0.25	0.25	0.50	0.448	0.434	0.492	0.508
0.50	0.50	1.00	0.448	0.419	0.483	0.517
1.00	1.00	2.00	0.448	0.381	0.459	0.541
2.00	2.00	4.00	0.448	0.322	0.419	0.581
KCl.	Na_2SO_4.					
0.00	0.00	0.00	0.448	(0.448)	*0.500*	*0.500*
0.10	0.10	0.20	0.448	0.441	0.496	0.504
0.50	0.50	1.00	0.448	0.420	0.484	0.516
1.00	1.00	2.00	0.448	0.407	0.476	0.524
1.50	1.50	3.00	0.448	0.402	0.473	0.527
K_2SO_4.	Na_2SO_4.					
0.00	0.00	0.00	0.448	(0.448)	*0.500*	*0.500*
0.10	0.10	0.20	0.448	0.434	0.492	0.508
0.50	0.50	1.00	0.448	0.432	0.491	0.509
1.00	1.00	2.00	0.448	0.429	0.489	0.511

The potassium ion fraction in the chloride-chloride mixtures decreases from 0.495 at 0.20 *N* to 0.419 at 4.0 *N*, while in the chloride-sulfate mixtures the potassium ion fraction decreases from 0.496 at 0.20 *N* to 0.473 at 3.0 *N*; in the sulfate-sulfate mixtures, on the other hand, the decrease is only from 0.492 to 0.489 between 0.20 and 2.0 *N*. The values of the ion fractions are plotted against the total concentrations of the salt solutions in Fig. 3. In the case of the chloride-chloride curve, the ion fraction appears to be a linear function of the total salt concentration; although, if it is true that C_c is a linear function of the salt concentration (Fig. 2), the ion fraction, calculated from the equations,

$$(\mathrm{K}^+)_c = \frac{\mathrm{C}_c}{\mathrm{C}_o + \mathrm{C}_c} \text{ and } (\mathrm{Na}^+)_c = 1 - (\mathrm{K}^+)_c,$$

should not determine a straight line when plotted against the total concentration of the salts. Since, however, only a relatively small change in the value of the ion fraction is produced up to a concentration of 4.0 *N* (0.500 to 0.419), the function may properly be considered linear over this portion of the curve.

In the case of the chloride-sulfate mixture the curve has the same general form as that in Fig. 2. The potassium ion fraction decreases at a diminishing rate as the salt concentration increases.

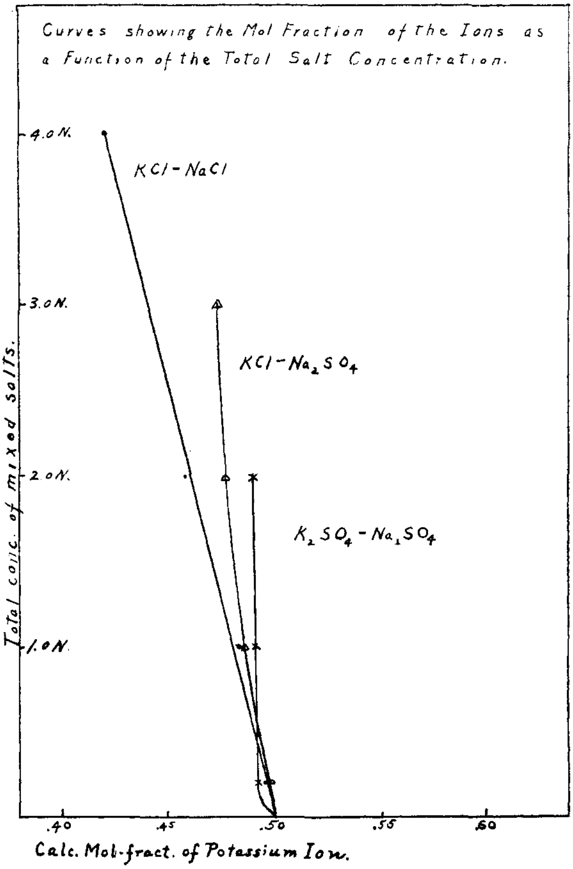

Fig. 3.

In calculating the ion fractions of the sodium and potassium in the sulfate-sulfate mixtures we are confronted with the task of assigning a value to C_0 from the data at hand. Extrapolation on the curve of Fig. 2 gives a value of 0.434 for C_0, whereas, the other two curves give a value of 0.448. Theoretically, an equivalent mixture of any two salts of sodium and potassium should give the same equilibrium constant when each salt in the mixture is completely ionized—*i. e.*, at infinite dilution—and it is probable that the sulfate-sulfate curve in Fig. 2 would take a different form below 0.20 *N* and actually cut the axis at a point that is common to the other two curves; but that would require a very abrupt change. It might possibly be thought that the whole curve should be raised by 0.014, so that it would terminate at 0.448 instead of at 0.434; but the concordance of the data in Table XII (as well as that of the data in Table XI and XIII) renders it very improbable that an experimental error of this magnitude has been made. Each of the three points on the curve represents the mean of eight individual determinations, in which the equilibrium was approached from both sides, and in no case does the value of C_c differ from the mean value of the series by more than 1.6%; in most cases the agreement is within 1.0%. In the light of these facts, it is probable that the results are very nearly correct for the conditions which prevailed.

The difference in value of C_c in the case of the sulfate-sulfate and of the chloride-sulfate mixture at 0.20 *N* cannot be attributed to a difference in concentration of the amalgams; as a matter of fact the amalgams were identical. In the former series (Table XII) the mean weight of mixed chlorides obtained from the amalgams was 0.2725 g., while in the latter series (Table XIII) it was 0.2783 g.

It is true, then, in the case of the sulfate-sulfate mixtures, that from 0.20 *N* to 2.0 *N* the value of C_c decreases by only about 1.1% and that the ion fractions of the sodium and potassium are practically constant over that range.

5. The Effect of Varying the Concentration Ratio of the Salts at a Fixed (high) **Total Salt Concentration.**—If the reaction between alkali metal amalgams and alkali salt solutions is ionic, the mass law expression,

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

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

$$\frac{(\mathrm{KHg}_m)(\mathrm{Na\ salt})_c}{(\mathrm{NaHg}_n)(\mathrm{K\ salt})_c} = C_c.$$

The results of experiments carried out with undiluted amalgams, and recorded in the first four tables, 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. The chloride-chloride mixtures had a total concentration of 0.20 *N* (see Table I) and the relative salt concentrations varied from 1NaCl : 4KCl to 4NaCl : 1KCl, and in the experiments recorded in Tables II, III and IV the total concentration of each mixture was 0.60 *N* and the ratio between the salt concentrations varied from five to one, to one to five; but no appreciable variation in the value of C_c was observed.

When dilute 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. It was thought that at higher total salt concentrations the magnitude of any variation which a change in the ratio might produce would be likely to increase. Table XI contains the results obtained with dilute amalgams and solutions whose total concentration was 2.0 *N*. Expts. 13–20, which were carried out with a solution 1.666 N with respect to KCl and 0.333 N with respect to NaCl, gave as a mean value, C_c = 0.383, whereas, Expts. 21–27, in which the concentrations of the respective salts in the mixture were reversed, gave a mean of 0.376. The difference between these values is less than 2.0%, and since the limit of accuracy with which each mean value can be determined is about 1.0%, no great significance can be attached to the difference at the present time.

Similar data for mixtures of the sulfates at a total concentration of 1.0 N are given in Expts. 17–30, Table XII. Expts. 17–22, in which the aqueous solution was 0.833 N with respect to K_2SO_4 and 0.166 N with respect to Na_2SO_4, gave as a mean value, C_c = 0.434; while Expts. 23–30, in which the reverse mixture was used, gave a mean of 0.423. The difference, while larger than was observed in the case of the chloride-chloride mixtures, is still too small to be considered conclusive. Nevertheless, in both the chloride-chloride and the sulfate-sulfate mixtures an excess of potassium salt produced the higher value of C_c, and this agreement in the direction of the change, together with the fact that an equivalent mixture of the chlorides or sulfates, at the same total concentration, yielded a value between those obtained with excess of potassium, and excess of sodium salt, makes it seem likely that the change may be significant. By varying the ratio over still wider limits this difference, if real, should be magnified; this point will be taken up in a future investigation, as will also the case of chloride-sulfate mixtures, chloride-iodide mixtures, etc.

E. Discussion of the Results.

This study has shown that, in equivalent mixtures of the chlorides, and of the chlorides and sulfates of sodium and potassium, the ion fraction of the potassium decreases with increasing total salt concentration; but that in the case of equivalent mixtures of the sulfates, at total concentrations ranging from 0.20 to 2.0 N, the ion fractions are almost, if not quite, independent of the total salt concentration of the solution. In the case of the chloride mixtures, this result agrees with that previously obtained.[1] The phenomenon is anomalous in view of the fact that, assuming the correctness of conclusions derived from the conductance data, potassium salts are slightly more highly ionized than the corresponding sodium salts; and we should, therefore, expect the same relations to exist in the mixture. Use has already been made[1] of A. Werner's theory of "Higher Order Compounds" in order to account for this apparent anomaly. According to this theory, the alkali halides should be capable of forming addition compounds with one another, as well as with other substances, and in support of this assumption the following evidence is introduced.

The recent introduction of the methods of "thermal analysis" into the field of organic chemistry has brought to light the fact that the property

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[1] G. McP. Smith, *Loc. cit.*

of forming addition compounds is characteristic of a great many substances and has even led some chemists to the belief that no chemical reaction takes place except through the preliminary formation of intermediate addition compounds. This property of forming addition compounds with other substances is ascribed by Werner[1] to all substances except the saturated hydrocarbons.

Alkali halides are known to add water in solution and to yield hydrated ions. They are capable also of forming addition compounds with ammonia.[2] Numerous double halides, such as K_2PtCl_6, K_2HgI_4, Na_3AlF_6, and $2KCl.MgCl_2.6H_2O$, may be cited as familiar instances in which the tendency of the alkali halides to form addition compounds with other halides comes into play. In addition to this tendency to add other halides, the alkali halides also show a tendency to polymerize. Lithium chloride, for example, appears to exist in the form of double molecules in glacial acetic acid,[3] and to polymerize in amyl alcohol,[4] and transference experiments carried out by E. W. Washburn[5] point strongly to the existence of polymers of caesium iodide in 0.50 normal aqueous solution.

During the last five or six years Hantzsch[6] and his students have published, in the *Berichte* and the *Annalen*, a great many articles which are based upon absorption spectra data and which tend to show that the alkali metals, through secondary valence unions, are capable of effecting closed ring structures with the formation of inner complex salts. And conductance measurements which have been carried out by Lifschitz[7] on the alkali salts of the oximino-ketonic and of the nitrolic acids have led him also to conclude that in some cases inner complex salts of these metals are formed.

In a very recent study, C. Sandonnini[8] has carried out conductance measurements with mixed sodium and potassium chloride solutions in which he finds that the experimentally obtained values are somewhat lower than the calculated values. Furthermore, Sandonnini finds that the sodium chloride-sodium sulfate mixture studied has a conductance which is 2.2% lower than the calculated value, while solutions in which complexes are known to exist have conductances that are but seven or eight per cent. lower than the calculated values; the pair KCl-$HgCl_2$,

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[1] A. Werner, "Neuere Auschauungen a. d. Gebiete d. anorg. Chemie," p. 28, Braunschweig (1913).

[2] Joannis, *Compt. rend.*, **112**, 338 (1891); Abegg and Riesenfeld, *Z. physik. Chem.*, **40**, 84 (1902).

[3] Zannovich-Tessarin, *Z. physik. Chem.*, **19**, 251 (1896).

[4] Andrews and Ende, *Ibid.*, **17**, 136 (1895).

[5] *Trans. Am. Electrochem. Soc.*, **21**, 137 (1912).

[6] *Ber.*, **43**, 3049 (1910); **45**, 85 (1912).

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

[8] *Atti. r. inst. Veneto*, **74**, 519 (1915); cf. *Chem. Abs.*, 10, 993 (1916).

at 5 mol per cent. of KCl gives a difference of only 7%. If a decrease in conductance is taken to indicate the presence of complexes in the solution, it would seem that they should be present to a considerable extent in the $NaCl\text{-}Na_2SO_4$ mixture, and not altogether lacking in the NaCl-KCl mixture.

Assuming, then, that the alkali metal halides may polymerize or combine with one another in aqueous solution to form higher order compounds, we have in the case of mixed sodium and potassium chloride solutions the following simplest possible types of equilibria:

$$1.\ NaCl + NaCl \rightleftarrows NaCl\text{---}NaCl \begin{array}{l} \nearrow\!\!\!\swarrow Na^+ + (Cl\text{---}NaCl)^- \quad (a) \\ \searrow\!\!\!\nwarrow (NaCl\text{---}Na)^+ + Cl^- \quad (b) \end{array}$$

$$2.\ NaCl + KCl \rightleftarrows NaCl\text{---}KCl \begin{array}{l} \nearrow\!\!\!\swarrow Na^+ + (Cl\text{---}KCl)^- \quad (a) \\ \searrow\!\!\!\nwarrow (NaCl\text{---}K)^+ + Cl^- \quad (b) \end{array}$$

$$3.\ KCl + NaCl \rightleftarrows KCl\text{---}NaCl \begin{array}{l} \nearrow\!\!\!\swarrow K^+ + (Cl\text{---}NaCl)^- \quad (a) \\ \searrow\!\!\!\nwarrow (KCl\text{---}Na)^+ + Cl^- \quad (b) \end{array}$$

$$4.\ KCl + KCl \rightleftarrows KCl\text{---}KCl \begin{array}{l} \nearrow\!\!\!\swarrow K^+ + (Cl\text{---}KCl)^- \quad (a) \\ \searrow\!\!\!\nwarrow (KCl\text{---}K)^+ + Cl^- \quad (b) \end{array}$$

The broken lines indicate secondary valence linkages as suggested by Werner. For the sake of simplicity, compounds which may possibly be formed with more than two molecules of alkali halide have not been represented in the equilibria.

These higher order compounds may ionize, as indicated, in two ways: (*a*) into simple metallic ions and complex negative ions containing one atom of alkali metal and two of chlorine, and (*b*) into simple chloride ions and positive complexes containing one atom of chlorine and two of alkali metal.[1]

It is well known that most ions are hydrated in aqueous solutions. If the equilibria represented above do exist, the complex ions which are

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[1] It is interesting to note in this connection that, as early as 1893, Mejer Wildermann (*Ber.*, **26**, 1773, 2881 (1893)) recognized the possibility of the formation of double molecules in aqueous solutions. He says, "Haben wir z. B. eine ClK-Lösung, und nehmen wir an, dass in der Lösung $(ClK)_2$, ClK, und ihre Ionen ClK_2, Cl (resp. Cl_2K, K) vorhanden sind—etc." These ions are identical with the ones given above in Equation 4. Wildermann discusses the electrical conductivity of salt solutions which do not follow the dilution law applicable to weak acids and bases, and by an extended mathematical treatment shows that such an assumption is in accordance, at least in a qualitative way, with the experimental data.

formed may be regarded as alkali-metal or chloride ions, as the case may be, which carry alkali halide instead of (or in addition to) water.[1]

Both forms of ionization of complex compounds which are represented above are known. Nearly all of the stable double halides, such as K_2PtCl_6, ionize, at least primarily, to give a simple metallic ion and a complex ion containing all of the halogen. This is in accordance with the scheme of ionization represented above under (*a*). On the other hand, certain complex cobalt salts are known[2] which ionize according to the scheme represented above under (*b*).

With our present knowledge, speculations as to just what complexes exist in the solutions are more or less futile, and all that we can say with certainty is that as the concentration of the chloride-chloride solution is increased the equilibrium is shifted in such a way as to decrease the ion fraction of the potassium in the solution. Nevertheless, there is some reason for believing that the observed results may be due to an increasing preponderance of $(Cl{-}{-}{-}{-}KCl)^-$ over $(Cl{-}{-}{-}{-}NaCl)^-$, or of $(KCl{-}{-}{-}{-}K)^+$ over $(NaCl{-}{-}{-}{-}K)^+$, etc., with increasing total salt concentration of the solution, or to the presence of complexes of the type $[Na{-}{-}{-}{-}(ClK)_n]^+$, where n is greater than 1; the formation of such complexes would tend to remove potassium faster than sodium ions, but the final result would, of course, be dependent upon the relative stability of complexes of this composition and of the corresponding complexes containing potassium as the central atom, $[K{-}{-}{-}{-}(ClNa)_n]^+$, as well as upon the existence of different values of n in the two complexes. The sodium ion is more highly hydrated in aqueous solution than the potassium ion,[3] and we should therefore expect the sodium ion to combine with more alkali halide. Moreover, it has been pointed out by G. H. Hansen[4] that the elements with the lowest atomic volumes are the ones which form the most stable complexes. Fritz Ephraim[5] has studied this principle in the case of many of the hexammines of bivalent metals, and he finds that their stabilities increase with decreasing atomic volumes of the central elements. Since the atomic volume of sodium is 23.7 while that of potassium is 45.5 we should expect the complex containing the sodium as the central atom to be the more stable. The formation by the sodium ion of more stable complexes, $[Na{-}{-}{-}{-}(ClK)_n]^+$, especially if connected with the presence in these complexes of more molecules of alkali halide than are contained in the corresponding potassium ion complexes, $[K{-}{-}{-}{-}(ClNa)_m]^+$, would lead us, in the case of equivalent chloride-chloride mixtures, to expect that an in-

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[1] Cf. E. W. Washburn, *Trans. Am. Electrochem. Soc.*, 21, 137 (1912).

[2] Cf. Werner, "Neuere Auschauungen, etc.," pp. 225–228, 304–309.

[3] Cf. E. W. Washburn, *Technology Quarterly*, 21, 360–449 (1908); also, see G. McP. Smith, This Journal, 37, 722 (1916).

[4] *Z. anorg. Chem.*, 79, 324 (1912).

[5] *Z. physik. Chem.*, 81, 513 (1913).

creasing total salt concentration should lead to a decreasing potassium ion fraction. In any case this is in agreement with the observed facts, but transference experiments would probably throw additional light upon this subject.

In the case of the equivalent chloride-sulfate mixtures similar reasoning may be applied, the only differences being that a still greater variety of complexes, together with a mixed salt yielding intermediate ions, is possible and that the preponderance of any complexes which tend to lower the potassium ion fraction increases at a continually decreasing rate, instead of at a constant rate, as the total concentration of the solution increases.

The sulfate-sulfate mixtures may or may not yield complexes. If complexes are formed they are of such a nature that from 0.2 *N* to 2.0 *N* concentration they remove sodium and potassium ions at very nearly the same rate, since in this case the ion fractions of the two metals are practically independent of the total concentration of the solution. However, the interaction of the two salts seems rather to result mainly in a simple metathesis, giving the mixed sodium and potassium sulfate,[1] $NaKSO_4$, in which the two metals ionize at a ratio which is practically constant between 0.2 and 2.0 *N*. The ion fractions of sodium and potassium which exist between these two concentrations (Table XIV) point somewhat strongly to the existence in such solutions of the intermediate ions, $(NaSO_4)^-$ and $(KSO_4)^-$, and to the preponderance and greater stability of the latter.[2]

F. Summary.

1. The value of the mass law expression, C_c, for the equilibrium between sodium and potassium salt solutions and liquid sodium and potassium amalgams is dependent upon the concentration of the amalgams. The effect of changing the concentration is very marked in the case of amalgams containing at equilibrium about 0.09% of potassium.

2. In the case of equivalent mixtures of sodium and potassium chlorides, up to 4.0 *N*, the value of C_c, at 25°, falls lineally with increasing total salt concentration. This decrease in value is in accordance with the data of G. McP. Smith, who worked at 18° with more concentrated amalgams.

3. In the case of equivalent mixtures of potassium chloride and sodium

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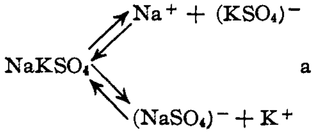
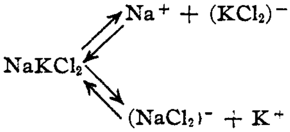
[1] This conclusion is further supported by certain experiments concerning the solubility of K_2SO_4 in Na_2SO_4 solutions; these experiments are described in an Appendix to this paper.

[2] It is of particular interest in this connection to note the similarity of the equilibria,



$$\mathrm{NaKSO_4} \rightleftharpoons \mathrm{Na^+ + (KSO_4)^-}, \quad \mathrm{NaKSO_4} \rightleftharpoons \mathrm{(NaSO_4)^- + K^+}$$

and



$$\mathrm{NaKCl_2} \rightleftharpoons \mathrm{Na^+ + (KCl_2)^-}, \quad \mathrm{NaKCl_2} \rightleftharpoons \mathrm{(NaCl_2)^- + K^+}$$

sulfate, up to 3.0 *N*, the value of C_c, at 25°, falls with increasing salt concentration, but the decrease is not linear.

4. In the case of equivalent mixtures of sodium and potassium sulfates, from 0.2 *N* to 2.0 *N*, the value of C_c, at 25°, is practically independent of the total salt concentration.

5. In the case of equivalent mixtures of sodium and potassium chlorides at a total concentration of 0.20 *N*, the value of C_c decreases with increasing temperature between 15° and 30°. Determinations were made at 15°, 20°, 25° and 30°.

The heat of the reaction,

$$\mathrm{KHg}_m + \mathrm{NaCl} = \mathrm{NaHg}_n + \mathrm{KCl} + (m - n)\mathrm{Hg},$$

is about —3000 calories.

6. These results are interpreted as indicating in Cases 2 and 3 the formation of complexes such as $\mathrm{NaKCl_2}$, etc., in the solutions, and in Case 4 the formation of a mixed sulfate, $\mathrm{NaKSO_4}$, which upon ionization yields the intermediate ions $\mathrm{NaSO_4^-}$ and $\mathrm{KSO_4^-}$, the latter being the more stable.

G. Appendix.

In connection with the effect of concentration changes upon the values of C_c in the case of mixtures containing sodium and potassium sulfates in equivalent proportions, it was pointed out in the previous discussion that the experimental data indicate the existence in such solutions of equilibria of the following nature:

$$\begin{array}{lll}
\mathrm{Na_2SO_4} \rightleftarrows \{ & \mathrm{NaSO_4^-} & \rightleftarrows \mathrm{Na^+} + \mathrm{SO_4^{--}} \\
 & \left.\begin{array}{l}\mathrm{Na^+} \\ \mathrm{K^+}\end{array}\right\} & \rightleftarrows 2\mathrm{NaKSO_4} \\
\mathrm{K_2SO_4} \rightleftarrows \{ & \mathrm{KSO_4^-} & \rightleftarrows \mathrm{K^+} + \mathrm{SO_4^{--}}
\end{array}$$

in which the intermediate ion $\mathrm{KSO_4^-}$ is more stable, and therefore exists at a higher concentration, than the corresponding intermediate ion $\mathrm{NaSO_4^-}$.

If this conclusion is valid, and in case the equilibria which exist in a saturated solution of potassium sulfate in contact with the solid salt are correctly represented by the scheme

$$\underset{\text{(solid)}}{\mathrm{K_2SO_4}} \rightleftarrows \underset{\text{(dissolved)}}{\mathrm{K_2SO_4}} \rightleftarrows \left\{\begin{array}{l}\mathrm{K^+} \\ \mathrm{KSO_4^-} \rightleftarrows \mathrm{K^+} + \mathrm{SO_4^{--}}\end{array}\right. ,$$

then in view of the solubility relationships of sodium and potassium sulfates we should expect the solubility of potassium sulfate in pure water to be less than its solubility in aqueous solutions of sodium sulfate, because the potassium sulfate equilibrium should be displaced to the right, owing to the removal of $\mathrm{K^+}$ and $\mathrm{KSO_4^-}$ ions by $\mathrm{NaSO_4^-}$ and $\mathrm{Na^+}$ ions from the sodium sulfate. Moreover, the solubility of potassium sulfate in aqueous sodium sulfate solutions containing a fixed quantity of water should become greater with increasing concentration of the sodium sulfate. Experiments which have been carried out in order to test this point have shown this to be the case.

In these experiments, determinations were made of the solubility of potassium sulfate in pure water[1] and in sodium sulfate solutions ranging in concentration from 0.25–1.00 *N*. The sodium sulfate solutions were first analyzed by evaporating weighed portions of the solutions, thoroughly drying the residues, and then weighing them, the results being calculated in terms of the weight of sodium sulfate per 100 g. of water. In carrying out the solubility determinations, the liquids were shaken in the thermostat with identical weights of pulverized potassium sulfate, in great excess, for at least 18 hrs. At the end of this time, portions of the clear solutions were drawn off for analysis. The mixtures were then shaken for a further period of five or six hours, after which fresh portions of solution were removed for analysis. The solutions were analyzed by evaporating off the water and weighing the thoroughly dried residues, the results being calculated in terms of the weight of the two salts per 100 g. of water. In each case, this result less the previously determined weight of sodium sulfate per 100 g. of water was assumed to give the weight of potassium sulfate which was dissolved by a quantity of the sodium sulfate solution containing 100 g. of water. Check results after 18 and 24 hrs. were assumed to indicate the complete saturation of the solution with respect to potassium sulfate. The results are given in Table XV, and in Fig. 4 are plotted the solubilities of potassium sulfate in a fixed quantity of water containing sodium sulfate in increasing amounts.

TABLE XV.

Solubility of Potassium Sulfate in Water and in Sodium Sulfate Solutions.
Solutions of Varying Concentration. Temperature 25°.

	Anal. of Na_2SO_4 sol.				Anal. of the Na_2SO_4 sol. sat. with K_2SO_4.			
Normal conc. of Na_2SO_4 at start.	Wt. Na_2SO_4 sol. G.	Wt Na_2SO_4. G.	Wt. Na_2SO_4 per 100 g. of water. G.	Total time of shaking with solid K_2SO_4. Hrs.	Wt. of sat. sol. G.	Wt. K_2SO_4 plus Na_2SO_4. G.	Wt. K_2SO_4 plus Na_2SO_4 per 100 g. of water. G.	Wt. K_2SO_4 per 100 grams of water. G.
0.00	.....	....	....	21	11.480	1.2353	...	12.05
0.00	.....	....	....	26	12.142	1.3060	...	12.05
0.25	11.362	0.1992	1.78	18	12.342	1.5292	14.14	12.36
0.25	10.111	0.1765	1.78	24	12.034	1.4862	14.09	12.31
0.50	10.994	0.3800	3.58	18	11.357	1.5855	16.22	12.64
0.50	10.296	0.3545	3.58	24	12.716	1.7777	16.25	12.67
0.75	11.161	0.5700	5.38	18	13.199	2.0393	18.27	12.90
0.75	10.485	0.5342	5.37	24	15.398	2.3753	18.24	12.87
1.00	11.588	0.7750	7.17	18	14.314	2.4163	20.31	13.13
1.00	11.515	0.7736	7.20	24	14.502	2.4472	20.30	13.12

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[1] In this connection it may be mentioned that J. E. Trevor (*Z. physik. Chem.*, 7, 470 (1891)) has determined the solubility of potassium sulfate in water at 25°, and that his value is practically identical with that given in Table XV.

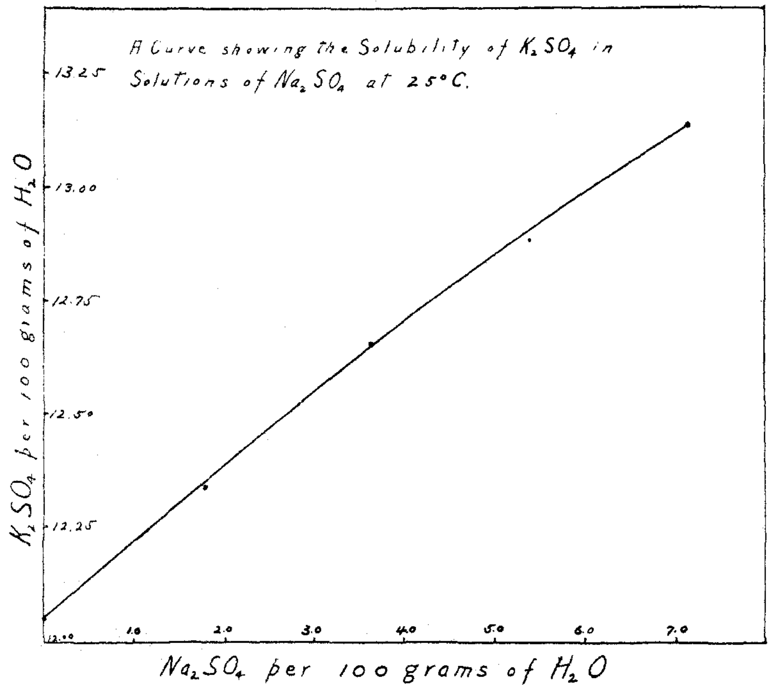

Fig. 4.

This method is open to the objection that sodium sulfate may to some extent have been removed from the solutions, owing to the presence of the solid potassium sulfate. It should be pointed out, however, that the solutions were at the start all far from saturation with respect to sodium sulfate; that if any sodium sulfate was removed it was probably removed in quantities increasing with the sodium sulfate concentration; and that the correction of any error arising from this cause would most likely result in exposing a still more marked rise in solubility of potassium sulfate with increasing amounts of sodium sulfate.

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THE INCONSTANCY OF THE SOLUBILITY PRODUCT. II.

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In an earlier publication,[1] it was shown that the solubility product of thallous chloride decreases in value upon addition of acetic acid to the aqueous solution, and that tetramethyl ammonium iodide behaves in the same fashion when treated with potassium hydroxide. The present

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[1] Hill, THIS JOURNAL, 32, 1186 (1910).