

other hand, by adding a large excess of sodium chloride initially to the reaction mixture, so that the amount of sodium chloride formed in the reaction was rendered negligible. Under these conditions concordant velocity constants were obtained as may be seen from Expts. 1, 2 and 7.

The experimental part of this work was begun at the Kent Chemical Laboratory of Yale University.

SEATTLE, WASH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]
THE EFFECT UPON THEIR SOLUTION TENSIONS OF DISSOLVING THE ALKALI AND ALKALI EARTH METALS IN MERCURY, AND THE CONSTITUTION OF SUCH SOLUTIONS.

BY GEORGE MCPHAIL SMITH.

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In a discussion of the constitution of liquid amalgams, C. H. Desch¹ makes the following statements: "In simple eutectiferous series, in which the freezing-point curve shows no indication of the formation of compounds, we may safely accept the conclusion arrived at by the three methods described above (*i. e.*, the cryoscopic, vapor-pressure, and electromotive-force methods), that the dissolved metals are monatomic. *In series in which compounds occur, it remains as yet an open question whether the same condition prevails, or whether compounds containing a single atom of the dissolved metal in each molecule, are also present.*"² The only experimental method which gives any indication of a definite answer to this question is that of measuring the velocity of diffusion in liquid metals." He then proceeds to describe a portion of a paper by the writer³ in which this method is developed by the latter by means of M. von Wogau's⁴ experimental measurements of the rate of diffusion of various metals in mercury, and in which it is shown by this method that, in the case of the alkali and alkali earth amalgams, such compounds do actually exist in the mercurial solutions.⁵

In the above-mentioned paper,³ however, another experimental method is also developed, which, although it is at least capable of furnishing confirmatory evidence of the same thing, was in that paper apparently not explained sufficiently in detail. It is with the purpose of furnishing a clearer exposition of the latter method that the present paper is written.

¹ "Text-Books of Physical Chemistry," edited by Sir William Ramsay; "Metallography," by Cecil H. Desch, ed. 1910, p. 333f.

² The italics are the writer's.

³ G. Mc. P. Smith, *Z. anorg. Chem.*, **58**, 381 (1908).

⁴ Max von Wogau, *Ann. Physik*, **23**, 345 (1907).

⁵ The diffusion method as applied to the study of the constitution of metallic solutions has subsequently been placed upon a firm theoretical basis (cf. G. Mc. P. Smith, *THIS JOURNAL*, **36**, 859 (1914)).

When a metal is immersed in a salt solution (in which, if present at all, its ions are limited in concentration), the solution tension of the metal tends to drive some of its ions into the solution, whereat the latter becomes positively charged, and the metal negatively charged. These charges give rise to a force component, which on the one hand tends to prevent the entrance of more positive ions into the solution, and on the other hand seeks to drive the positive ions in the solution back to the metal. One of two things must now take place. Either the solution tension of the metal is exactly compensated by the electrostatic charges, in which case there results an equilibrium; or, as a result of the magnitude of the solution tension, the electrostatic charge attains so high a value, that other positive ions which are contained in the solution are forced out of it and deposited on the metal.

In general, when a metal is immersed in a salt solution of another metal (which may or may not contain its own ions), the ions of the second metal will separate the more readily, the higher their own concentration, the greater the solution tension of the first metal, and the lower the ionic concentration of the first metal. If we designate the electromotive force necessary for the electrolytic separation of the first metal by ϵ , we have,

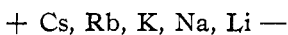
$$\epsilon = \frac{RT}{n} \ln \frac{P}{p},$$

(in which R is the gas constant, T the absolute temperature, P the electrolytic solution tension of the metal, p the osmotic pressure of its ions, and n the valency of its ions), and the separation of the second metal must take place as soon as the osmotic pressure of its ions and the electrostatic pull are able to overcome the electrolytic solution tension of the second metal, *i. e.*, the relation,

$$\epsilon_1 > \epsilon_2, \text{ or } \sqrt[n_1]{\frac{P_1}{p_1}} > \sqrt[n_2]{\frac{P_2}{p_2}},$$

must hold, in which the index 1 refers to the first metal, 2 to the second metal, and n_1 and n_2 are the valencies of the two metals.

The electromotive series of the univalent alkali metals reads:



Disregarding their action upon water, we should expect each metal in the series, beginning at the positive end, to be capable of displacing from aqueous salt solutions any metal which follows it in the series, and, under like conditions, this displacement should take place the more readily, the farther apart the two metals stand in the series. In other words, we should expect, under ordinary conditions, to have the relation

$$\frac{P_+}{p_+} > \frac{P_-}{p_-},$$

and the more electropositive metal should displace the more electro-negative one from its salt solutions.

Now, the relative magnitudes of the above two expressions, on which depends the direction of the displacement, can be affected in two ways, with the possibility of reversing them altogether. First, the values of p_+ and p_- can be changed at will, by regulating the ionic concentrations, and, second, the values of P_+ and P_- can be altered by substituting metallic solutions, or compounds, of the metals, in place of the metals themselves.

To take a concrete example, it appears very probable that finely divided sodium and potassium might be found capable of readily displacing one another from concentrated aqueous salt solutions, were it not for the action of the metals upon the aqueous solvent. On providing, however, for very much lower solution tensions of the metals—by the substitution of liquid amalgams for the free metals—their action upon the water is almost entirely prevented, and the reversible displacement of sodium and potassium from their aqueous salt solutions can be realized without difficulty.

In the experiments to be detailed in this paper, each amalgam of the respective pairs, Na and K, Na and Rb, and Na and Cs, in dilute equimolar mercurial solution, was allowed to act at 24° upon the corresponding one of three equivalent aqueous solutions, containing equimolar quantities of NaCl and KCl, of NaCl and RbCl, and of NaCl and CsCl, respectively; and, as will be seen from the data in Table I, equilibria were attained in all cases.¹

TABLE I.—EQUILIBRIUM DATA AT 24° .²

No.	Amalgam.	Total normal concentration of salt solution.	Quantity of solution taken. Cc.	Quantity of amalgam taken. G.	Equiv. fractions of salts present in the solution.		Atomic fract. of the alkali metals in the amalgam.		Equilibrium constant $\frac{(\text{MeHg}_x)(\text{NaCl})}{(\text{NaHg}_x)(\text{MeCl})}$	Mean value.
					(NaCl).	(MeCl).	(MeHg _x)	(NaHg _x)		
1a	0.167% Na	4.000	50.0	50	0.50	0.50	0.2290	0.7710	0.297	0.31
1b	0.28% K	4.000	50.0	50	0.50	0.50	0.2461	0.7539	0.326	
2a	0.167% Na	4.000	25.0	57	0.50	0.50	0.2635	0.7364	0.358	0.37
2b	0.62% Rb	4.000	25.0	50	0.50	0.50	0.2739	0.7260	0.377	
3a	0.167% Na	4.000	25.0	25	0.50	0.50	0.3244	0.6755	0.480	0.49
3b	0.98% Cs	4.000	25.0	25	0.50	0.50	0.3295	0.6705	0.491	

Now, at equilibrium, we have in the cases of these univalent metals the relationships, $P_{\text{Na}}/p_{\text{Na}} = P_{\text{Me}}/p_{\text{Me}}$; and, since $p_{\text{Na}} = p_{\text{Me}}$ in each

¹ Full details of these experiments have been published elsewhere by the writer (cf. *Z. anorg. Chem.*, 58, 381 (1908); *Z. physik. Chem.*, 73, 424 (1910)).

² The general formula MeHg_x is in this table used to represent either hydrargyride molecules (each containing only one atom of the amalgamated metal), or simply monatomic molecules of Me. In the latter case $x = 0$.

of the equimolal mixed-salt solutions employed in these experiments,¹ it follows that, in each amalgam at equilibrium, $P_{\text{Na}} = P_{\text{Me}}$. If, now, we are justified in the conclusion that, in dilute mercurial solution, the solution tension of a given alkali metal is roughly proportional to its concentration in the metallic solution,² then we are in a position to calculate the relative magnitudes of the solution tensions of these four metals in their dilute equimolal mercurial solutions. We have, at 24° , the relationships:³

$$P_{(\text{Cs})} = \frac{0.6730}{0.3270} P_{(\text{Na})}; \quad P_{(\text{Rb})} = \frac{0.7312}{0.2688} P_{(\text{Na})}; \quad P_{(\text{K})} = \frac{0.7625}{0.2375} P_{(\text{Na})};$$

$$i. e., P_{(\text{Na})} : P_{(\text{Cs})} : P_{(\text{Rb})} : P_{(\text{K})} = 1.00 : 2.06 : 2.72 : 3.21$$

It is thus seen that the solution-tension magnitudes of the free metals—which decrease in the order, Cs, Rb, K, Na—are, in the case of the first three metals, reversed upon dissolving the metals in an excess of mercury; they then decrease in the order K, Rb, Cs, Na. The same is true of the alkali earth metals: while the solution tensions of the free metals decrease in the order Ba, Sr, Ca, those of the metals in equimolal liquid mercurial solution decrease in the order Ca, Sr, Ba. It may be added that lithium, the least electropositive of the free alkali metals, becomes, in mercurial solution, the most electropositive of them all.⁴

Taken in connection with the contents of our introductory paragraph, these facts are regarded by the writer as furnishing very good evidence that dilute mercurial solutions of the alkali and alkali earth metals are solutions of mercury compounds of the respective metals. It has been shown by Ramsay,⁵ Heycock and Neville,⁶ G. Meyer,⁷ and others, that dilute mercurial solutions of metals are governed by the same laws with respect to the depression of the vapor pressure, the freezing point, etc., of the solvent, as are ordinary dilute solutions. Therefore, upon dissolving small, equimolal quantities of the alkali or alkali earth metals in equal, large quantities of mercury, if, as has often been assumed,⁸ they exist in solution in the form

¹ Cf. G. McP. Smith, *THIS JOURNAL*, 32, 502 (1910); 35, 39 (1913).

² Cf. G. Meyer, *Z. physik. Chem.*, 7, 447 (1891); T. W. Richards and R. N. Garrod-Thomas, *Ibid.*, 72, 165 (1910). It would, however, be more exact to consider the solution tension of the alkali metal as proportional to the concentration of MeHg_x in the dilute solution; but in the case of very dilute amalgams both considerations lead to results that are practically identical (cf. F. Haber, *Z. physik. Chem.*, 41, 399 (1902)).

³ The symbols $P_{(\text{Na})}$, etc., are used to indicate the relative solution-tension magnitudes of the metals in dilute equimolal mercurial solutions, such as those listed in the first column of Table I.

⁴ Concerning the behavior of the alkali earth metals and of lithium, Cf. G. McP. Smith, *Am. Chem. J.*, 37, 507 (1907); *Z. anorg. Chem.*, 58, 381 (1908).

⁵ *J. Chem. Soc.*, 55, 521 (1889).

⁶ *Ibid.*, 55, 666 (1889); 57, 376 (1890).

⁷ *Z. physik. Chem.*, 7, 447 (1891).

⁸ G. Meyer, *Ibid.*, 7, 447 (1891); M. von Wogau, *Ann. Physik*, 23, 345 (1907).

of free monatomic molecules, then we should expect their solution tensions to be indeed lowered, but in a more or less uniform manner; the relative magnitudes of their solution tensions should not be greatly altered. If, however, they enter into combination with mercury to form compounds containing only one atom of the amalgamated metal to the molecule, and if it is these compounds which are present in solution in the excess of mercury, then we should expect the solution tensions of the metals to be lowered to a very much greater degree, and *not* uniformly, but differently, depending upon the relative affinities of the metals for mercury.¹ The latter is what actually does happen; and, moreover, it would be difficult to explain the analogous behavior in this respect of the metals K, Rb, and Cs, on the one hand, and of Ca, Sr, and Ba, on the other—the members of two neighboring triads in the periodic system—on any other basis than that of the existence in mercurial solution of the corresponding members of the two triads in the form of analogously constituted compounds. Furthermore, it is well known that alkali metals are capable of entering into combination with mercury, even at ordinary temperatures, with the formation of crystalline compounds; and, *in the light of the mass law, it would indeed be a remarkable fact if such compounds were caused to undergo dissociation by the addition of a large excess of one of their constituent metals.*

In conclusion it may be added that the writer² has recently succeeded in showing, by means of the diffusion method already referred to, that, in mercurial solutions of these metals, the compounds present very probably correspond to the following formulas, in which, it will be noted, each compound contains but one atom of the amalgamated metal to the molecule: LiHg_3 , NaHg_5 , KHg_6 , RbHg_6 , CsHg_6 , CaHg_5 , SrHg_6 , and BaHg_6 .³

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¹ The solution tensions of these metals in their amalgams are best explained as being due to the presence of their free monatomic molecules in the mercurial solutions; these metals are present in the mercury either wholly in the free state, or only partially so. In the latter event, we have the equilibrium: $\text{MeHg}_n \rightleftharpoons \text{Me} + n\text{Hg}$; and in dilute liquid amalgams mercury is present in such great excess, that $(\text{Me})/(\text{MeHg}_n) = \text{const.}$; that is, in the case of a given metal, C_{Me} , and therefore P_{Me} , is proportional to the total concentration of the metal in the dilute solution.

But, for the different metals in their dilute equimolar mercurial solutions, the different values of $(\text{Me})/(\text{MeHg}_n)$ depend upon the different degrees of dissociation of the compounds, MeHg_n , and these in turn depend upon the different affinities of the metals for mercury.

² THIS JOURNAL, 36, 859 (1914); *Z. anorg. Chem.*, 88, 161 (1914).

³ The crystals of the approximate composition KHg_{12} , etc., which have been mentioned in the literature (cf. *e. g.*, Kerp and Böttger, *Z. anorg. Chem.*, 25, 1 (1900); Smith and Bennett, THIS JOURNAL, 32, 622 (1910)), are probably solid, or semi-solid solutions of the above compounds with mercury.