tive force of cells of the type Sn, $Sn(NO_3)_2$ (0.007 to 0.10 N), KNO_3 (0.5 N), KCl (1 N), Hg_2Cl_2 + Hg, and of corresponding cells in which the tin was replaced by lead and the stannous nitrate by lead nitrate. In view of the instability of stannous nitrate and the liquid potentials involved, these results seem far less conclusive than the equilibrium measurements with the perchlorates.

11. Summary.

In this article have been described determinations of the equilibrium between metallic tin and lead and lead perchlorate and stannous perchlorate in dilute perchloric acid solution at 25°. These determinations have given the value *2.98* for the equilibrium ratio of the tin and lead concentrations in this solution, while Sackur found for this ratio the value 3.34 to 3.45 in dilute solutions of the two chlorides.

Assuming that the value 2.98 represents also the ratio $(Sn^{++})/(Pb^{++})$ of the concentrations of the tin ion and lead ion in the perchlorate solution, the specific electrode potential of tin is computed to be *0.0140* volt larger than that of lead.

From electromotive force data existing in the literature the specific electrode potential of lead referred to the molal hydrogen electrode has been recomputed and found to be + *0.132* volt. That of tin then becomes + *0.146* volt. These values are probably accurate within ± 0.002 volt, so far as they are influenced only by experimental errors.

CAMBRIDGE, MASS.

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

HETEROGENEOUS EQUILIBRIA BETWEEN AQUEOUS AND METALLIC SOLUTIONS: THE INTERACTION OF MIXED SALT SOLUTIONS AND LIQUID AMALGAMS.

[FOURTH PAPER.]

A STUDY OF THE IONIZATION RELATIONS OF SODIUM AND STRONTIUM CHLORIDES IN MIXTURES.

BY G. MCP. SMITH AND S. A. BRALEY.[1]

Received May 29, 1917.

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[1] Thesis submitted to the Graduate School of the University of Illinois by S. A. Braley in partial fulfilment of the requirements for the degrees of Doctor of Philosophy.

of the Degree of Dissociation of the Amalgams with Change of Concentration. E. Discussion of the Results. F. Summary.

A. Introduction.

1. Purpose of the Investigation.—This investigation, in which the salts studied belong to different ionic types, is the fourth of the series being carried out in this laboratory with the object of studying by an independent method the ionic relationships which exist in mixed salt solutions. It is based upon the equilibrium found to exist between sodium and strontium salts and the liquid amalgams,[1] and the method used is that originally developed by G. McP. Smith.[2]

2. Principles Relating to the Ionization of Salts in Mixtures.—Calculations from conductance data indicate that in general salts of the same ionic type are ionized to the same extent.[3] From the work of Macgregor, Archibald, McIntosh and McKay[4] the conclusion has been drawn 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 equal to that which it has when alone present in a solution in which its positive or negative ions have a concentration equivalent to that of the common ion in the solution.[5] M. S. Sherrill[6] has studied by conductance methods the ionization of salts without a common ion in mixtures, and he arrives at the same conclusion in this case also. G. M. J. McKay,[7] however, has later shown by transference experiments on solutions of KCl and K_2SO_4 that, in solutions 0.2009 N, with respect to each salt, the specific conductance of the KCl is 2% lower and that of the K_2SO_4 is 5.2% higher than the above principle would predict. But nevertheless he notes that the measured conductance of the solution does not differ by more than 1% from that calculated on the assumption that the principle holds. He, therefore, concludes that the principle of the ionization of salts in mixtures is subject to serious inaccuracy especially in the case of salts of two different types such as studied. C. Sandonnini[8] has given experimental evidence showing that the measured conductivity of a mixture of a uni-univalent and a uni-bivalent salt differs markedly from the value obtained by adding the measured conductivities of the individual salts. G. McP. Smith and T. R. Ball[9] have shown by

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[1] G. McP. Smith, *Am. Chem. J.*, 37, 506 (1907).

[2] THIS JOURNAL, 32, 502 (1910); 35, 39 (1913).

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

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

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

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

[7] *Ibid.*, 33, 308 (1911).

[8] *Atti inst. Veneto*, 74, 519 (1915); *Gazz. chim. ital.*, [2] 46, 205 (1916); *C. A.*, 10, 993 (1916).

[9] THIS JOURNAL, 39, 179 (1917).

the method used in this investigation that in mixed sodium and potassium chloride and sulfate solutions, containing the alkali salts in equivalent quantities, the ion fraction of the potassium is in all cases less than that of the sodium, although from the conductivity data and the principles of ionization as stated above it should be somewhat greater.

It should be noted that most of the principles hitherto arrived at have been based almost exclusively upon conductance data, and that a disagreement exists between the values obtained by the conductivity methods and by other methods.

B. Theoretical.

1. The Aqueous Solution.—When a liquid sodium amalgam is placed in contact with a strontium salt solution, the sodium, owing to its solution tension, tends to pass into the solution, 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, and, in case there are no impurities present, the strontium ions alone are discharged into the amalgam; this action continues until the solution tension of the strontium in the amalgam has assumed a value sufficiently large to prevent the further entrance of strontium from the solution. At this point equilibrium is established. This reversible reaction has been shown to be reversible, so that if a liquid strontium amalgam is placed in contact with a sodium salt solution the opposite reaction will take place, with the final establishment of the same equilibrium. This reversible reaction may be expressed by the equation

$$2\mathrm{NaHg}_n + \mathrm{Sr}^{++} \rightleftarrows \mathrm{SrHg}_m + 2\mathrm{Na}^+ + (2n - m)\mathrm{Hg}.$$

In case a large excess of mercury is present, mercury may be eliminated from the mass-law expression, and the expression may be written as follows:

$$\frac{(\mathrm{SrHg}_m)(\mathrm{Na}^+)^2}{(\mathrm{NaHg}_n)^2(\mathrm{Sr}^{++})} = C_o \qquad (1)$$

But this equation is of no value unless we can determine either the ion-concentration ratio of the metals or the value of C_o.

In a mixed salt solution, however, the concentration of the salts may readily be determined, and the ratio of these concentrations must be some function of the ion-concentration ratio, *i. e.*,

$$\frac{(\mathrm{Na\ Salt})^2}{(\mathrm{Sr\ Salt})} = n\,\frac{(\mathrm{Na}^+)^2}{(\mathrm{Sr}^{++})} \qquad (2)$$

in which n is some unknown quantity, constant or otherwise. But if the salt solution is made infinitely dilute, n of necessity must be equal to unity, since the salts will then be completely ionized. At infinite dilution, then, the salt concentrations can be substituted for the ion concentrations, and we obtain the following expression:

$$\frac{(\text{SrHg}_m)(\text{Na Salt})_o^2}{(\text{NaHg}_n)^2(\text{Sr Salt})_o} = C_o \qquad (3)$$

in which the subscript o indicates infinite dilution of the salts. But at any other concentration c an expression may be written:

$$\frac{(\text{SrHg}_m)(\text{Na Salt})_c^2}{(\text{NaHg}_n)^2(\text{Sr Salt})_c} = C_c \qquad (4)$$

and, since the value of C_c will approach that of C_o as the concentration approaches zero, it follows that the value of C_o may be obtained by plotting the values of C_c determined in the case of a fixed salt-concentration ratio at several different total salt concentrations, against the total salt concentrations, and extrapolating the curve to infinite dilution.

Now, in the case of any given equilibrium mixture, it follows from the preceding equations that

$$\frac{(\text{SrHg}_m)}{(\text{NaHg}_n)^2} = C_o\frac{(\text{Sr}^{++})}{(\text{Na}^+)^2} \qquad (5)$$

and that

$$\frac{(\text{SrHg}_m)}{(\text{NaHg}_n)^2} = C_c\frac{(\text{Sr Salt})_c}{(\text{Na Salt})_c^2}. \qquad (6)$$

That is, in the case of each specific equilibrium mixture, the relationship exists, that

$$C_o\frac{(\text{Sr}^{++})}{(\text{Na}^+)^2} = C_c\frac{(\text{Sr Salt})_c}{(\text{Na Salt})_c^2}, \qquad (7)$$

or

$$\frac{(\text{Sr}^{++})}{(\text{Na}^+)^2} = \frac{C_c(\text{Sr Salt})_c}{C_o(\text{Na Salt})_c^2} = a. \qquad (8)$$

If the concentrations be expressed in terms of mol fractions, then

$$(\text{Sr}^{++}) + (\text{Na}^+) = 1, \text{ and } (\text{Sr}^{++}) = 1 - (\text{Na}^+).$$

Substituting this value of (Sr^{++}) in Equation 8, we obtain:

$$\frac{1-(\text{Na}^+)}{(\text{Na}^+)^2} = a, \qquad (9)$$

whence,

$$(\text{Na}^+) = \frac{-1+\sqrt{1+4a}}{2a}, \qquad (10)$$

in which a is equal to

$$\frac{C_c(\text{Sr Salt})_c}{C_o(\text{Na Salt})_c^2}.$$

Therefore, after having determined the value of C_o, it is possible to determine the ion fractions of the metals in solutions containing the salts at a fixed mol-fraction ratio and also in mixtures in which the salts are present in different mol-fraction ratios, for according to the mass law the same value of C_o will also obtain in the latter case.

2. **The Metallic Solution.**—In the case of the system sodium–potassium, with the use of solutions of fixed composition and concentration, G. McP. Smith and T. R. Ball[1] have found that changes in the concentration of the amalgam lead to changes in the value of C_c. Now if in the expression,

$$\frac{(\text{SrHg}_m)(\text{Na Salt})_c^2}{(\text{NaHg}_n)^2(\text{Sr Salt})_c} = C_c,$$

the concentrations of the salts are kept constant and the value of C_c is found to change with changing total amalgam concentration, then it follows of necessity that the ratio of the amalgam concentrations must also change in proportion. In such case, the conclusion may be drawn that the relative tendency of each metal to react is not proportional to its relative concentration in the amalgam. Since the reactive tendency or solution tension of the amalgam is dependent upon its degree of dissociation into mercury and other free metallic atoms, and since we are now in a position to determine the relative tendencies of the two metals to react, it should, therefore, be possible to determine in a relative manner the effect of concentration changes upon the degree of dissociation of either amalgam.

In any liquid amalgam the following equilibrium exists:

$$\text{MeHg}_x = \text{Me} + x\text{Hg} \qquad (11)$$

for which the mass-law expression may be written

$$\frac{(\text{Me})(\text{Hg})^x}{(\text{MeHg}_x)} = K. \qquad (12)$$

But since the solvent in which this equilibrium exists is mercury, and since in the case of the amalgams under consideration the degrees of dissociation are undoubtedly exceedingly small, the concentration of the mercury in the above expression may be neglected, and it then becomes:

$$\frac{(\text{Me})}{(\text{MeHg}_x)} = k \qquad (13)$$

Upon analysis of the equilibrium amalgam, the total equivalents, y, of Me may be determined, and we have:

$$\text{Me} + \text{MeHg}_x = y \qquad (14)$$

By substituting the value of MeHg_x from Equation 14 into Equation 13, it becomes

$$\frac{\text{Me}_1}{y_1 - \text{Me}_1} = k \qquad (15)$$

at a given concentration, *1*; at a second concentration, *2*, it becomes

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[1] *Loc. cit.*

$$\frac{Me_2}{y_2 - Me_2} = k, \tag{16}$$

or, at a concentration *n*, it becomes

$$\frac{Me_n}{y_n - Me_n} = k. \tag{17}$$

Equating these expressions one to the other and solving for Me_1, we obtain:

$$Me_1 = \frac{y_1}{y_2} Me_2 = \frac{y_1}{y_3} Me_3 = \frac{y_1}{y_n} Me_n, \tag{18}$$

or, if the degree of dissociation in the amalgam at concentration *1* be considered as unity, then at any concentration *n*,

$$Me_n = \frac{y_n}{y_1}. \tag{19}$$

From this equation, with the use of the analytical data obtained in equilibrium experiments carried out with mixed solutions of fixed composition and concentration, but with liquid amalgams of varying total concentration, it is possible to calculate the proportional number of free atoms, existing at equilibrium, in the amalgams.

C. Materials, Apparatus and Method of Experimentation.

1. **Materials.**—The decomposition of the amalgams by the water of the salt solutions is catalyzed by dust particles on the surface of the mercury or by heavy metals contaminating the solution or the amalgam. The catalytic action of the heavy metals is especially pronouned; upon using materials contaminated with traces of aluminum, lead, or other metals, there is invariably a vigorous evolution of hydrogen, and in some cases the amalgams are entirely decomposed in a very short time. When, however, dust particles contaminate the solution or the amalgam, the action is quite different; it is then localized on the surface of the amalgam and may be stopped by removing the spot from which the action comes, or in many cases the action will spontaneously cease, owing to the removal of the dust particle from the surface of the amalgam by the gas evolved. On account of the extreme ease with which the decomposition of the amalgams is catalyzed, it is necessary to use only the purest of materials.

(*a*) **Water, Mercury and Sodium Chloride.**—These substances were purified according to methods already described in a preceding paper of this series.[1]

(*b*) **Strontium Chloride.**—A good grade of commercial salt was first recrystallized from hot water containing hydrochloric acid. The mother liquor was removed as far as possible, first by filtration on the suction pump, and later by means of a high-speed electric centrifuge. A second

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

crystallization was made from pure water, and the mother liquor removed as before. After this the crystals were dried for several days over calcium chloride, and the hydrated salt finally placed in tightly stoppered bottles.

Towards the latter part of the work a fresh supply of the commercial salt from a different source was found to be insufficiently purified by this treatment. The cause of this was not investigated, but a fresh supply of the pure salt was obtained by converting high-grade strontium carbonate into the chloride, and subjecting this to the treatment outlined above.

(*c*) **Amalgams.**—The amalgams were prepared by electrolysis as described by G. McP. Smith and H. C. Bennett.[1] The liquid stock amalgams were not made to conform to any particular concentration, but in most cases they were made rather concentrated; in all cases they were analyzed and diluted with mercury before using.

2. **Apparatus.**—A description of the apparatus used in this investigation will be found in the paper[2] by G. McP. Smith and T. R. Ball, already referred to; no changes were found to be necessary.

3. **Method of Experimentation.** (*a*) **Solutions.**—Separate solutions of sodium chloride and strontium chloride were made up, each equal in concentration to the total concentration desired for the mixed salt solution. Then by mixing these two solutions in the proper volume proportions, it was possible to prepare solutions having the same total concentration and any salt-concentration ratio desired.

For the sodium-chloride solution, the dry salt was weighed out in the calculated quantity, dissolved in water, transferred quantitatively to a volumetric flask, and diluted to the mark at 25°.

For the strontium chloride solution, the hydrated salt was weighed out in sufficient quantity to give a solution slightly more concentrated than that desired. This amount was dissolved in water, diluted to a convenient volume, and the normality determined by the Volhard volumetric method for chlorine.[3] This solution was then accurately diluted to the normality desired.

(*b*) **Equilibrium.**—As it was desirable in each run to start with amalgams having as nearly as possible the same equivalent concentration, the analyzed stock amalgams were in each run diluted with mercury to the concentration decided upon. The mercury for the dilution was weighed out on a small trip balance, with an accuracy of 0.1–0.2 g. and placed in the reaction flask. Fifty cc. of the mixed salt solution were added, and the whole balanced on the trip balance. A sufficient quantity of the analyzed stock amalgam was then added to furnish altogether about 4.7

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[1] This Journal, **31**, 799 (1909).

[2] *Ibid.*, **39**, 179 (1917).

[3] Treadwell-Hall, "Analytical Chemistry," **2**, 707 (1913).

milli-equivalents of the amalgamated metal. The flask containing the reaction mixture was at once placed in the thermostat, and shaken for fifteen minutes, after which the solution was decanted from the amalgam; a fresh portion of the solution was immediately added, the flask again placed in the thermostat, shaken for fifteen minutes, and the solution again decanted. When dilute solutions were used, the amalgams were treated in this manner with six successive portions of the solution, while in the case of the more concentrated solutions not so many renewals were required to produce the desired equilibrium. After decanting the last portion of the solution, the amalgam was in each case washed and decomposed according to the procedure described in the earlier papers. Each run was made with six separate reaction mixtures, three of which were started with sodium amalgam and three with strontium amalgam.

(*c*) **Treatment of the Decomposition Products.**—The hydrochloric acid solution containing the sodium and strontium from the equilibrium amalgam was in each case quantitatively withdrawn from the mercury in the decomposition flask, evaporated to dryness on the steam bath (to remove the excess of acid), and then analyzed for strontium and sodium. The mercury itself was dried and accurately weighed to 0.1–0.2 g.

(*d*) **Determination of Sodium and Strontium.**—Preliminary studies were made of several methods for the determination of the sodium and strontium in the solution. Owing to the hygroscopic nature of the anhydrous strontium chloride, it was found almost impossible to weigh with convenience and accuracy the mixed chlorides. This fact made it desirable to weigh each of the two metals in some convenient form. The regular method of first precipitating the strontium as carbonate, with subsequent precipitation as sulfate, was excluded because of errors likely to be introduced in driving off large quantities of ammonium salts in the determination of the sodium. The method finally decided upon was the following: The acid-free mixed chloride residue was dissolved in about 50 cc. of water, dilute sulfuric acid was added in slight excess, and then a quantity of alcohol equal to the volume of the solution. This solution was allowed to stand for some hours, usually overnight. At the end of this time it was filtered through a Gooch filter,[1] washed thoroughly with 50% alcohol containing a small amount of sulfuric acid, and finally with pure alcohol. The crucible containing the strontium sulfate was then dried in the electric oven, and finally it was ignited in the electric furnace. For the ignition, the crucible was placed in the cold muffle, and the current turned on and allowed to run for one hour; at the end of

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[1] The Gooch filters were prepared from a very good grade of commercial asbestos, which had been boiled for several hours with two separate portions of strong hydrochloric acid, thoroughly washed with water, mixed into a soup with dilute nitric acid, and preserved in a glass-stoppered bottle.

this time the temperature was about 750°. The Gooch filter used had previously been dried and ignited under the same conditions.[1]

The filtrate from the strontium sulfate was evaporated to a small volume, transferred to a weighed platinum dish, and evaporated to dryness. The sodium sulfate residue was very cautiously heated until sulfur trioxide fumes were no longer given off, and then it was carefully fused.

Preliminary trial analyses of known mixtures proved this method to be capable of giving excellent results.

D. Experimental Data.

The following tables contain the data that have been obtained in this investigation. Unless otherwise stated, the figures in the first column in each table refer to the number of the experiment; the second column indicates the amalgam used at the start; the third, fourth, and fifth columns contain data, in g., obtained in the analysis of the equilibrium amalgam; column six shows the concentration of the amalgam, at equilibrium, in total milli-equivalents of amalgamated metals per 10 g. of mercury, as calculated from the data in columns three, four and five; columns seven and eight give the atomic fractions of the metals in the equilibrium amalgam, as calculated from columns three and four; column nine contains the value of the expression

$$\frac{(\mathrm{SrHg}_m)(\mathrm{NaCl})_c^2}{(\mathrm{NaHg}_n)^2(\mathrm{SrCl_2})_c} = C_c,$$

in which (NaHg_n) and (SrHg_m) are the atomic fractions of the amalgamated metals from columns seven and eight, and (NaCl) and $(\mathrm{SrCl_2})$ are the respective mol fractions in the salt solution.

1. Effect of Varying the Concentration of the Liquid Amalgam.—In the case of the sodium-potassium equilibrium, Smith and Ball have observed that changing the concentration of the liquid amalgam exerts a decided effect upon the value of C_c, and it, therefore, seemed advisable to first investigate this effect in the case of the sodium-strontium equilibrium.

The data for this study will be found in Table I. In this series of experiments, with solutions at a total concentration of 0.2 *N*, the concentration of the original amalgam was decreased by one-half for each successive set of determinations. It was noted that the mean values of C_c obtained in the different sets decrease in direct proportion to the mean values of the amalgam concentration, but that the individual values found for any one initial concentration of amalgam do not check. However, upon plotting the individual values of C_c against the corresponding amalgam con-

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[1] To show the constancy in weight of the Gooch filters, six were prepared and ignited as above. After being weighed they were washed, dried, and re-ignited. The greatest difference in weight found was of a magnitude insufficient to cause an error of 1% in an average determination of the value of C_c.

centrations at equilibrium, a straight line (Fig. 1) was found, showing that the value of C_c is a linear function of the amalgam concentration. Since this is true, it is possible by a simple proportion to correct the individual values of C_c to some definite concentration of amalgam and obtain values suitable for direct comparison. For this reason, column ten has been added to the tables; it contains the values of C_c corrected to some concentration "A," in total milli-equivalents of amalgamated metals per 10 grams of mercury.

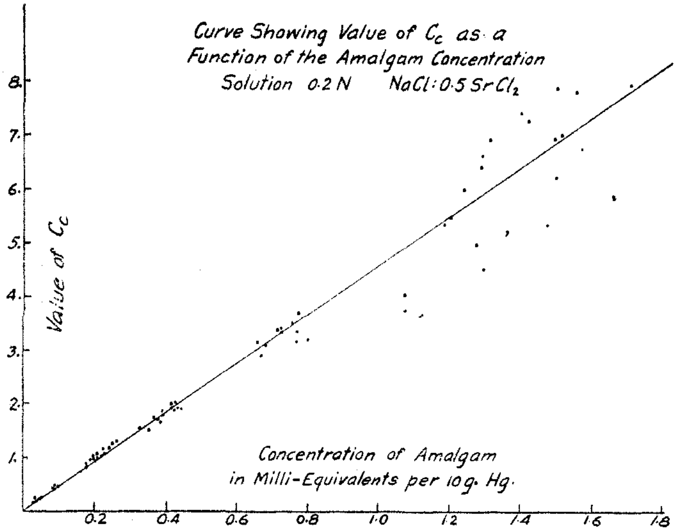

Fig. 1.

TABLE I.

Showing the Effect of Varying the Concentration of the Liquid Amalgam. Total Concentration 0.2 *N*. NaCl : $^1/_2$ $SrCl_2$. Temperature 25°.

No.	Amal. at start.	Eq'm amalgam gave on analysis. Na_2SO_4.	SrSO₄.	Hg.	Amalg. conc. in milli-equivs. per 10 g. Hg.	Atomic fractions of amalgamated metals. Na.	Sr.	C_c.	C_c cor. to *A* milli-equivs. per 10 g. Hg. *A*=1.369.
1	Sr	0.0695	0.2808	28.98	1.399	0.3436	0.6564	7.41	7.25
2	Sr	0.0702	0.3129	29.16	1.499	0.3687	0.6313	6.19	5.69
3	Sr	0.0506	0.2043	20.56	1.426	0.3907	0.6093	5.32	5.11
4	Na	0.0593	0.2197	24.84	1.296	0.4111	0.5889	4.54	4.80
5	Na	0.0700	0.2515	29.23	1.277	0.4016	0.5984	4.95	5.31
6	Na	0.0616	0.1918	26.59	1.116	0.4525	0.5475	3.57	4.38
7	Sr	0.0674	0.3383	27.58	1.715	0.3347	0.6653	7.92	6.32
8	Sr	0.0656	0.3058	26.82	1.585	0.3569	0.6431	6.73	6.99
9	Sr	0.0629	0.3082	25.50	1.663	0.3458	0.6542	5.80	4.78
10	Na	0.0617	0.2015	28.79	1.062	0.4431	0.5569	3.78	4.87
11	Na	0.0537	0.1827	25.66	1.070	0.4317	0.5683	4.06	5.20
12	Sr	0.0583	0.2976	27.00	1.504	0.3363	0.6637	7.84	7.14
13	Sr	0.0521	0.2538	24.50	1.427	0.3469	0.6531	7.25	6.96

TABLE I (*continued*).

No.	Amal. at start.	Eq'm amalgam gave on analysis.			Amalg. conc. in milli-equivs. per 10 g. Hg.	Atomic fractions of amalgamated metals.		C_c.	C_c cor. to A milli-equivs. per 10 g. Hg. A=1.269.
		Na_2SO_4.	$SrSO_4$.	Hg.		Na.	Sr.		
14	Na	0.0543	0.2508	27.00	1.294	0.3591	0.6409	6.64	7.03
15	Na	0.0523	0.2470	26.00	1.314	0.3540	0.6460	6.89	7.18
16	Na	0.0522	0.2268	26.00	1.232	0.3737	0.6263	5.98	6.65
17	Sr	0.0527	0.2623	23.50	1.557	0.3367	0.6633	7.82	6.88
18	Sr	0.0524	0.2480	23.00	1.496	0.3534	0.6466	6.92	6.33
19	Sr	0.0575	0.2735	25.00	1.515	0.3523	0.6477	6.97	6.30
20	Na	0.0568	0.2563	28.00	1.283	0.3643	0.6357	6.40	5.42
21	Na	0.0440	0.1809	21.50	1.204	0.3863	0.6137	5.50	6.25
22	Na	0.0479	0.1943	23.50	1.183	0.3906	0.6094	5.34	6.18
				Mean,	1.369			6.08	6.05
									A=0.753.
23	Sr	0.0737	0.2352	46.39	0.775	0.4477	0.5523	3.67	3.57
24	Sr	0.0805	0.2482	50.14	0.757	0.4561	0.5439	3.49	3.47
25	Sr	0.0727	0.2110	50.34	0.659	0.4712	0.5288	3.18	3.63
26	Na	0.0761	0.2155	50.12	0.682	0.4726	0.5274	3.15	3.49
27	Na	0.0794	0.2341	50.60	0.724	0.4672	0.5328	3.33	3.46
28	Na	0.0740	0.2174	50.19	0.678	0.4660	0.5340	3.35	3.72
29	Sr	0.0875[1]	0.2520	51.70	(0.768)	0.4731	0.5269	(3.14)	(3.08)
30	Sr	0.0815	0.2448	49.50	0.772	0.4626	0.5374	3.35	3.27
31	Sr	0.0910[1]	0.2695	52.90	(0.801)	0.4734	0.5266	(3.21)	(2.98)
32	Na	0.0849	0.2566	54.90	0.727	0.4613	0.5387	3.38	3.50
33	Na	0.0800	0.2388	52.00	0.717	0.4641	0.5359	3.32	3.49
34	Na	0.0652	0.1697	44.00	(0.669)	0.4986	0.5014	(2.71)	(3.05)
				Mean,	0.721			3.36	3.51
									A=0.390.
35	Sr	0.1214	0.2520	102.0	0.436	0.5562	0.4438	1.91	1.79
36	Sr	0.1242	0.2540	102.0	0.444	0.5605	0.4395	1.87	1.64
37	Sr	0.1190	0.2408	102.0	0.426	0.5573	0.4427	1.86	1.70
38	Na	0.1167	0.2115	102.0	0.387	0.5878	0.4122	1.59	1.61
39	Na	0.1116	0.2128	102.0	0.380	0.5756	0.4244	1.71	1.76
40	Na	0.1124	0.2155	101.6	0.368	0.5743	0.4257	1.74	1.84
41	Sr	0.1150	0.2446	101.0	0.424	0.5486	0.4514	2.00	1.84
42	Sr	0.1170	0.2371	101.8	0.417	0.5598	0.4402	1.88	1.76
43	Sr	0.1083	0.2260	95.5	0.419	0.5536	0.4464	1.94	1.81
44	Na	0.0985	0.1745	101.5	0.324	0.5932	0.4068	1.54	1.85
45	Na	0.1079	0.1914	102.5	0.351	0.5972	0.4028	1.51	1.68
46	Na	0.1140	0.2293	105.0	0.390	0.5627	0.4373	1.85	1.85
				Mean,	0.394			1.78	1.76
									A=0.225.
47	Sr	0.1442	0.1903	194.0	0.217	0.6621	0.3379	1.03	1.07
48	Sr	0.1560	0.2160	217.0	0.209	0.6511	0.3489	1.12	1.23
49	Sr	0.1442	0.1909	202.0	0.203	0.6614	0.3386	1.04	1.15
50	Na	0.1399	0.1794	199.5	0.197	0.6685	0.3315	0.991	1.13

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[1] Sodium sulfate slightly contaminated.

TABLE I (*continued*).

No.	Amal. at start.	Eq'm amalgam gave on analysis.			Amalg. conc. in milli-equivs. per 10 g. Hg.	Atomic fractions of amalgamated metals.			C_c cor. to *A* milli-equivs. per 10 g. Hg.
		Na_2SO_4.	$SrSO_4$.	Hg.		Na.	Sr.	C_c.	*A* = 0.225.
51	Na	0.1352	0.1678	199.5	0.187	0.6756	0.3244	0.950	1.14
52	Na	0.1279	0.1556	182.5	0.197	0.6663	0.3337	1.00	1.14
53	Sr	0.1333	0.2162	199.0	0.226	0.6478	0.3522	1.12	1.11
54	Sr	0.1644	0.2431	207.0	0.240	0.6371	0.3629	1.19	1.11
55	Sr	0.1540	0.2187	202.5	0.224	0.6455	0.3545	1.14	1.14
56	Na	0.1264	0.1432	193.0	0.173	0.6953	0.3047	0.842	1.09
57	Na	0.1298	0.1541	198.0	0.177	0.6854	0.3146	0.895	1.14
58	Na	0.1175	0.1278	194.5	0.157	0.7149	0.2851	0.745	1.07
59	Sr	0.1665	0.2486	202.5	0.249	0.6339	0.3661	1.22	1.10
60	Sr	0.1666	0.2553	204.0	0.251	0.6279	0.3721	1.26	1.13
61	Sr	0.1573	0.2215	206.0	0.224	0.6474	0.3526	1.12	1.12
62	Na	0.1430	0.1870	204.0	0.199	0.6635	0.3365	1.02	1.15
63	Na	0.1290	0.1514	202.0	0.173	0.6841	0.3159	0.902	1.17
64	Na	0.1308	0.1613	193.0	0.186	0.6772	0.3228	0.941	1.14
				Mean,	0.205			1.01	1.14
									A = 0.0935.
65	Sr	0.1537	0.1035	397.0	0.083	0.7936	0.2064	0.438	0.494
66	Sr	0.1649	0.1218	392.5	0.093	0.7779	0.2221	0.490	0.493
67	Sr	0.1769	0.1510	406.0	(0.103)	0.7519	0.2481	(0.586)	(0.529)
68	Na	0.1605	0.1144	393.0	0.089	0.7834	0.2166	0.472	0.495
69	Na	0.1557	0.1035	396.0	0.084	0.7957	0.2043	0.431	0.482
70	Na	0.1557	0.1047	395.5	0.084	0.7937	0.2063	0.438	0.486
				Mean,	0.086			0.454	0.490
									A = 0.043.
71	Sr	0.1893	0.0866	796.5	0.045	0.8498	0.1502	0.278	0.265
72	Sr	0.1985	0.0926	793.5	0.048	0.8473	0.1527	0.284	0.255
73	Sr	0.1925	0.0826	804.0	0.045	0.8576	0.1424	0.258	0.247
74	Na	0.1535	0.0534	811.0	0.034	0.8795	0.1205	0.208	0.264
75	Na	0.1402	0.0489	802.0	0.031	0.8812	0.1188	0.205	0.280
76	Na	0.1376	0.0458	797.5	0.030	0.8861	0.1139	0.194	0.274
				Mean.	0.039			0.238	0.263

Smith and Ball have also found that when highly concentrated sodium and potassium amalgams are used the values of C_c obtained are apt to be non-concordant. In this connection attention should be called to the wide variation in the values of C_c in the first twenty-two experiments in Table I, in which very concentrated sodium and strontium amalgams were used, and in which even the corrected values vary from 7.35 to 4.38; in the succeeding experiments, with more and more dilute amalgams, the values of C_c are much more concordant. This may be seen at a glance, in Fig. 1.

Tables II, III and IV contain data showing the effect of variations in amalgam concentration of the above order, but with solutions of total normality of 0.4, 0.8 and 1.2, respectively. The results for Expts. 19–24 of Table IV are far from concordant, but this will be referred to later in connection with Table XI. While the results vary widely for the different concentrations of the salt solution, they are nevertheless for a given total salt concentration a linear function of the amalgam concentration, as may be seen in Fig. 2, in which the mean (uncorrected) values of C_c are plotted against the mean values of the amalgam concentration. Since these values are all linear functions of the concentration of the amalgam, it, of course,

TABLE II.

Showing the Effect of Varying the Concentration of the Liquid Amalgam.
Total Concentration 0.4 *N*. NaCl : $^1/_2$ $SrCl_2$. Temperature 25°.

No.	Amal. at start.	Eq'm amalgam gave on analysis.			Amal. conc. in milli-equivs. per 10 g. Hg.	Atomic fractions of amalgamated metals.		C_c.	C_c cor. to *A* milli-equivs. per 10 g. Hg.
		Na_2SO_4.	$SrSO_4$.	Hg.		Na.	Sr.		*A* = 0.753.
1	Sr	0.1115	0.2390	50.3	0.830	0.5469	0.4531	2.03	1.79
2	Sr	0.1115	0.2402	50.0	0.837	0.5455	0.4545	2.04	1.75
3	Sr	0.1115	0.2395	49.7	0.843	0.5463	0.4537	2.03	1.77
4	Na	0.1256	0.2763	51.0	0.853	0.5403	0.4597	2.10	1.68
5	Na	0.1190	0.2525	50.0	0.885	0.5496	0.4504	1.99	1.65
6	Na	0.1236	0.2770	50.5	0.942	0.5359	0.4641	2.16	1.68
				Mean,	0.865			2.06	1.72
									A = 0.390.
7	Sr	0.1471	0.1755	100.5	0.396	0.6845	0.3155	0.900	0.886
8	Sr	0.1526	0.1955	100.0	0.428	0.6688	0.3312	0.990	0.902
9	Sr	0.1479	0.1802	100.5	0.404	0.6776	0.3224	0.938	0.905
10	Na	0.1774	0.1774	101.5	0.396	0.6833	0.3167	0.909	0.895
11	Na	0.1435	0.1695	100.5	0.385	0.6865	0.3135	0.889	0.901
12	Na	0.1410	0.1789	98.2	0.384	0.6896	0.3104	0.872	0.886
				Mean,	0.399			0.916	0.896
									A = 0.225.
13	Sr	0.2119	0.1814	200.0	0.248	0.7512	0.2488	0.589	0.534
14	Sr	0.2151	0.1893	202.1	0.252	0.7461	0.2539	0.610	0.545
15	Sr	0.2077	0.1807	198.8	0.246	0.7482	0.2518	0.601	0.549
16	Na	0.1887	0.1432	199.7	0.211	0.7731	0.2269	0.506	0.539
17	Na	0.1890	0.1431	200.4	0.206	0.7734	0.2266	0.506	0.554
18	Na	0.1870	0.1417	200.0	0.209	0.7735	0.2265	0.506	0.545
				Mean,	0.228			0.553	0.546
									A = 0.0935.
19	Sr	0.2226	0.0980	400.0	0.0950	0.8546	0.1454	0.266	0.237
20	Sr	0.2091	0.0872	400.0	(0.0937)	0.8739	0.1261	(0.221)	(0.221)
21	Sr	0.2152	0.1005	398.0	0.1040	0.8471	0.1529	0.285	0.257
22	Na	0.1593	0.0558	377.0	0.0756	0.8811	0.1189	0.205	0.253
23	Na	0.1840	0.0776	381.5	0.0900	0.8599	0.1401	0.253	0.258
24	Na	0.2065	0.0915	393.0	0.0995	0.8533	0.1467	0.269	0.252
				Mean,	0.0928			0.256	0.251

TABLE III.

Showing the Effect of Varying the Concentration of the Liquid Amalgam.
Total Concentration 0.8 *N*. NaCl : $^1/_2$ $SrCl_2$. Temperature 25°.

No.	Amal. at start.	Eq'm amalgam gave on analysis			Amal. conc. in milli-equivs. per 10 g. Hg.	Atomic fractions of amalgamated metals.		C_c.	C_c cor. to *A* milli-equivs. per 10 g. Hg.
		Na_2SO_4.	$SrSO_4$.	Hg.		Na.	Sr.		*A* = 0.753.
1	Sr	0.1520	0.1900	50.0	0.842	0.6741	0.3259	0.958	0.857
2	Sr	0.1527	0.1910	49.0	0.827	0.6739	0.3261	0.959	0.828
3	Sr	....	....	...	Lost	....	....	...	...
4	Na	0.1486	0.1715	51.0	0.777	0.6914	0.3086	0.862	0.836
5	Na	0.1365	0.1610	47.0	0.783	0.6873	0.3127	0.885	0.850
6	Na	0.1436	0.1685	52.0	(0.742)	0.6879	0.3121	(0.885)	(0.898)
				Mean,	0.807			0.916	0.843
									A = 0.390.
7	Sr	0.1843	0.1359	100.0	0.408	0.7782	0.2218	0.489	0.468
8	Sr	0.1935	0.1545	102.5	0.430	0.7642	0.2358	0.539	0.489
9	Sr	0.1855	0.1315	100.0	0.404	0.7848	0.2152	0.467	0.450
10	Na	0.1751	0.1150	100.0	0.372	0.7975	0.2025	0.425	0.446
11	Na	0.1700	0.1137	100.5	0.361	0.7945	0.2055	0.435	0.469
12	Na	0.1741	0.1149	99.7	0.371	0.7969	0.2031	0.427	0.449
				Mean,	0.391			0.463	0.462
									A = 0.225.
13	Sr	0.2270	0.1060	198.4	0.219	0.8471	0.1529	0.285	0.292
14	Sr	0.2315	0.1063	200.5	0.220	0.8492	0.1508	0.279	0.285
15	Sr	0.2292	0.1078	200.3	0.220	0.8461	0.1539	0.287	0.294
16	Na	0.2247	0.1055	200.0	0.206	0.8467	0.1533	0.285	0.298
17	Na	0.2288	0.1073	200.0	0.220	0.8465	0.1535	0.286	0.293
18	Na	0.2288	0.1100	200.2	0.220	0.8434	0.1566	0.293	0.299
19	Sr	0.2290	0.1012	200.0	0.216	0.8540	0.1460	0.268	0.288
20	Sr	0.2301	0.1003	200.4	0.216	0.8558	0.1442	0.263	0.274
21	Sr	0.2278	0.1000	200.3	0.215	0.8548	0.1452	0.266	0.279
22	Na	0.2288	0.1057	196.4	0.223	0.8485	0.1515	0.281	0.284
23	Na	0.2289	0.1064	196.4	0.223	0.8477	0.1523	0.283	0.285
24	Na	0.2340	0.0994	196.4	(0.224)	0.8594	0.1406	(0.256)	(0.257)
25	Sr	0.2313	0.1042	201.0	0.219	0.8542	0.1458	0.267	0.274
26	Sr	0.2330	0.1027	199.5	0.221	0.8540	0.1460	0.268	0.273
27	Sr	0.2263	0.1005	200.1	0.214	0.8535	0.1465	0.269	0.282
28	Na	0.2342	0.1022	200.8	0.220	0.8559	0.1441	0.263	0.269
29	Na	0.2248	0.1112	201.5	(0.217)	0.8398	0.1602	(0.304)	(0.314)
30	Na	0.2326	0.0985	201.0	0.217	0.8593	0.1407	0.256	0.263
				Mean,	0.218			0.275	0.283
									A = 0.0935
31	Sr	0.2335	0.0800	398.0	0.1045	0.8832	0.1168	0.200	0.178
32	Sr	0.2425	0.0810	401.0	0.1071	0.8856	0.1144	0.195	0.169
33	Sr	0.2455	0.0660	402.6	0.1073	0.9059	0.0941	0.153	0.137
34	Na	0.2316	0.0635	401.0	0.0985	0.9041	0.0959	0.157	0.148
35	Na	0.2325	0.0610	402.0	0.0979	0.9079	0.0921	0.149	0.142
36	Na	0.1803	0.0350	392.7	0.0743	0.9300	0.0700	0.108	0.136
				Mean,	0.0983			0.160	0.151

TABLE IV

Showing the Effect of Varying the Concentration of the Liquid Amalgam.

Total Concentration 1.2 *N*. NaCl : $^1/_2$ $SrCl_2$. Temperature 25°.

No.	Amal. at start.	Eq'm amalgam gave on analysis.			Amal. conc. in milli-equivs. per 10 g. Hg.	Atomic fractions of amalgamated metals.		C_c.	C_c cor. to *A* milli-equivs. per 10 g. Hg.
		Na_2SO_4.	$SrSO_4$.	Hg.		Na.	Sr.		*A*=0.753.
1	Sr	0.1765	0.1740	48.7	0.899	0.7241	0.2759	0.703	0.589
2	Sr	0.1695	0.1612	48.1	0.861	0.7311	0.2689	0.675	0.590
3	Sr	0.1735	0.1700	47.3	0.908	0.7252	0.2748	0.698	0.579
4	Na	0.1706	0.1545	50.3	0.812	0.7413	0.2587	0.629	0.583
5	Na	0.1710	0.1505	50.3	0.805	0.7462	0.2538	0.609	0.570
6	Na	0.1696	0.1560	49.5	0.826	0.7378	0.2622	0.644	0.587
				Mean,	0.852			0.660	0.583
									A=0.390.
7	Sr	0.2190	0.1155	100.0	0.434	0.8306	0.1694	0.328	0.295
8	Sr	0.2150	0.1195	100.0	0.433	0.8230	0.1770	0.349	0.314
9	Sr	0.2165	0.1140	100.7	0.426	0.8308	0.1692	0.328	0.300
10	Na	0.2012	0.1075	100.3	0.399	0.8290	0.1710	0.332	0.325
11	Na	0.2035	0.1040	100.7	0.397	0.8352	0.1648	0.315	0.310
12	Na	0.2056	0.1021	100.4	0.400	0.8389	0.1611	0.306	0.298
				Mean,	0.415			0.326	0.307
									A=0.225.
13	Sr	0.2420	0.0825	199.4	0.216	0.8842	0.1158	0.198	0.206
14	Sr	0.2494	0.0845	200.3	0.221	0.8842	0.1158	0.198	0.201
15	Sr	0.2488	0.0837	198.7	0.223	0.8848	0.1152	0.198	0.199
16	Na	0.2440	0.0823	200.2	0.216	0.8847	0.1153	0.198	0.206
17	Na	0.2540	0.0819	200.7	0.223	0.8891	0.1109	0.188	0.190
18	Na	0.2500	0.0825	200.5	0.215	0.8892	0.1108	0.188	0.196
				Mean,	0.219			0.195	0.200
									A=0.0935.
19	Sr	0.2440	0.0755	401.8	0.1060	0.8932	0.1068	0.196	0.173
20	Sr	0.2265[1]	0.0647	398.3	(0.0962)	0.9080	0.0920	(0.149)	(0.145)
21	Sr	0.2400	0.0665	402.0	0.1020	0.9032	0.0968	0.159	0.145
22	Na	0.2373	0.0536	401.0	0.0978	0.9221	0.0779	0.122	0.117
23	Na	0.2320	0.0435	400.5	0.0933	0.9323	0.0677	0.104	0.104
24	Na	0.2416	0.0415	401.5	0.0959	0.9376	0.0624	0.0949	0.0946
				Mean,	0.0990			0.161	0.127

follows that in the case of a given salt concentration the value of C_c can be corrected to a definite amalgam concentration, by means of the proportion which obtains for that specific salt concentration.

The necessity for this correction arises from the fact that, owing to the variable evolution of hydrogen by the amalgam, the concentration of the latter at equilibrium is not constant, and hence the results would otherwise not be strictly comparable.

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[1] Sodium sulfate spattered.

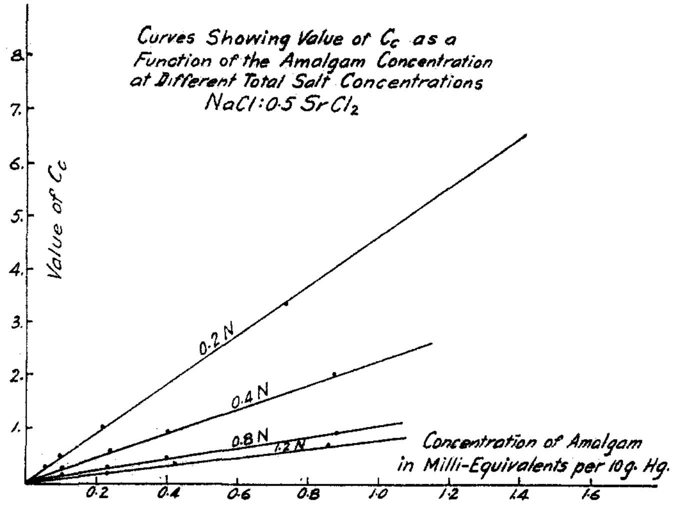

Fig. 2.

2. Effect of Increasing the Total Salt Concentration at a Fixed (Equivalent) Salt-concentration Ratio, and at Various Fixed Amalgam Concentrations.—Table V contains the data obtained on increasing the total salt concentration, in stages, from 0.2 to 3.2 *N*, the sodium and strontium chlorides being present in all cases in equivalent quantities. While the mean values of C_c found in these series of experiments, corrected to 0.225 milli-equivalents per 10 g. of mercury, vary all the way from 1.14 to 0.158, they nevertheless bear a regular relationship to the total salt concentra-

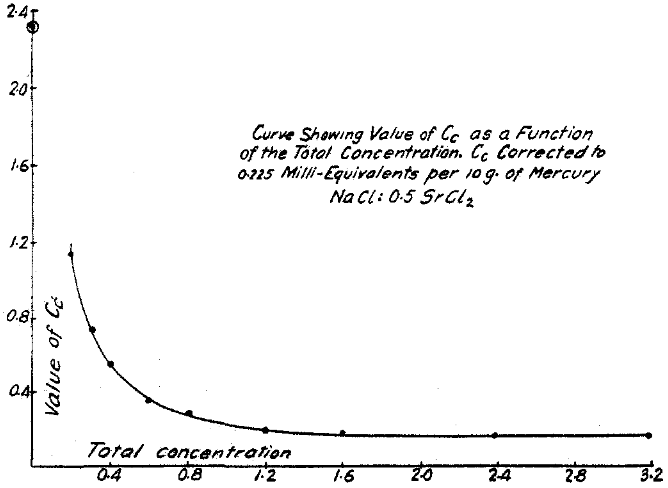

Fig. 3.

tions, as may be seen in Fig. 3; from 0.2 N up to about 1.2 N the value of C_c varies inversely as the total salt concentration, and between these limits the curve is an equilateral hyperbola. If, therefore, instead of plotting the values of C_c and of the total concentration, the logarithmic values are plotted, the logarithm of C_c is approximately a linear function of the logarithm of the total concentration; this is shown by Curve 3 of Fig. 4.

TABLE V.

Showing the Effect of Increasing the Total Salt Concentration at a Fixed (Equivalent) Salt-Concentration Ratio.

NaCl : $^1/_2$ $SrCl_2$. Temperature 25°.

No.	Amal. at start.	Eq'm amalgam gave on analysis. Na_2SO_4.	$SrSO_4$.	Hg.	Amal. conc. in milli-equivs. per 10 g. Hg.	Atomic fractions of amalgamated metals. Na.	Sr.	C_c.	C_c cor. to 0.225 milli-equivs. per 10 g. Hg.
Total Concentration 0.2 N (see Nos. 47–64, Table I), Mean									1.14
Total Concentration 0.3 N.									
1	Sr	0.1699	0.1675	200.4	0.210	0.7240	0.2760	0.704	0.749
2	Sr	0.1715	0.1702	200.3	0.213	0.7223	0.2777	0.711	0.748
3	Sr	0.1737	0.1697	201.1	0.213	0.7229	0.2771	0.715	0.750
4	Na	0.1666	0.1621	195.5	0.210	0.7266	0.2734	0.692	0.737
5	Na	0.1703	0.1656	200.0	0.210	0.7266	0.2734	0.692	0.738
6	Na	0.1714	0.1647	200.3	0.210	0.7291	0.2709	0.681	0.726
				Mean,	0.211			0.699	0.741
Total Concentration 0.4 N (see Nos. 13–18, Table II), Mean									0.546
Total Concentration 0.6 N.									
7	Sr	0.2108	0.1148	199.4	0.212	0.8261	0.1739	0.341	0.362
8	Sr	0.2147	0.1180	201.2	0.216	0.8262	0.1738	0.339	0.354
9	Sr	0.2116	0.1150	200.3	0.211	0.8264	0.1736	0.340	0.362
10	Na	0.2133	0.1175	198.7	0.216	0.8243	0.1757	0.346	0.361
11	Na	0.2100	0.1145	198.7	0.212	0.8283	0.1717	0.334	0.355
12	Na	0.2135	0.1132	198.2	0.213	0.8322	0.1678	0.331	0.350
				Mean,	0.213			0.339	0.357
Total Concentration 0.8 N (see Nos. 13–30, Table III), Mean									0.283
Total Concentration 1.2 N (see Nos. 13–18, Table IV), Mean									0.200
Total Concentration 1.6 N.									
13	Sr	0.2935	0.0958	197.2	0.263	0.8871	0.1129	0.192	0.164
14	Sr	0.2847	0.0903	199.2	0.251	0.8901	0.1099	0.185	0.166
15	Sr	0.2847	0.0944	199.3	0.253	0.8856	0.1144	0.194	0.172
16	Na	0.2548	0.0739	200.2	0.229	0.8986	0.1014	0.166	0.171
17	Na	0.2618	0.0759	200.3	0.225	0.8986	0.1014	0.166	0.166
18	Na	0.2528	0.0720	199.7	0.218	0.9001	0.0999	0.165	0.171
				Mean,	0.240			0.178	0.168

TABLE V (*Continued*)

No.	Amal. at start.	Eq'm amalgam gave on analysis.			Amal. conc. in milli-equivs. per 10 g. Hg.	Atomic fractions of amalgamated metals.		C_c.	C_c cor. to 0.225 milli-equivs. per 10 g. Hg.
		Na_2SO_4.	$SrSO_4$.	Hg.		Na.	Sr.		
Total Concentration 2.4 N.									
19	Sr	0.2722	0.0676	200.2	0.228	0.9124	0.0876	0.141	0.139
20	Sr	0.2571	0.0815	200.5	0.225	0.8910	0.1090	0.183	0.183
21	Sr	0.2725	0.0705	201.2	0.229	0.9090	0.0910	0.147	0.144
22	Na	0.2717	0.0608	200.5	0.224	0.9204	0.0796	0.126	0.127
23	Na	0.2760	0.0558	201.0	0.224	0.9274	0.0726	0.142	0.143
24	Na	0.2598	0.0813	201.3	0.222	0.9001	0.0999	0.165	0.167
				Mean,	0.225			0.151	0.150
Total Concentration 3.2 N.									
25	Sr	0.2902	0.0985	198.7	0.259	0.8841	0.1159	0.198	0.161
26	Sr	0.2991	0.0908	199.2	0.261	0.8950	0.1050	0.175	0.151
27	Sr	0.2970	0.0930	198.5	0.262	0.8924	0.1076	0.181	0.155
28	Na	0.2656	0.0826	201.4	0.227	0.9005	0.0995	0.164	0.163
29	Na	0.2575	0.0879	201.0	(0.228)	0.8835	0.1165	(0.199)	(0.195)[1]
30	Na	0.2628	0.0817	201.7	0.228	0.8926	0.1074	0.180	0.175
31	Sr	0.3260	0.1100	206.0	0.281	0.8986	0.1014	0.166	0.133
32	Sr	0.3312	0.1096	205.0	0.286	0.8863	0.1137	0.193	0.152
33	Sr	0.2908	0.0961	199.5	0.258	0.8868	0.1132	0.192	0.167
34	Na	0.2480	0.0880	200.1	(0.222)	0.8794	0.1206	(0.208)	(0.211)[1]
35	Na	0.2505	0.0841	200.0	(0.225)	0.8868	0.1132	(0.192)	(0.192)[1]
36	Na	0.2650	0.0836	200.2	0.228	0.8992	0.1008	0.167	0.164
				Mean,	0.254			0.163	0.158

With the exception of Expts. 19–24, in which the total salt concentration is very high, the results in Table V are fairly concordant, *i. e.*, the extremes differ in each set by not over 4 or 5%, this being the limit of accuracy with which the values of C_c could be checked. However, this variation is small in comparison with the large variation due to differences in concentration in the amalgams and solutions.

The values in Table V were all determined and corrected for a single specific concentration of amalgam; but data suitable for studying the effect of increasing the salt concentrations at other fixed amalgam concentrations are to be found in the preceding tables, and with this end in view the mean values in all cases are assembled in Table VI. In this table Col. 1 gives the total concentration of the solution; Col. 2 the number of the table in which the individual experiments are tabulated; Col. 3 refers numerically to the experiments; and Col. 4 contains the mean corrected values of C_c.

For each amalgam concentration, the logarithms of these mean values are plotted against the logarithms of the total salt concentrations, in Fig. 4. The resulting curves, which are practicaly parallel, show very conclusively that the effect due to increasing the total salt concentration of the

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[1] Hydrogen evolved quite freely.

solution is entirely independent of that due to varying the concentration of the amalgam. This will be again referred to under the discussion of the ion fractions.

3. Effect of Varying the Concentration Ratio of the Salts at a Fixed Total Concentration.—Tables VII and VIII give the data obtained at total concentrations of 0.3 *N* and 0.6 *N*, respectively, upon varying the ratio of the salts from $^1/_2$ SrCl$_2$: NaCl = 4 : 1 to $^1/_2$ SrCl$_2$: NaCl = 1 : 4. The mean values of C_c in this case do not follow any regular order of change.

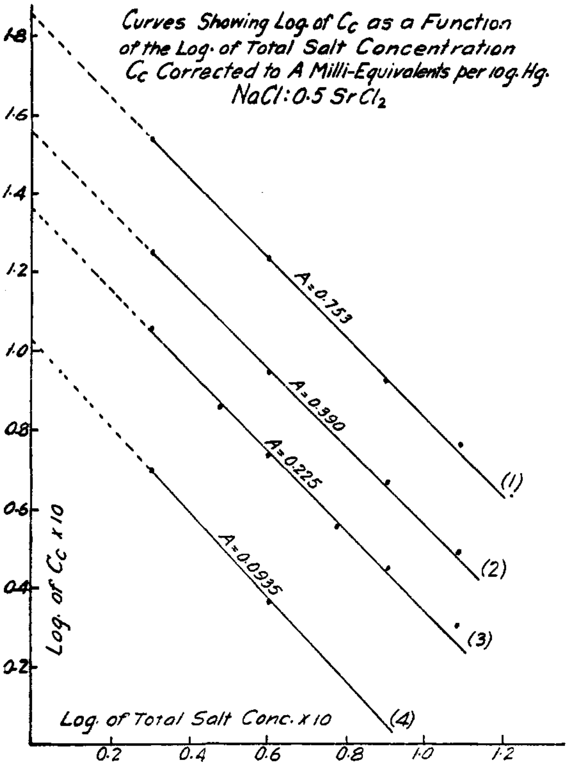

Fig. 4.

TABLE VI.

NaCl : $^1/_2$ SrCl$_2$. Temperature 25°.

Total concentration of solution.	Table No.	Expt. Nos.	Mean values of C_c corrected to *A* milli-equivalents per 10 g. mercury.
			A = 0.753.
0.2 *N*	I	23–34	3.51
0.4 *N*	II	1–6	1.72
0.8 *N*	III	1–6	0.843
1.2 *N*	IV	1–6	0.583
			A = 0.390.
0.2 *N*	I	35–46	1.76
0.4 *N*	II	7–12	0.896
0.8 *N*	III	7–12	0.462
1.2 *N*	IV	7–12	0.307
			A = 0.225.
0.2 *N*	I	47–64	1.14
0.4 *N*	II	13–18	0.546
0.8 *N*	III	13–30	0.283
1.2 *N*	IV	13–18	0.200
			A = 0.0935.
0.2 *N*	I	65–70	0.490
0.4 *N*	II	19–24	0.251
0.8 *N*	III	31–36	0.151
1.2 *N*	IV	19–24	0.127

It should be noted that the normality ratios for Experiments 1–6 of Table VII are 0.071 NaCl to 0.229 $SrCl_2$, instead of 0.06 and 0.24 as was intended. Since the mean values are not regular, this discrepancy was not detected until the ion fractions were calculated, when it was found they did not agree. Upon analysis of some of the remaining solution the

TABLE VII.

Showing the Effect of Varying the Concentration Ratio of the Salts at a Fixed Total Salt Concentration.

Total Concentration 0.3 *N*. Temperature 25°.

No.	Amal. at start.	Eq'm amalgam gave on analysis. Na_2SO_4.			Amal. conc. in milli-equivs. per 10 g. Hg.	Atomic fractions of amalgamated metals. Na.		C_C.	C_C cor. to 0.225 milli-equivs. per 10 g. Hg.
		Na_2SO_4.	$SrSO_4$.	Hg.		Na.	Sr.		
NaCl = 0.071 N, $SrCl_2$ = 0.229 N.									
1	Sr	0.0860	0.2760	200.8	0.210	0.4462	0.5538	0.668	0.716
2	Sr	0.0885	0.2973	202.4	0.220	0.4293	0.5707	0.744	0.760
3	Sr	0.0855	0.2806	201.0	0.212	0.4407	0.5593	0.692	0.734
4	Na	0.0824	0.2634	200.5	0.201	0.4471	0.5529	0.664	0.744
5	Na	0.0840	0.2613	200.4	0.201	0.4539	0.5461	0.637	0.713
6	Na	0.0818	0.2475	200.4	0.192	0.4608	0.5392	0.610	0.715
				Mean,	0.206			0.669	0.730
NaCl = 0.10 N, $SrCl_2$ = 0.20 N.									
7	Sr	0.1195	0.2535	200.1	0.210	0.5705	0.4295	0.660	0.706
8	Sr	0.1147	0.2212	197.5	0.204	0.5729	0.4271	0.651	0.719
9	Sr	0.1164	0.2288	200.0	0.207	0.5681	0.4319	0.669	0.729
10	Na	0.1127	0.2117	200.0	0.195	0.5792	0.4208	0.627	0.725
11	Na	0.1145	0.2129	200.0	0.197	0.5819	0.4181	0.617	0.708
12	Na	0.1130	0.2147	200.8	0.196	0.5764	0.4236	0.638	0.733
				Mean,	0.202			0.644	0.720
NaCl = 0.15 N, $SrCl_2$ = 0.15 N (see Nos. 1–6, Table V), Mean									0.741
NaCl = 0.20 N, $SrCl_2$ = 0.10 N.									
13	Sr	0.2235	0.0935	199.4	0.209	0.8608	0.1392	0.601	0.649
14	Sr	0.2117	0.0853	199.8	0.196	0.8653	0.1347	0.576	0.662
15	Sr	0.2200	0.0923	200.3	0.205	0.8605	0.1395	0.603	0.662
16	Na	0.2028	0.0802	200.5	0.186	0.8737	0.1263	0.530	0.640
17	Na	0.2097	0.0838	200.3	0.193	0.8662	0.1338	0.571	0.688
18	Na	0.2127	0.0842	199.3	0.196	0.8674	0.1326	0.564	0.646
				Mean,	0.198			0.574	0.654
NaCl = 0.24 N, $SrCl_2$ = 0.06 N.									
19	Sr	0.2580	0.0585	200.6	0.213	0.9208	0.0792	0.664	0.706
20	Sr	0.2507	0.0530	199.8	0.206	0.9231	0.0769	0.642	0.701
21	Sr	0.2560	0.0560	200.3	0.210	0.9220	0.0780	0.652	0.698
22	Na	0.2523	0.0528	200.0	0.206	0.9253	0.0747	0.620	0.679
23	Na	0.2495	0.0515	200.0	0.204	0.9262	0.0738	0.612	0.677
24	Na	0.2500	0.0510	200.5	0.203	0.9270	0.0730	0.604	0.669
				Mean,	0.207			0.632	0.688

NaCl was found to be 0.0710 and 0.0711 N and the $SrCl_2$ to be 0.2289 and 0.2290 N. Therefore, these values were used.

The first six experiments in Table VII also show a greater variation than usual in the different values of C_c, the range being from 0.713 to 0.760, or a difference of about 7%.

TABLE VIII.

Showing the Effect of Varying the Concentration Ratio of the Salts at a Fixed Total Concentration.

Total Concentration 0.6 N. Temperature 25°.

No.	Amal. at start.	Eq'm amalgam gave on analysis.			Amal. conc. in milli-equivs. per 10 g. Hg.	Atomic fractions of amalgamated metals.		C_c.	C_c cor. to 0.225 milli-equivs. per 10 g. Hg.
		Na_2SO_4.	$SrSO_4$.	Hg.		Na.	Sr.		
NaCl = 0.12 N, $SrCl_2$ = 0.48 N.									
1	Sr	0.0815	0.2190	193.5	0.183	0.4906	0.5094	0.353	0.435
2	Sr	0.0845	0.2318	194.5	0.191	0.4894	0.5106	0.355	0.419
3	Sr	0.0910	0.2470	199.5	0.199	0.4878	0.5122	0.358	0.406
4	Na	0.0833	0.2125	191.5	0.182	0.5034	0.4966	0.326	0.404
5	Na	0.0835	0.2195	201.5	0.177	0.4960	0.5040	0.341	0.435
6	Na	0.0813	0.2125	200.0	0.173	0.4978	0.5022	0.337	0.445
				Mean,	0.184			0.345	0.424
NaCl = 0.20 N, $SrCl_2$ = 0.40 N.									
7	Sr	0.1450	0.1639	200.0	0.191	0.6959	0.3041	0.314	0.369
8	Sr	0.1494	0.1665	200.2	0.196	0.6990	0.3010	0.314	0.362
9	Sr	0.1470	0.1715	195.2	0.202	0.6891	0.3109	0.327	0.365
10	Na	0.1354	0.1427	200.7	0.172	0.7105	0.2895	0.287	0.374
11	Na	0.1335	0.1435	195.5	0.176	0.7065	0.2935	0.294	0.376
12	Na	0.1396	0.1555	200.0	0.183	0.6985	0.3015	0.309	0.380
				Mean,	0.170			0.307	0.371
NaCl = 0.30 N, $SrCl_2$ = 0.30 N (see Nos. 7–12, Table V), Mean									0.357
NaCl = 0.40 N, $SrCl_2$ = 0.20 N.									
13	Sr	0.2575	0.0585	198.3	0.213	0.9186	0.0814	0.369	0.333
14	Sr	0.2585	0.0613	200.0	0.216	0.9160	0.0840	0.319	0.333
15	Sr	0.2620	0.0615	199.8	0.218	0.9175	0.0825	0.314	0.324
16	Na	0.2348	0.0500	200.0	0.193	0.9240	0.0760	0.285	0.333
17	Na	0.2467	0.0545	198.4	0.204	0.9209	0.0791	0.298	0.330
18	Na	0.2457	0.0553	201.2	0.202	0.9200	0.0800	0.303	0.337
				Mean,	0.208			0.305	0.331
NaCl = 0.48N, $SrCl_2$ = 0.12 N.									
19	Sr	0.2300	0.0230	191.0	0.183	0.9622	0.0378	0.291	0.357
20	Sr	0.2730	0.0300	200.0	0.209	0.9593	0.0407	0.314	0.339
21	Sr	0.2717	0.0305	199.6	0.208	0.9584	0.0416	0.322	0.349
22	Na	0.2691	0.0301	200.3	0.206	0.9573	0.0427	0.331	0 362
23	Na	0.2674	0.0305	200.0	0.205	0.9578	0.0422	0.327	0.367
24	Na	0.2606	0.0278	200.3	0.198	0.9605	0.0395	0.304	0.343
				Mean,	0.201			0.315	0.353

4. Effect of Changing the Temperature: Heat of Reaction.—The heat of the reaction,

$$2NaHg_n + SrCl_2 = 2NaCl + SrHg_m + (2n - m)Hg,$$

may be determined from the values of C_c at different temperatures, other conditions remaining constant, by the van't Hoff equation,

$$2.303 \log \frac{C_{c_1}}{C_{c_2}} = \frac{Q}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right],$$

in which C_{c_1} and C_{c_2} are the equilibrium values at the temperatures T_1 and T_2, respectively, R the gas constant in calories, or 1.986, and Q the heat evolved when the substances in the numerator react to form those in the denominator of the mass-law expression, or when the above reaction takes place from right to left.

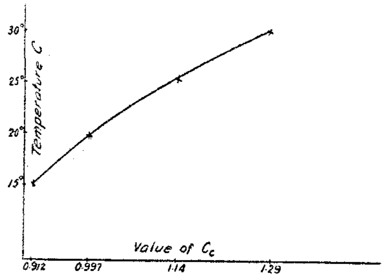

Fig. 5.

The values of C_c as determined at 15, 20, 25 and 30° will be found in Table IX; and the effect of changing the temperature is shown graphically in Fig. 5. By substituting the mean values of C_c into the van't Hoff equation, the heat of the reaction was found to be 2987 cal. between 15 and 20°; 4665 cal. between 20 and 25°; and 4430 cal. between 25 and 30°, the mean value between 15 and 30° being 4024 cal.

The discordance of the results is rather startling, in spite of the fact that a difference of approximately 1% in the determination of the C_c value makes a difference of 400 to 500 cal. in the heat of the reaction as calculated, and that the individual determinations of C_c could not be checked within narrower limits than 4 or 5%. When it is considered, however, that the heat of the reaction, as determined, includes the heats of ionization of the salts, as well as the heats of dissociation of the metallic mercury compounds, and that these may (and probably do) change very materially with the temperature, the results perhaps are not so surprising.[1] Since the "Heat of Reaction" as determined is in reality the algebraic sum of the heats of several (at least five) individual reactions, not to mention the heats of dilution of the amalgams, the values obtained are of significance mainly with respect to the order of magnitude and direction. Since the heat of the reaction is positive, the reaction as a whole is exothermic.

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[1] In the case of the sodium-potassium equilibrium, heats of reaction showing a similar disagreement were obtained by Smith and Ball (*Loc. cit.*).

TABLE IX.

Showing Effect of Changing the Temperature.

Total Concentration 0.2 *N*. NaCl : $^1/_2$ $SrCl_2$.

No.	Amal. at start.	Eq'm amalgam gave on analysis. Na_2SO_4.	SrSO$_4$.	Hg.	Amal. conc. in milli-equivs. per 10 g. Hg.	Atomic fractions of amalgamated metals. Na.	Sr.	C_c.	C_c cor. to 0.225 milli-equivs. per 10 g. Hg.
Temperature 15°.									
1	Sr	0.1442	0.1587	189.2	0.199	0.7015	0.2985	0.811	0.919
2	Sr	0.1511	0.1700	195.0	0.204	0.6968	0.3032	0.835	0.920
3	Sr	0.1465	0.1590	198.0	0.192	0.7043	0.2957	0.797	0.935
4	Na	0.1395	0.1405	189.0	0.184	0.7179	0.2821	0.749	0.915
5	Na	0.1430	0.1428	194.5	0.184	0.7215	0.2785	0.715	0.877
6	Na	0.1121	0.0985	179.4	0.148	0.7466	0.2534	0.610	0.919
				Mean,	0.185.			0.753	0.912
Temperature 20°.									
7	Sr	0.1431	0.1675	190.0	0.201	0.6877	0.3123	0.882	0.988
8	Sr	0.1355	0.1659	189.5	0.196	0.6788	0.3212	0.931	1.07
9	Sr	0.1340	0.1510	191.5	0.184	0.6965	0.3035	0.836	1.02
10	Na	0.1361	0.1495	191.5	0.185	0.7019	0.2981	0.821	0.998
11	Na	0.1500	0.1735	200.5	0.200	0.6909	0.3091	0.865	0.973
12	Na	0.1455	0.1622	201.0	0.190	0.6992	0.3008	0.841	0.997
13	Sr	0.1570	0.1902	195.5	0.219	0.6809	0.3191	0.920	0.945
14	Sr	0.1588	0.2007	200.3	0.221	0.6717	0.3283	0.972	0.991
15	Sr	0.1602	0.2023	202.0	0.221	0.6717	0.3283	0.972	0.991
16	Na	0.1461	0.1613	200.4	0.191	0.7008	0.2992	0.812	0.962
17	Na	0.1445	0.1602	199.5	0.189	0.7000	0.3000	0.820	0.979
18	Na	0.1401	0.1646	200.0	0.188	0.6877	0.3123	0.882	1.05
				Mean,	0.199			0.879	0.997
Temperature 25° (see Nos. 47–64, Table I), Mean									1.14
Temperature 30°									
19	Sr	0.1095	0.1320	194.0	0.154	0.6820	0.3180	0.913	1.34
20	Sr	0.1131	0.1334	200.5	0.152	0.6869	0.3131	0.887	1.31
21	Sr	0.1205	0.1450	198.8	0.168	0.6832	0.3168	0.907	1.24
22	Na	0.1115	0.1208	200.3	0.148	0.6921	0.3079	0.859	1.31
23	Na	0.1116	0.1273	200.5	0.148	0.6941	0.3069	0.851	1.30
24	Na	0.1185	0.1423	201.0	0.161	0.6828	0.3172	0.907	1.25
				Mean,	0.155			0.887	1.29

5. Calculation of the Ion Fractions in Cases 2 and 3.—In the theoretical part, an expression, $(\mathrm{Na}^+) = \dfrac{-1 + \sqrt{1 + 4a}}{2a}$, has been developed, in which $a = \dfrac{C_c(\mathrm{SrCl_2})}{C_o(\mathrm{NaCl})^2}$. From the data now at hand it is possible to calculate the change of ion fraction (*a*) with the change of total concentration of the solution at a fixed salt-concentration ratio, and (*b*) with the change of concentration ratio at a fixed total-salt concentration.

(*a*) **Increasing Salt Concentration at a Fixed Concentration Ratio.**—By the extrapolation of the logarithmic curve (No. 3, Fig. 4), a C_o value of 2.32 is obtained at an amalgam concentration of 0.225 milli-equivalents per 10 g. of mercury. By using this value and the necessary data in Table V, the ion fractions have been calculated over a total concentration range of from 0.2 *N* to 3.2 *N*, and are given in Table X. Col. 1 gives the total normality of the solution; Col. 2 the value of C_o; Col. 3 the value of C_c from Table V; and Cols. 5 and 6 the calculated ion-fraction values.

TABLE X.

$NaCl : {}^1/_2 SrCl_2$. Temperature 25°.

Amalgam Concentration: 0.225 Milli-equivalents per 10 g. of Mercury.

Total normality.	C_o.	C_c.	Calculated ion fractions.	
			Na^+.	Sr^{++}.
0.00	2.32	2.32	0.666	0.333
0.20	2.32	1.14	0.777	0.223
0.30	2.32	0.741	0.835	0.165
0.40	2.32	0.546	0.866	0.134
0.60	2.32	0.357	0.900	0.100
0.80	2.32	0.283	0.920	0.080
1.20	2.32	0.200	0.943	0.057
1.60	2.32	0.168	0.951	0.049
2.40	2.32	0.150	0.955	0.045
3.20	2.32	0.158	0.955	0.045

From these data it will be noted that the sodium-ion fraction increases from 0.777 at a total concentration of 0.2 *N* to 0.951 at 1.6 *N*, and that above the latter concentration it remains practically constant; the strontium-ion fraction decreases correspondingly. The rate of this change may be seen more plainly by referring to Fig. 6, in which the ion fractions are plotted against the total salt concentration. The curve is extrapolated to an ion-fraction ratio of 0.666 sodium to 0.333 strontium, the theoretical ratio at infinite dilution when the salts have equal normality in the solution.

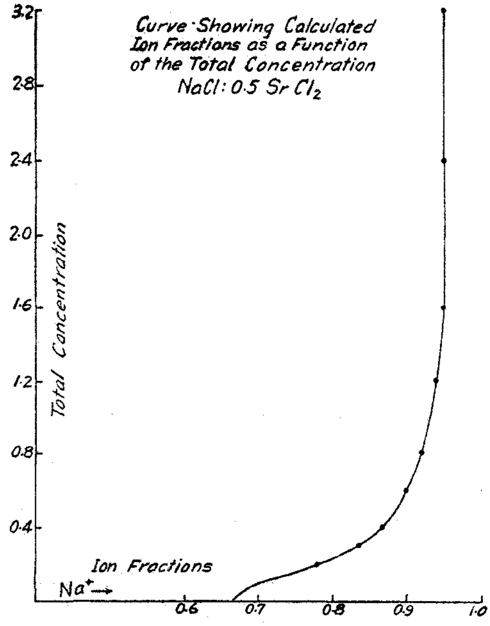

Fig. 6.

From the previous data it has been shown that the value of C_c changes with the concentration of the amalgam, and that upon plotting the logarithmic values of C_c against the logarithmic values of the total salt concentration for each of four different specific amalgam concentrations, a series of four parallel curves is obtained; and the statement was made that the change in value of C_c caused by varying the concentration of the amalgam is independent of the change caused by increasing the total salt concentration at a fixed (equivalent) concentration ratio. If this is true, the ion-fraction values calculated from the four sets of data should be identical. Also, if the principle upon which this investigation is based, namely the mass law, is true, then the ion fractions calculated in all four cases for a given concentration of solution should agree; the constitution of a solution of any specific salt ratio and concentration must of necessity remain constant regardless of the composition of the amalgam with which it is in equilibrium.

On extrapolating Curves 1, 2 and 4, in Fig. 6, C_o values are obtained as follows: When $A = 0.753$, $C_o = 6.92$; when $A = 0.390$, $C_o = 3.51$; and when $A = 0.0935$, $C_o = 1.07$, A being the number of milli-equivalents of amalgamated metals per 10 g. of mercury.

TABLE XI.

					Calculated ion fractions.	
No.	Total normality.	A.	C_o.	C_c.	Na^+.	Sr^{++}.
1	0.2	0.753	6.92	3.51	0.776	0.223
2		0.390	3.51	1.76	0.750	0.250
3		0.225	2.32	1.14	0.777	0.223
4		0.0935	1.07	0.490	0.786	0.214
				Mean,	0.772	0.228
5	0.4	0.753	6.92	1.72	0.861	0.139
6		0.390	3.51	0.896	0.860	0.140
7		0.225	2.32	0.546	0.866	0.134
8		0.0935	1.07	0.251	0.873	0.127
				Mean,	0.865	0.135
9	0.8	0.753	6.92	0.843	0.922	0.078
10		0.390	3.51	0.462	0.898	0.102
11		0.225	2.32	0.283	0.920	0.080
12		0.0935	1.07	0.151	0.913	0.087
				Mean,	0.913	0.087
13	1.2	0.753	6.92	0.583	0.942	0.058
14		0.390	3.51	0.307	0.941	0.059
15		0.225	2.32	0.200	0.943	0.057
16		0.0935	1.07	(0.127)	(0.914)	(0.086)
				Mean,	0.942	0.058

For purposes of comparison, the ion fractions as calculated from the data in Table VI, at total salt concentrations of 0.2, 0.4, 0.8 and 1.2 *N*, and for the amalgam concentrations given above, are tabulated in Table XI; in this table Col. 1 gives the number of the calculation, Col. 2 the total normality of the solution, Col. 3 the value of "A," Cols. 4 and 5 the respective C_o and C_c values, and Cols. 6 and 7 the calculated ion fractions.

The ion-fraction values found are in the case of each individual salt solution very concordant for the different amalgam concentrations, with the single exception of those in No. 16, and the C_c value upon which these ion fractions are based is not reliable, it being the mean value of Expts. 19–24 in Table IV. Attention has already been called to the variation of these values; at this very high total salt concentration the strontium ion exists at a very low concentration in the solution, and since the very low concentration (*i. e.*, large volume) of the amalgam decreased the active mass of the strontium in the amalgam, it is easily seen—especially upon referring to the original data in Table IV—that equilibrium probably was not attained in the case of these experiments.

The concordance of these values, then, may be taken as further evidence that, in so far as the simple ions are concerned, the mass law does hold for concentrated solutions of strong electrolytes, and that the principles upon which this investigation is based are true.

(*b*) **Varying Concentration Ratio of Salts at a Fixed Total Salt Concentration.**—The change of ion fraction with the change of mol fraction at a fixed total-salt concentration may be calculated from the data in Tables VII and VIII. As these determinations were performed at a total amalgam concentration of 0.225 milli-equivalents per 10 g. mercury, the previously determined value of C_o at this amalgam concentration, 2.32, is the value used here. The results of these calculations at 0.3 and 0.6 *N* are given

TABLE XII.

Mol fractions of the salts in the solution.			Calculated ion fractions.	
NaCl.	$SrCl_2$.	C_c.	Na^+.	Sr^{++}.
Total concentration 0.3 N (see Table VII).				
0.3845	0.6155	0.730	0.567	0.431
0.5000	0.5000	0.720	0.697	0.303
0.6666	0.3333	0.741	0.835	0.165
0.8000	0.2000	0.654	0.926	0.074
0.8888	0.1111	0.688	0.966	0.034
Total concentration 0.6 N (see Table VIII).				
0.3333	0.6666	0.424	0.602	0.398
0.5000	0.5000	0.371	0.797	0.203
0.6666	0.3333	0.357	0.900	0.100
0.8000	0.2000	0.331	0.969	0.031
0.8888	0.1111	0.353	0.980	0.020

in Table XII, in which Cols. 1 and 2 represent the mol fractions of the NaCl and the $SrCl_2$ in the solution, Col. 3 the C_c value, and Cols. 4 and 5 the calculated ion fractions of sodium and strontium, respectively.

In Fig. 7, the mol fractions in which the salts are present in the solutions are plotted against the corresponding ion fractions, and it is apparent that the latter are by no means proportional to the former. If they were proportional these ratios would be identical and the curve would be a straight line cutting the plot diagonally as shown by the broken line. The fact that at a given total salt concentration the ion fractions are not proportional to the mol fractions in the solutions is a point which has been used to prove that the mass law does not hold for concentrated solutions of the strong electrolytes. In this paper an application of the mass law itself shows that the ion fractions are not proportional to the mol fractions in the solutions; that is, *the use of the mass law leads to the very conclusion that has been used against it*, so that it may after all hold for concentrated solutions. If the mass law does hold in such solutions then it follows that in the case of mol-fractional variations at other total salt concentrations, a series of curves should be found which would approach the theoretical straight line as their limit at zero concentration. The two curves already given (Fig. 7), showing the change of ion fraction at total concentrations of 0.6 N and 0.3 N, respectively, seem to point to the correctness of this conclusion. Moreover, upon also plotting in Fig. 7 the mean values of the ion fractions found to be present in equivalent mixtures at total concentrations of 0.2 N, 0.4 N, 0.8 N and 1.2 N, as taken from Table X, all six points are seen to occupy positions in harmony with the same conclusion.

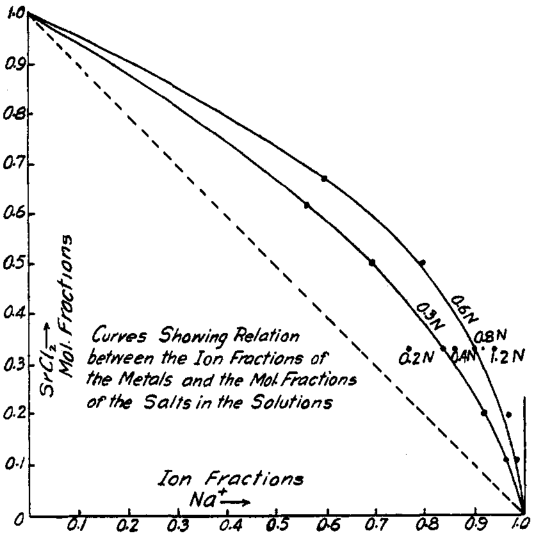

Fig. 7.

6. Calculation of the Change of the Degree of Dissociation of the Amalgams with Change of Concentration.—From the data given in Table I, by means of the formula $Me_n = y_n/y_1$ which was developed in the theoretical part, the change in the degree of dissociation of each amalgam in the mixture with changing concentration may be calculated.

The results of these calculations, derived from mean values only, are given in Table XIII, in which the first column refers numerically to the experiments in Table I from which the calculations are made, Cols. 2 and 3 to the concentration of the amalgam with respect to each metal in terms of milli-equivalents per 10 g. of mercury, Col. 4 to the concentration of the amalgam in total milli-equivalents of metals per 10 g. of mercury, Cols. 5 and 6 to the calculated concentration of the free atoms of each metal in the amalgam at successive dilutions, based upon the assumption that in the case of each metal the concentration of these atoms is equal to unity in the most concentrated amalgam.

Table XIII.

Nos. of the expts. in Table I.	Conc. in milli-equivs. of each metal per 10 g. of mercury.		Conc. in total milli-equivs. of metals per 10 g. of mercury.	Relative decrease in conc. of free atoms with increasing dilution witn mercury.	
	Na.	Sr.		Na.	Sr.
1–22	0.317	1.043	1.360	1.00	1.00
23–34	0.242	0.505	0.747	0.763	0.485
35–46	0.156	0.239	0.395	0.492	0.232
47–64	0.102	0.102	0.204	0.320	0.0974
65–70	0.0562	0.0302	0.0864	0.177	0.0289
71–76	0.0303	0.0105	0.0408	0.0956	0.0101

From these results it is readily seen that the increase of association, in the sense of the equation $Me + xHg = MeHg_x$, upon dilution with mercury is much more pronounced in the case of the strontium amalgam than in that of the sodium amalgam.

E. Discussion of the Results.

This investigation has shown that in equivalent mixtures of sodium and strontium chlorides the ion fraction of the strontium decreases, while the ion fraction of the sodium correspondingly increases, with increasing total salt concentration. This holds true up to about 1.6 *N*, above which the ion fractions remain constant. While we are able by means of the data obtained to calculate the ion fractions of the two metals, these data nevertheless do not enable us to calculate the actual concentrations of the ions in the mixed solution.

The ion-fraction changes above referred to may be due to any one or more of the following causes: (*a*) the existence of intermediate ions; (*b*) the existence of hydrated ions, and (*c*) the existence of complex halide ions.

(*a*) There no longer seems to be a question as to the existence of intermediate ions in solutions of uni-bivalent salts. On this basis strontium chloride would first ionize as follows:

$$SrCl_2 = SrCl^+ + Cl^-, \qquad (1)$$

and the $SrCl^+$ ion would again ionize to give the simple Sr^{++} ion;

$$SrCl^+ = Sr^{++} + Cl^-. \qquad (2)$$

In the case of sodium chloride, only one simple form of ionization is possible.

$$NaCl = Na^+ + Cl^-. \qquad (3)$$

Therefore, upon mixing solutions of these two salts in equivalent quantities, we should expect the common Cl^- ion to lower the concentration of the simple Sr^{++} ion much more rapidly than that of the Na^+ ion.

Concerning the degree of ionization of salts, A. A. Noyes and K. G. Falk[1] have pointed out the great differences which exist in the results, depending upon whether the calculations are made from conductivity data or from freezing-point data. The greatest differences occur in the case of the bivalent-metal halides; for $CaCl_2$ and $MgCl_2$, in solutions of less than normal concentration, the differences range from 3 to 9%, depending upon the concentration. W. D. Harkins and H. M. Paine[2] in their study of the effect of salts on the solubility of other salts give evidence pointing to the existence of the $SrCl^+$ ion; they also make the following statement: "The first step in the ionization of strontium chloride is

$$SrClCl = SrCl^+ + Cl^-,$$

and in very concentrated solutions this should be almost the only form of ionization." In other words, the concentration of the simple Sr^{++} ion is very small in very concentrated solutions of strontium chloride. While the present work gives no evidence of the actual concentrations of the ions in the mixed solution, an exceedingly rough comparison may nevertheless be based upon it. In solutions of $1.6\ N$ or above, it has been shown that the ion fractions are $0.95\ Na^+ : 0.05\ Sr^{++}$, and since, according to conductivity methods, sodium chloride is approximately 70% ionized at $1.6\ N$ concentration, it follows that, on the assumption of the isohydric principle, an approximate Sr^{++} ion concentration of 0.05–$0.06\ N$ exists in an equivalent mixture of sodium and strontium chlorides of the above concentration.[3] This is in good agreement with the conclusions of Harkins and Paine.

(*b*) A second basis upon which the results might be explained is at hand, namely, the existence of hydrated ions in solution.[4] This is in reality a case of complex formation. The ions of sodium and strontium are both known to be highly hydrated in dilute aqueous solution, and the explanation referred to is obviously self evident.

(*c*) Complexes like K_2PtCl_6, K_2HgI_4, $2KCl.MgCl_2.6H_2O$, etc., are,

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[1] *Loc. cit.*

[2] This Journal, 38, 2709 (1916).

[3] Even assuming the NaCl to be completely ionized in this mixture (*i. e.*, Conc. $Na^+ = 0.8\ N$), since $Na^+ : Sr^{++} = 0.95 : 0.05$, the Sr^{++} ion concentration could be at most only $0.084\ N$.

[4] E. W. Washburn, *Tech. Quarterly*, 21, 360 (1908); G. McP. Smith, This Journal, 37, 722 (1915).

of course, commonplace; but H. C. Jones and Nicholas Knight,[1] H. W. Foote and L. H. Levy,[2] K. Sudhaus,[3] C. Sandonnini,[4] F. Rudorff,[5] G. S. Jamieson,[6] and many others have furnished proof of the existence of complexes in the most ordinary salt solutions.

H. C. Jones and K. Ota[7] have shown that the data obtained by conductivity and freezing-point lowering, which they interpret from the standpoint of the existence of complexes in solution, point towards a decrease in relative concentration of such complexes with the dilution of the solution, thus indicating a gradual dissociation of the complexes with dilution into simpler forms. Sandonnini has also noted this behavior; upon plotting his values he obtained a curve without sharp breaks, and, therefore, he concludes that the complex is gradually formed or dissociated with increasing or decreasing concentration. There should, of course, be no sharp breaks in the curve if the complexes present are formed in accordance with the mass law. The data obtained in the present investigation upon changing the mol-fraction ratio of the salts at a fixed total-salt concentration, give further evidence in this direction (Fig. 7). Also the fact that, with increasing dilution, the ion-fraction ratio of the metals in equivalent salt mixtures approaches the theoretical value for infinite dilution (Fig. 6) is in good agreement with this view, since the gradual formation or dissociation of complexes would lead to a gradual change in the value of the ion-fraction ratio.

Even if we were to assume the formation of complexes in order to account for the results obtained, we still have no indication as to exactly what these complexes might be.[8] Complexes such as those referred to are characterized by A. Werner[9] as "Higher Order Compounds," and are often capable of furnishing upon dissociation several different ionic species. If the simplest complex possible in the case under consideration were formed, namely, $SrCl_2.NaCl$, then whether the formula were written $Na(SrCl_3)$ or $Sr(NaCl_3)$ this compound would be capable of giving several different ions in the solution; but since the reaction with which we are concerned deals only with the simple Na^+ and Sr^{++} ions, these alone will be considered. The compound $Na(SrCl_3)$ would primarily give

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[1] *Am. Chem. J.*, 22, 111 (1899).

[2] *Ibid.*, 35, 239 (1906).

[3] *Neues Jahrb. Min. Geol.*, 37, 1–50 (Beil. Bd.); *C. A.*. 8, 1714 (1914).

[4] *Loc. cit.*

[5] *Ber.*, 21, 3048 (1888).

[6] *Am. Chem. J.*, 38, 614 (1907); *Am. J. Sci.*, 43, 67 (1917); *C. A.*, 11, 426 (1917).

[7] *Ibid.*, 22, 11 (1899).

[8] It is of interest to note in this connection that G. S. Jamieson (*C. A.*, 11, 426 (1917)) has obtained from mixed salt solutions crystallized double salts corresponding in composition to the formulas $2CsCl.CaCl_2.2H_2O$ and $5CsCl.2SrCl_2.8H_2O$.

[9] "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," Braunschweig, 1913, p. 28.

Na^+ and $(SrCl_3)^-$ ions, and the mass law would require that with increasing concentration of the solution greater amounts of this complex should be formed and that its ionization should at the same time decrease, that is, that the Sr^{++}-ion concentration in the solution should decrease more rapidly than the Na^+-ion concentration. This explanation also agrees with the experimental data, according to which the Sr^{++}-ion concentration does decrease more rapidly than the Na^+-ion concentration. The second formula $Sr(NaCl_3)$, on the other hand, would give an excess of Sr^{++} ions, and, therefore, it is not in harmony with the experimental data obtained in this investigation.[1]

Mixed salt solutions, or simple ones even of uni-univalent salts for that matter, are undoubtedly very complex as regards their constitution, and all of the phenomena mentioned above probably do take place to a more or less considerable extent.[2] It seems, however, hardly worth while to attempt to draw from the data at hand any specific conclusions in this direction. But it may nevertheless be pointed out in this connection that practically all of the discussions which have been entered upon concerning the application of the mass law to the ionization of strong electrolytes, *e. g.*, of uni-univalent salts such as potassium chloride,[3] have been based upon the simple assumption that the equilibrium in question corresponds more or less closely to $KCl \rightleftarrows K^+ + Cl^-$; or, possibly, to $KCl.(x + y)H_2O \rightleftarrows K^+.(H_2O)_x + Cl^-.(H_2O)_y$; the existence of equilibria such as

$$\begin{tikzcd}
 & KCl.(x + y)KCl \arrow[r, shift left] \arrow[r, leftarrow, shift right] & K^+.(ClK)_x + Cl.^-(KCl)_y & \\
H_2O + KCl \arrow[r, shift left] \arrow[r, leftarrow, shift right] \arrow[ur, shift left] \arrow[ur, leftarrow, shift right] \arrow[dr, shift left] \arrow[dr, leftarrow, shift right] & K^+ + Cl^- & + & \text{etc., etc.} \\
 & KCl.(x + y)H_2O \arrow[r, shift left] \arrow[r, leftarrow, shift right] & Cl^-.(H_2O)_y + K^+.(OH_2)_x \arrow[d, shift right] \arrow[d, leftarrow, shift left] & \\
 & & K(ClK)_x.Cl(H_2O)_y &
\end{tikzcd}$$

has never seriously been taken into consideration.

F. Summary.

1. The value of the "mass-law" expression C_c for the equilibrium between the mixed chloride solutions and the liquid amalgams increases directly with the concentration of the amalgams.

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[1] Nevertheless, the possibility of the existence in the solution of the latter complex in relatively small amount, as compared with the former, is not excluded by the data obtained.

[2] See the discussion in the preceding paper of this series, THIS JOURNAL, 39, 211 (1917).

[3] See, for example, Stuart J. Bates, *Ibid.*, 37, 1421 (1915).

2. With increasing total salt concentration, at a fixed (equivalent) salt-concentration ratio, (*a*) the value of C_c decreases very rapidly up to about 0.8 *N*, after which it decreases more and more slowly until it reaches a limit at 1.6 *N*; (*b*) the ion fraction of the sodium increases with increasing salt concentration up to about 1.6 *N*, where it reaches a limit value of 0.95 Na^+ : 0.05 Sr^{++}.

3. With equivalent mixtures at a total concentration of 0.2 *N*, the value of C_c increases with increase of temperature between 15° and 30°. The heat of the reaction

$$2NaHg_n + SrCl_2 = SrHg_m + 2NaCl + (2n - m)Hg,$$

as determined from the van't Hoff equation, using values of C_c at 15°, 20°, 25° and 30°, is about + 4000 Cal.

4. In solutions of fixed concentration, the ion fractions of the two metals vary in the direction of, but not in proportion to, the mol-fractional variation of the salts in the solutions. The fact that the ion fractions are not proportional to the mol fractions in such solutions of strong electrolytes has been used as an argument that the mass law does not hold in the case of these solutions. In this investigation, however, the use of the mass law has led to the very conclusion that has been used against it.

5. The change in the degree of association of the metals ($Me + xHg \rightleftarrows MeHg_x$) with the dilution of the amalgams with mercury is much more rapid in the case of the strontium amalgam than in the case of the sodium amalgam.

URBANA, ILL.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE NATIONAL CARBON COMPANY.]

THE DECOMPOSITION OF CEROUS OXALATE IN A REDUCING OR INERT ATMOSPHERE AND A NEW PROPERTY OF THE HIGHER OXIDES OF CERIUM.

BY WALLACE S. CHASE.

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General.

In the course of certain investigations in this laboratory some cerous oxide was desired and its preparation was attempted by decomposing cerous oxalate in an atmosphere of hydrogen. While this experiment was unsuccessful from the standpoint of Ce_2O_3 yield, its results were of enough interest to prompt an investigation of the decomposition of this oxalate in the absence of oxygen. The present paper constitutes a brief description of the work done and its results.

An extended review of the literature showed that Mosander[1] claimed

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[1] *J. prakt. Chem.*, 30, 276 (1843).