[Contribution from the Chemical Laboratory of the University of California]

THE VAPOR PRESSURE OF SODIUM AND CESIUM AMALGAMS

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The following investigation was undertaken as an extension of the work carried out by the senior author and his collaborators on the vapor pressures of amalgams in relation to the theory of metallic solutions.[1] It was hoped also that data might be secured which would permit the indirect determination of the e.m.f. of the cesium electrode.

The standard electrode potential of the alkali metals cannot be determined directly on account of the reaction between the metal and water. Lewis and Kraus[2] first showed that the electrode potential could be obtained by interposing a dilute amalgam of the alkali metal. The amalgam was used in aqueous solution with but little reaction with water. A second cell composed of an electrolyte other than water then gave the free energy change in going from the pure metal to the amalgam. The sum of the electromotive forces of the two cells gave the standard electrode potential.

This method was found successful with all the alkali metals except cesium. No solvent could be found for a salt of cesium which would not dissolve the metal. Consequently the method had to be abandoned. There seems to be no doubt that the e.m.f. of a dilute cesium amalgam could be measured against a hydrogen electrode using an aqueous electrolyte, so that the problem could be solved by an indirect determination of the e.m.f. between metallic cesium and the dilute amalgam. This could be accomplished by applying the Duhem equation to accurate data on the vapor pressure of cesium amalgams and so obtaining the relation between the activity of cesium and the composition of the amalgam. Some preliminary calculations showed that the results of the application of the Duhem equation would be sufficiently accurate to obtain satisfactory values for the activity of the cesium at the temperatures used in the investigation, although leaving somewhat doubtful the possibility of getting a sufficiently accurate temperature coefficient to make possible the extrapolation to 25°. An inspection of the freezing-point diagrams for the alkali metals led us to hope the hydrargyrates of cesium to be more dissociated than those of sodium, although the measurements showed this not to be the case.

The Materials Used

The sodium used was a good grade of commercial metal. No trace of other alkali metals was detected spectroscopically, nor could potassium be detected qualitatively, though one-tenth of one per cent. could have been observed.

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[1] Hildebrand, "Solubility," A. C. S. Monograph, Chemical Catalog Co., New York, **1924**, Chapter 16.

[2] Lewis and Kraus, This Journal, **32**, 1459 (1910).

The mercury was washed and distilled.

Kahlbaum's cesium bromide was tested spectroscopically for impurities without any positive test for metals other than cesium. The metal was prepared by mixing the dry salt with fresh calcium shavings in an iron tube. The tube was then placed in a glass tube, evacuated and heated to six or seven hundred degrees, which furnished a constant stream of cesium vapor. The metal was three times redistilled, leaving no residue the last time, and was found to melt above 25° in every case. The melting point of pure cesium is 26°.

The hydrogen was prepared by electrolysis of sodium hydroxide solution, dried by passing through concentrated sulfuric acid, phosphorus pentoxide and finally over an amalgam containing about eighty-five mole per cent. of sodium, which is liquid at room temperature. The hydrogen was then of sufficient purity to give no trace of oxide on the surface of the cesium in the upper part of the apparatus or in the tube containing the amalgam.

Experimental Method

The measurement of the vapor pressures was carried out essentially as in the previous work on vapor pressures of amalgams.[3] The apparatus with which the cesium was to come in contact was thoroughly evacuated by a mercury vapor pump and well baked out. The cesium was contained in a small glass tube, as shown in Fig. 1, drawn out to a fine tip. After the glass had been out-gassed, the tip was broken by means of a weight controlled magnetically and the cesium allowed to run into the tube in which the pressure was to be measured. The mercury was then distilled into the cesium until the proper concentration had been attained. The furnace was raised to the proper position, heated to the temperature of the run and the fused salt bath poured in. It was found convenient to filter the fused eutectic of sodium and potassium nitrate frequently through glass wool. After each run the salt was siphoned out of the furnace. The amalgam was allowed to heat for about an hour in order to eliminate part of the gas which might still be held by the glass. This was then boiled out and the amalgam allowed to stand for a time sufficient to allow the temperature to become constant and also to insure the amount of permanent gas above the amalgam being nearly constant during the run. Usually but four measurements of the pressure were taken on the amalgam and an equal number on the tube of pure mercury. This was sufficient to insure an accuracy due to chance errors of ob-

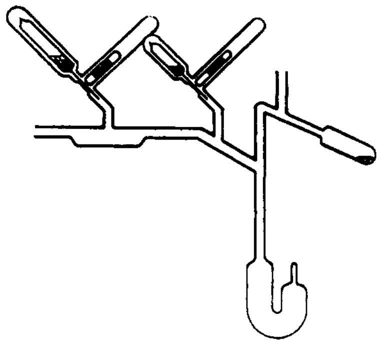

Fig. 1.—Apparatus for preparing amalgams and measuring vapor pressures.

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[3] (a) Hildebrand, *Trans. Am. Electrochem. Soc.*, **22,** 319 (1913); (b) Hildebrand and Eastman, This Journal, 36, 2020 (1914); (c) *ibid.*, **37,** 2452 (1915); (d) Hildebrand, Foster and Beebe, *ibid.*, **42,** 545 (1920).

servation and temperature fluctuations of the order of magnitude of 0.05%. Since other errors were larger than this it was not deemed advisable to take a greater number of measurements.

Inasmuch as a fluctuation of one degree in the temperature of the furnace changes the vapor pressure of the mercury by 3%, the furnace was designed with the intention of obtaining as constant a temperature as possible. Thus the bath which was the basis of the furnace was surrounded by three glass shields with horizontal layers of asbestos to prevent circulation of air. Two shields of asbestos paper outside the glass shields served to circulate the gases from the Fisher burner around the outside of the glass shields and to prevent radiation to the manometers. A gas pressure regulator maintained the gas pressure for the burner constant to within one-tenth of a millimeter. As a result the temperature remained constant during a run to within a few hundredths of a degree. The heating liquids were diphenylsulfone, anthraquinone, phenanthrene, diphenylamine and phthalic anhydride.

The analysis of the amalgam was carried out in such a way as to furnish with one sample two independent determinations of the mole fraction. The tube containing the amalgam was, therefore, first weighed and at the conclusion of the analysis the glass tube was weighed empty, thus giving the total weight of the amalgam. The amalgam was then treated with water until most of the alkali metal had been extracted and the solution poured into a flask to be titrated. The last of the alkali metal was removed by digestion with acid. Hydrochloric acid was found to dissolve some mercury in the presence of air. However, half normal sulfuric acid was found to have no appreciable effect even when mercury was boiled in it for more than an hour. The mercury distils with the steam in appreciable quantities during digestion, necessitating the use of a long-necked flask with a condenser, water cooled, inside the flask. A small tube prevented excessive bumping. A platinum wire was placed in contact with the amalgam near the end of the extraction to decrease the overvoltage of the hydrogen.

The acid was standardized against Kahlbaum's sodium carbonate, against sodium carbonate prepared by recrystallizing as bicarbonate and by weighing as sulfate. These methods agreed to within one-tenth of one per cent. At the conclusion of the experiments the acid was again standardized.

The mercury was transferred from the long-necked digestion flask to a small casserole by pouring under water to prevent spattering. It was then washed three times with filtered acetone, dried by filter paper and transferred to a ten cubic centimeter weighing bottle by means of a watch glass pulled out to a spout which would enter the weighing bottle. This method of handling the mercury was found to be thoroughly dependable. The mercury was heated to constant weight by placing in an oven at 115° for five-minute periods, cooling in a desiccator and weighing. Longer periods for heating were found to result in distillation of the mercury.

The check on the analysis was obtained by subtracting the weight of either metal from the total weight of the amalgam to obtain the weight of the other metal. In the analysis of the sodium amalgams a further check was obtained by evaporation of the solution after titration and weighing the sodium sulfate.

Errors and Corrections

The causes of error have been carefully evaluated and corrections applied where possible. A consideration of these errors indicated that the probable error of the measurements should be about 0.3%. This is about the average deviation observed in the experimental points from the smoothed curve. The methods of correcting for some of these errors will be discussed briefly.

One of the chief sources of error in vapor pressure measurements lies in the difficulty of obtaining a pure vapor. Rather than attempt to eliminate all vapors other than mercury a correction was applied. A small tip was placed on the end of the closed arm of the pressure tube which functioned in principle as the capillary of a McLeod gage. At the conclusion of each run the fixed gas was compressed into this tube and its pressure measured. The pressure of the fixed gas in the closed tube is given by the equation

$$p = H - (P + S + h\rho)$$

in which H is the pressure in the open arm as measured by the manometer, P is the pressure of the mercury in the amalgam, S is the capillary depression of the amalgam, h is the difference in height of the amalgam in the two arms of the tube and ρ is the density of the amalgam referred to mercury at 25° as unity. This pressure p usually varied from a few millimeters of mercury to two or three centimeters. The pressure of the fixed gas in the closed arm during the run was then found by multiplying this pressure by the ratio of the volume of the capillary tip to the volume of the vapor in the closed arm during the run. This ratio was of the order of magnitude of 1/30. Similar corrections were applied to the mercury tube and the final activity corrected by these two factors.

The chief source of error in making the above correction arises from assuming a density for the amalgam. It was necessary, therefore, to make measurements on the density, the data being recorded in Table I. The values are but approximate, as accurate values were unnecessary in this work and could not be obtained by the method used. It is interesting to note that the apparent molal volume of mercury in cesium appears to be negative until the concentration of mercury is more than thirty mole per cent.

Table I

Density and Partial Molal Volumes of Cesium Amalgams

N_1, mole fraction of mercury	ρ, density referred to mercury	N_1	$\overline{V}_1$, partial molal volume of mercury, cc.	$\overline{V}_2$, partial molal volume of cesium, cc.
0.937	0.85	1.0	14.8	42
.914	.80	0.8	13.3	57
.909	.84	.6	9.0	65
.877	.75	.4		69
.868	.77	.0		71
.779	.58			

Perhaps the greatest source of error was caused by the difficulty in sighting on the meniscus of concentrated amalgams. The amalgam presented a flat or concave surface on amalgams in which the concentration of cesium was more than about ten mole per cent. As the concentration increased the wetting of the glass increased until in about thirty mole per cent. amalgams the glass would be completely covered by a film of the amalgam which, of course, made readings impossible. This film could be readily removed by heating with a burner, but that necessitated removing the amalgam from the bath and destroying the temperature equilibrium. In a few cases it was possible to improve the conditions by treating the glass before the run with hydrofluoric acid. The commercial 50% acid was found most satisfactory for this purpose, a short treatment at the boiling point sufficing to give good results in amalgams of moderate concentration. However, even in these it was necessary to sight on the contact of amalgam with glass rather than on the center of the meniscus. This might account for several tenths of a millimeter error in the case of the more concentrated amalgams.

The tube leading to the furnace was made small to cut down diffusion of mercury vapor and heated to prevent condensation. In this manner the error due to distillation of mercury was cut down to less than 0.1%.

At the higher temperatures the more concentrated sodium amalgams attacked the glass, making it necessary to take observations in as short a time as possible while the glass was transparent. No such difficulty was encountered with the cesium amalgams.

Experimental Results

The data for sodium amalgams were obtained before those for cesium amalgams and consequently the latter are a little more accurate. Furthermore, the bearing of the cesium measurements on the value of the cesium electrode potential made it desirable to obtain more measurements on cesium amalgams. So many improvements were made after the first ten runs that these were not considered of sufficient value to tabulate. All of the experimental measurements from run eleven on are given in the tables. Table II gives the experimental data obtained for sodium amalgams and also values calculated by methods to be described.

The first column gives the average temperature of the runs. The temperature varied during a run by perhaps a tenth of a degree or less. The temperature varied from one run to another by half a degree. The first variation is of greater importance, due to the fact that the vapor pressure of mercury varies by about 3% per degree change in temperature, while the activity of mercury in an amalgam changes at the rate of about 0.05% per degree.

The second column of the table gives the mole fraction of mercury as obtained by the analysis. The two methods of obtaining the number of moles of mercury usually varied by about one part in ten thousand.

The two values obtained for the number of moles of sodium usually varied by about one part in a thousand. The third column gives the experimental values of p/p°.

Table II

Activity of Mercury in Sodium Amalgams

T	N_1	p/p°, obs.	p/p°, calcd. 1	p/p°, calcd. 2
648.1	0.872	0.701	0.686	0.701
	.627	.080	.080	.080
	.611	.066	.067	.065
608.5	.961	.941	.938	.942
	.939	.894	.888	.894
	.872	.692	.678	.688
	.773	.348	.351	.355
	.740	.272	.263	.264
	.541	.016	.021	.018
	.529	.021	.017	.015
	.511	.011	.013	.011
572.9	.774	.343		.340

Table III

Activity of Mercury in Cesium Amalgams

T	N_1	p/p°, obs.	p/p°, calcd. 1	p/p°, calcd. 2
651.4	0.940	0.865	0.856	0.833
	.909	.733	.733	.738
	.711	.090	.085	.083
609.9	.926	.800	.792	.800
	.877	.558	.571	.568
	.847	.417	.435	.423
	.831	.358	.370	.355
	.751	.129	.129	.134
	.713	.072	.070	.073
573.9	.914	.733	.731	.731
	.865	.495	.495	.493
	.728	.079	.076	.078
553.6	.937	.838	.824	.837
	.934	.822	.804	.820
	.868	.487	.488	.481
	.779	.153	.155	.149

The data from cesium amalgams given in Table III seem to be a little more accurate than those for sodium amalgams in the lower range of concentration, but inferior in the range of higher concentration. This was doubtless due to the greater tendency of the cesium amalgams to wet the glass. The temperature control was somewhat better than in the work on sodium. The variation of the temperature during a run was usually not more than one or two hundredths of a degree, while the variation of the temperature from one run to another was less than three tenths of a degree. The values of N_2 are probably in error by 0.1% or less.

Interpretation of Results

The experimental data may be treated in a variety of ways. The most obvious way to show deviations from Raoult's law is to plot activity against mole fraction. This has been done in Fig. 2, in which the activity of mercury is plotted against its mole fraction. As is evident from the figure, this method of plotting does not permit extrapolation far beyond the region of experimental measurements.

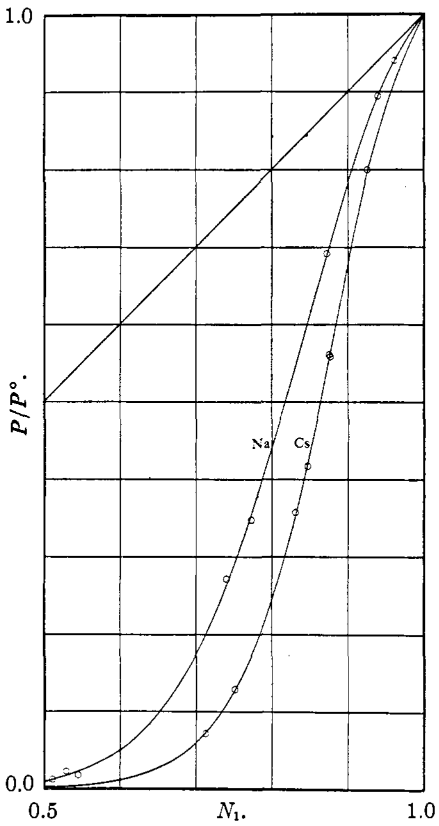

Fig. 2.—The activity of mercury in sodium and cesium amalgams.

A more useful method of plotting such data is to consider the deviations from perfect solution. For this purpose log a_1/N_1 may be plotted against some function of N_1. If Raoult's law is obeyed, the plot is a straight line, log a_1/N_1 being zero. It is very convenient in many instances to plot log a_1/N_1 against N_2^2.[4] Some of the data are so represented in Fig. 3, the points falling almost exactly on a straight line. The straight line is dotted in the figure, while the full curve is the best smooth curve which could be drawn through the experimental points.

The last columns of Tables II and III have been calculated from these curves. The fourth column of Table II has been calculated by means of the equation log $a_1/N_1 = {}^1/_2\beta N_2^2$. The value of the single constant $-\beta$, obtained graphically, is 12.81 at 648.1°K. and 13.33 at 608.5°K. The values in the fourth column of Table III were obtained in the same manner, assigning values to $-\beta$ of 22.16, 24.74, 26.52 and 28.66 for the four temperatures, the smallest value being for the highest temperature.

The values in the last column of Table II were obtained by a more roundabout method, but one which furnishes information concerning the relative partial molal heat contents of the amalgams and also fits the

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[4] (a) Ref. 1, p. 48; (b) Hildebrand, *Proc. Nat. Acad. Sci.*, **13**, 267 (1927).

experimental data better. The method consisted in first obtaining an equation which better fitted the experimental data for the temperature common to the greatest number of runs. Second, from this equation and the experimental values at other temperatures, the variation of the activity with the temperature was obtained. Third, from the change of activity with the temperature the relative partial molal heat content of mercury in the amalgams was obtained, which was then plotted against mole fraction and a smooth curve used to recalculate the activity at any temperature and concentration.

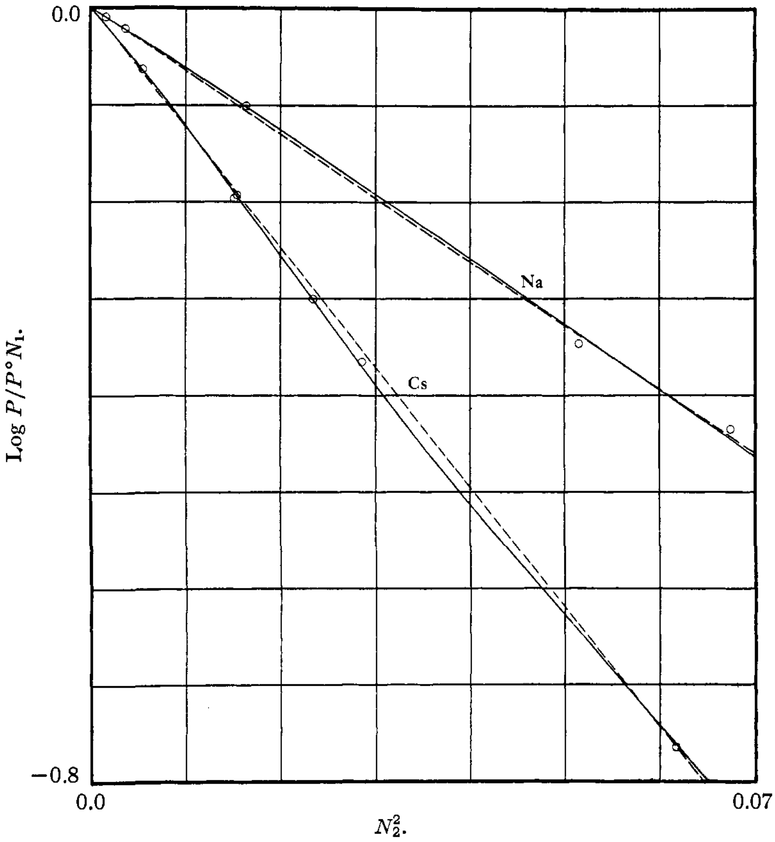

Fig. 3.—The activity of mercury in sodium and cesium amalgams.

The empirical equation which best fitted the experimental data is $\log a_1/N_1 = 2.082 (\log N_2 + 0.418)$. The value of the coefficient of $\log N_2$ gives an idea of the difference to be expected between the values given in the last two columns of Table II. A similar plot for the cesium data indicated a similar value for the coefficient of $\log N_2$ in dilute amalgams, but one which approached 2 in the more concentrated amalgams. The values at 608.5°K. in the sixth column of Table II were obtained from this equation.

From the above equation values of the activity were calculated at concentrations used in runs at other temperatures. The change in log a_1 with respect to $1/T$ multiplied by 2.303/1.988 gives the relative partial molal heat content of mercury in the amalgam, referred to pure mercury as the standard state. These values vary with the concentration and may be represented by the equation $\bar{L}_1 = 4300\ N_2^2$. Table IV gives the values obtained by the above method and those calculated from the equation, while Table V gives similar values for cesium. These values are subject to a rather large percentage error, inasmuch as the change of activity with the temperature is slight.

TABLE IV

RELATIVE PARTIAL MOLAL HEAT CONTENT OF MERCURY IN SODIUM AMALGAMS

N_2	$\bar{L}_1$ Obs.	$\bar{L}_1$ Calcd.
0.128	− 76	− 81
.226	−204	−255
.373	−665	−694
.389	−765	−752

TABLE V

RELATIVE PARTIAL MOLAL HEAT CONTENT OF MERCURY IN CESIUM AMALGAMS

T	N_2	$\bar{L}_1$ Obs.	$\bar{L}_1$ Calcd.
592	0.086	−107	− 56
	.135	−122	−136
	.272	−572	−548
582	.063	− 32	− 49
	.067	− 28	− 54
	.132	−211	−210
	.221	−560	−588

The values in the last column of Table II were calculated by this method and agree considerably better with the experimental points than those calculated by means of the more simple equation. The activity of mercury may now be calculated in an amalgam of any concentration and at any temperature, the accuracy depending on the range of extrapolation. If the range of extrapolation is great, doubtless the simpler equation would alone be justified.

In considering the data on cesium amalgams no simple empirical equation was found to represent the data accurately throughout the whole range studied. The curve was, therefore, treated in two portions, in the range from $N_1 = 1$ to $N_1 = 0.8$ being represented by the equation $\log a_1/N_1 = 8.954\ N_2^2 + 42.40\ N_2^3 - 110.3\ N_2^4$ and in the range of more concentrated amalgams by the equation $\log a_1/N_1 = 7.793/(1 + 0.7267\ r_1)$ in which r_1 is defined as N_1/N_2. The curves representing these two equations differ but slightly, but since the change of activity with the temperature is but slight it is essential to fit the experimental points as well as possible. The accuracy obtained in determining the relative partial molal heat content is greater for sodium amalgams than for cesium amalgams. The latter were found to be represented by the equation $\overline{L}_1 = AN_2^2$, in which the value for A was taken as 10,000, 6400 and 10,400 for the temperature intervals between the various runs, the first value being for the highest temperature. The values in the last column of Table V were calculated by means of these equations. Similar calculations were carried out by merely sliding a cut-out curve and gave values differing little from those calculated as above.

The Activity of the Alkali Metal

The calculation of the activity of the solute from the known activity of the solvent may be accomplished by either the graphical or analytical integration of the Duhem equation.[5] The former is accomplished by plotting $\ln a_1/N_1$ against N_1/N_2. The equation used is

$$\ln a_2/N_2 = -\int \frac{N_1}{N_2}\,\mathrm{d}\ln a_1/N_1$$

The latter method consists in expressing $\ln a_1/N_1$ as a function of N_2 and integrating analytically. In these calculations a_2, the activity of the alkali metal, will refer to the pure liquid metal as the standard state. On substituting the value of $\ln a_1/N_1$, namely $2.303\beta N_2^2/2$, and integrating we obtain the relation

$$\ln a_2/N_2 = 2.303[-\beta(N_2 - {}^1/_2N_2^2) + {}^1/_2\beta]$$

The right-hand member of this equation is identical with minus ${}^1/_2\beta N_1^2$.[4a] The form of the equation first given has been used in the calculations since the term involving N_2^2 can be neglected for small values of N_2. For a given value of N_2 the e.m.f of a cell in which the reaction is the transfer of sodium to amalgam of this concentration is then given by the relation

$$E = \frac{RT\ln a_2}{23074}$$

If we take N_2 as 0.01772, we find the e.m.f. of such a cell to be 1.07 volts at 648.1° and 1.03 volts at 608.5°K. If we extrapolate such a value over the long range to 298° we obtain the value 0.72 volt. Such a cell has been measured by Lewis and Kraus and was found to have the e.m.f. of 0.85 volt. The assumption used in the above extrapolation is that $\mathrm{d}E/\mathrm{d}T$ is constant over the range of extrapolation, which undoubtedly is incorrect. Lewis and Kraus determined $\mathrm{d}E/\mathrm{d}T$ at 298°. If an average value of $\mathrm{d}E/\mathrm{d}T$ is taken for the extrapolation, the e.m.f. is found to be 0.88 volt.

The foregoing calculations are of value in determining the reliability of similar calculations of the cesium cell. More data are available for the cesium calculations, but the difficulties of extrapolation are greater than for sodium due to the lower activity of the mercury in these amalgams.

[5] (a) Hildebrand and Eastman, This Journal, **37,** 2452 (1915); (b) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Compounds," McGraw-Hill Book Co., New York, **1923.**

Using the various empirical equations which expressed the experimental data, we find for the e.m.f. of the cell in which the reaction is a transfer of pure cesium into an amalgam whose concentration is 1.0 atom per cent. 1.43 to 1.47 volts at 609°K. Upon extrapolating to 25° we find a value of 1.71 volts, the agreement of the various methods of extrapolating being to the order of 0.05 volt. A further idea of the accuracy of such calculations may be obtained from Fig. 7.

The Deviation of Sodium, Potassium and Cesium Amalgams from Raoult's Law

It has been shown in Fig. 3 that the vapor pressure of mercury from sodium and cesium amalgams may be represented by the equation

$$\log a_1/N_1 = {}^1/_2\beta N_2^2 \tag{1}$$

in which β is a constant which varies with the temperature. The activity of the solute may be calculated from Equation (1) and the Duhem equation, giving

$$\log a_2/N_2 = -\beta(N_2 - {}^1/_2N_2^2) + {}^1/_2\beta \tag{2}$$

Equation (1) was derived from data extending over a concentration range of $N_1 = 1$ to $N_1 = 0.5$. We may test Equation (2) by means of the data obtained by Richards and Conant on sodium amalgams at 25°.[6] They measured the e.m.f. of cells in which the reaction is a transfer of sodium from one amalgam to another of different concentration. These data give activities of sodium in amalgams referred to each other or, by extrapolation, referred to infinite dilution. For the test of Equation (2) it is necessary to have the activity referred to pure sodium as the standard state. This may be accomplished by combining the data of Richards and Conant with those of Lewis and Kraus.[2] The latter have measured the e.m.f. of a cell in which the reaction is the transfer of sodium into a dilute amalgam. Since $E/.05915 - \log N_2$ differs from $\log a_2/N_2$ by a constant factor, the two sets of data may be combined by plotting $E/.05915 - \log N_2$ as ordinate against N_2 as abscissa and shifting the curve along the ordinate until it coincides with the single measurement of Lewis and Kraus of $\log a_2/N_2$. The resulting curve is A in Fig. 4. The experimental points fall on a straight line almost within the limits of experimental accuracy. This has been observed for similar data on barium amalgams by Anderson.[7]

That these points should fall on a straight line for small values of N_2 is evident from Equation (2), for when N_2 is small the term N_2^2 may be neglected. The slope of the curve gives the value for the constant β and the departure of the intercept at $N_2 = 0$ from ${}^1/_2\ \beta$ indicates the departure to be expected from Equation (1) for large values of N_2. The equation for the curve through the experimental points in Fig. 4 is log

[6] Richards and Conant, THIS JOURNAL, **44**, 601 (1922).

[7] Anderson, *ibid.*, **48**, 2285 (1926).

$a_2/N_2 = 20N_2 - 12.8935$. This value of β is in good accord with the values found at higher temperatures.

These data serve to emphasize again the importance of the constant β which expresses the deviation of both solvent and solute from Raoult's law.[4b] The more exactly Equation (1) corresponds to vapor pressures throughout the whole range of concentration the more nearly will the intercept in Fig. 4 equal one-half the slope of the curve. The value of the intercept gives the log of the ratio of the activity of sodium in infinitely dilute amalgam to pure sodium.

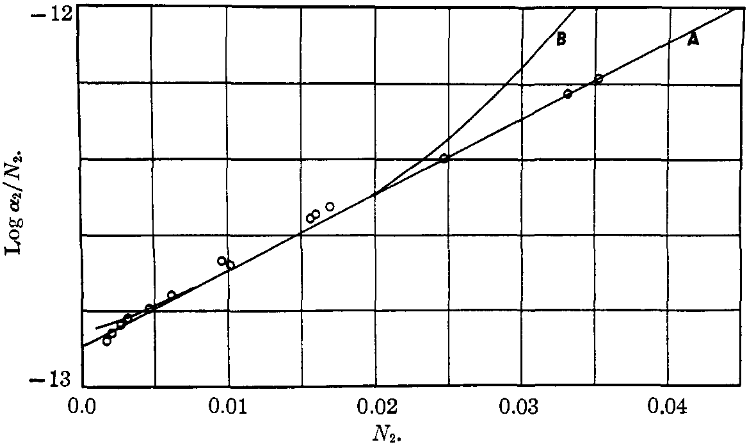

Fig. 4.—Activity of sodium in sodium amalgam at 25°.

The value of β obtained from Fig. 4 makes possible the calculation of the vapor pressure of mercury from liquid sodium amalgams at 25°, using the equation $\log a_1/N_1 = -10N_2^2$. Poindexter[8] has measured the vapor pressure of solid sodium amalgams, using the ionization gage. His data may be represented by an equation of the form of that above in which the constant at 298°K. is —22 ± 5. As would be expected, the escaping tendency from a solid amalgam is much less than from a supercooled liquid amalgam. Poindexter found much higher vapor pressures in the case of the dilute liquid amalgams.

Table VI gives values of β for sodium and cesium amalgams obtained from the experimental work of this paper. The value for sodium at 298° is obtained from the data of Richards and Conant. The value for cesium at 298° is obtained by extrapolation. The values for potassium are obtained from the data of Millar.[9] The value for barium is obtained from the data of Anderson.[7] Barium and cesium amalgams seem to vary from perfect solution to about the same extent. There is quite a difference,

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[8] Poindexter, *Phys. Rev.*, **28**, 208 (1926).

[9] Millar, THIS JOURNAL, **49**, 3003 (1927).

TABLE VI

THE DEVIATION OF AMALGAMS FROM RAOULT'S LAW AS EXPRESSED BY β IN THE EQUATION LOG $a_1/N_1 = \beta N_2^2$

Amalgam	Temp., °K.	$-\beta$
Sodium	648.1	12.82
	608.5	13.33
	298.1	20.0 ±0.4
Potassium	663.1	19.0
	583.1	20.4
	523.1	21.8
	473.1	23.6
Cesium	651.4	22.16
	609.9	24.74
	573.9	26.52
	553.6	28.66
	298.1	55.0 ±1.0
Barium	298.1	55.0

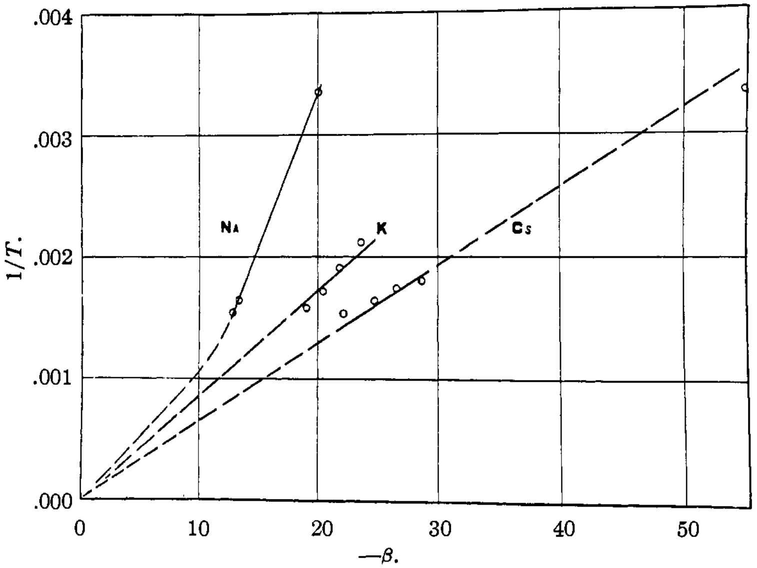

Fig. 5.—The variation of $-\beta$ (in the equation log $a_1/N_1 = \beta N_2^2$) with the temperature.

however, between cesium and sodium amalgams. The data of Table VI have been plotted in Fig. 5. It thus appears that the value for β is about the same for a sodium amalgam at 298°K., a potassium amalgam at 580° and a cesium amalgam at 770°. Doubtless the curves in Fig. 5 should not be straight lines, but since the data are not of sufficient accuracy to determine the curvature it has seemed better to draw them so. A straight line implies that the relative partial molal heat content of the mercury is independent of the temperature. The equations for these curves are: $\beta_{Cs} = 15{,}620/T$, $\beta_K = 11{,}630/T$ and β_{Na} $3930/T + 6.84$. Combining these equations with Equations (1) and (2) (simplified) we obtain the expressions

$$
\begin{aligned}
\log a_1/N_{1\text{Cs}} &= -\frac{7810}{T}N_2^2\\
\log a_1/N_{1\text{K}} &= -\frac{5815}{T}N_2^2\\
\log a_1/N_{1\text{Na}} &= -(1965/T + 3.42)\,N_2^2\\
\log a_2/N_{2\text{Cs}} &= -\frac{15{,}620}{T}N_2 + C\\
\log a_2/N_{2\text{K}} &= -\frac{11{,}630}{T}N_2 + C\\
\log a_2/N_{2\text{Na}} &= -(3930/T + 6.84)\,N_2 + C
\end{aligned}
$$

The expressions for the activity of the mercury a_1 are supported by experimental data up to a concentration of $N_2 = 0.5$. The expressions for the activity of the solute are of use in this simplified form to a concentration of $N_2 = 0.05$. Using the more exact expression of Equation (2), or its equivalent $\log a_2/N_2 = -{}^1/{}_2\beta N_1^2 + C'$, values for the activity of the solute may be obtained up to a concentration of $N_2 = 0.5$. The value of the constant C has been obtained only in the case of sodium amalgams at 25°, in which case it has been found to be 12.8935.

Compound Formation

Departure from perfect solution has frequently been explained by the assumption of compound formation.[10] A large number of compounds have been shown to exist[11] in the solid phase for sodium amalgams, suggesting the calculation of the vapor pressure of amalgams from these data.

Fig. 6 gives three curves, A, B, C, calculated by assuming in each case the formation of one compound, namely, $NaHg_2$, $NaHg_4$ and $NaHg_{16}$. The first two of these compounds are indicated by the cooling curve while the compound $NaHg_{16}$ merely indicates an approximate formula which would be necessary to explain the behavior of dilute amalgams if only compound formation is considered. It will be observed that through a limited range each curve corresponds more or less closely with the smooth curve through the experimental points. In more dilute solutions the first two curves give too high an activity, and in more concentrated solution too low an activity. The second of these deviations may be accounted for to some extent by assuming dissociation of the compound. This has been done in Curve D, Fig. 6, by assuming the equilibrium constant $K = a_{NaHg_2}/a_{Na}a^2_{Hg} = 1000$. By assuming similar dissociation for the other

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[10] Ref. 1, p. 72.

[11] Schüller, *Z. anorg. Chem.*, **40**, 385 (1904).

compounds it is possible to approach the experimental data through a narrow range of concentration, the agreement suggesting that compound formation is involved, but the results are far from satisfactory.

Doubtless the true state of affairs is to be represented by the existence of a large number of compounds simultaneously, each with its characteristic dissociation constant. The attempt has been made to see to what extent such an assumption accounts for the behavior of the amalgams.

The following solution of the problem has been suggested by Professor Scatchard and is based on the assumption of definite compounds, dissociating in accord with the mass law, each molecular species obeying Raoult's law.

"Given a system made up from 1 mole of sodium and n moles of mercury. The activity of the mercury is a; the number of moles of mercury in the system is (Hg); the number of moles of sodium (0); the number of moles of $NaHg_2$ (2); of $NaHg_4$ (4); of $NaHg_6$ (6). We have the following equations

$$(2) = Ka^2(0) \qquad (1)$$

$$(4) = K'a^4(0) \qquad (2)$$

$$(6) = K''a^6(0) \qquad (3)$$

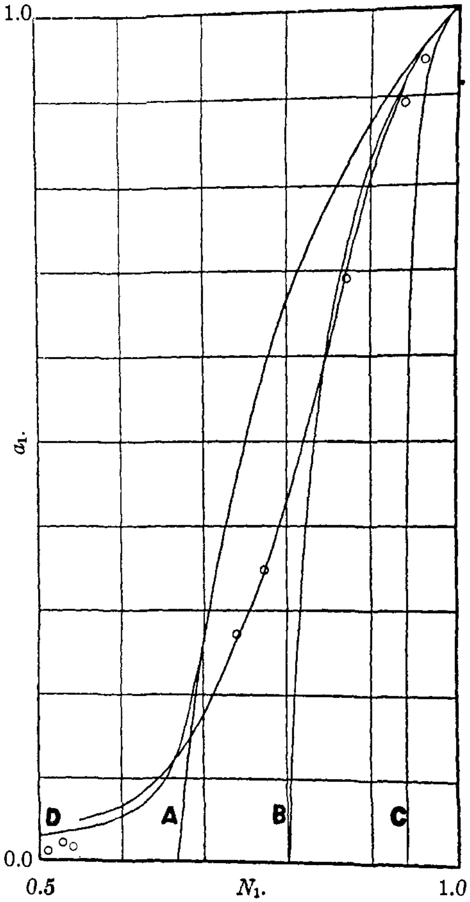
$$n = (Hg) + 2(2) + 4(4) + 6(6) \qquad (4)$$

$$1 = (0) + (2) + (4) + (6) \qquad (5)$$

From (5)

$$a = \frac{Hg}{1 + (Hg)}$$

$$(Hg) = \frac{a}{1 - a} \qquad (6)$$



Curves A, B and C are calculated by assuming complete formation of the compounds $NaHg_2$, $NaHg_4$ and $NaHg_{16}$, respectively, while D is calculated by assuming partial dissociation of $NaHg_2$.

Fig. 6.—The activity of mercury calculated by assuming compound formation, compared with experimental values.

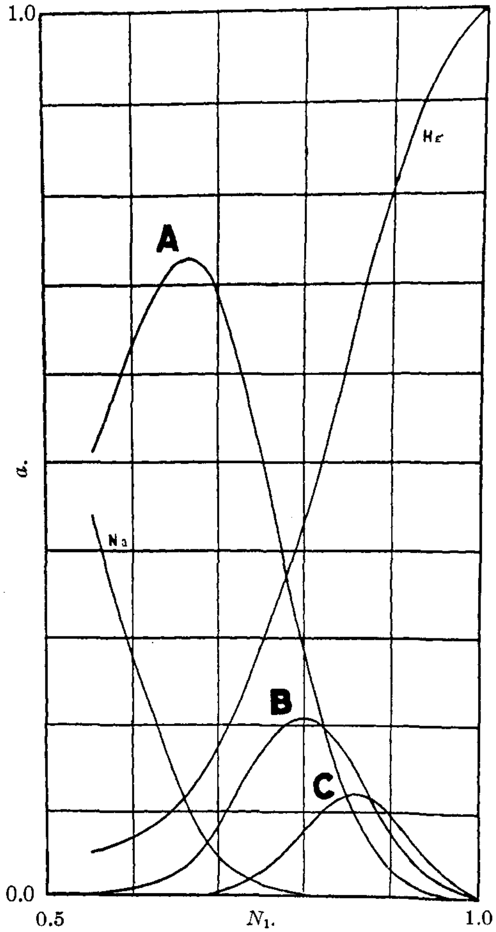
Substituting from Equations (1), (2) and (3) in (5) gives

$$1 = (1 + Ka^2 + K'a^4 + K''a^6)\cdot(0) \qquad (7)$$

Substituting from (1), (2), (3), (6) and (7) in (4) gives

$$n = \frac{a}{1 - a} + \frac{2Ka^2 + 4K'a^4 + 6K''a^6}{1 + Ka^2 + K'a^4 + K''a^6} \qquad (8)"$$

By means of Equation (8) very good agreement with the experimental data was obtained for a limited range of concentration by allowing K'' to equal zero and determining K and K' by successive approximations. The smooth curve through the experimental points in Fig. 6 is calculated by assigning values to all three constants and agrees, within the limits of experimental error, with the experimental data from $a_1 = 0.1$ to $a_1 = 0.9$. The values chosen for the constants are as follows: $K = 500$; $K' = 2000$; and $K'' = 4000$.



Curves A, B and C represent the mole fraction of $NaHg_2$, $NaHg_4$ and $NaHg_6$, respectively.

Fig. 7.—The constituents of sodium amalgam calculated by assuming three compounds existing simultaneously.

The assumptions involved in the above calculations are that there are five molecular species present in a sodium amalgam and that these all obey Raoult's law. Doubtless other compounds are present and other factors would have to be considered for an exact treatment of the behavior of these amalgams. It is interesting, however, that such a simple picture should account so well for their behavior. A clearer idea of the constitution of the amalgams suggested by these calculations is obtained from Fig. 7. In Fig. 7 the activity (or mole fraction) of each constituent is plotted against the mole fraction of mercury in the amalgam.

The existence of such a compound as $NaHg_{16}$ (C, Fig. 6) is also suggested by the work of Poindexter. This author suggests that n may be larger than 15.7. Millar has pointed out that n may be larger than 10 for potassium amalgams. It is interesting to note that if no change in atomic volume is experienced on the formation of such a compound, there is room on the surface of a sodium atom for 16 mercury atoms. A further test of the validity of the assumption of this compound is obtained by calculating the dissociation constant for the compound from the measurement of Lewis and Kraus and then calculating the data of Richards and Conant from this constant. Curve B, Fig. 4, has been calculated in this manner and agrees within the limits of experimental error to a concentration of $N_2 = 0.02$. The value found for the dissociation constant is 12.8579.

Summary

1. The vapor pressures of sodium and cesium amalgams have been measured at temperatures from 554 to 651°K. and at concentrations from $N_1 = 1$ to $N_1 = 0.5$. The data may be represented by the equation $\log a_1/N_1 = KN_2^2/T$.

2. The relative partial molal heat content of mercury in the amalgams has been calculated from the temperature coefficient of the activity, making possible the calculation of the free energy of transfer of mercury in amalgams at intermediate temperatures and over the range of concentration studied.

3. Approximate values have been obtained for the free energy of transfer of alkali metal to amalgam.

4. Values of the constant β, which expresses the deviation of both solvent and solute from Raoult's law, are compared for sodium, potassium, cesium and barium.

5. The whole of the deviation from perfect solution exhibited by sodium amalgams can be explained on the assumption of compound formation. The compounds $NaHg_2$, $NaHg_4$ and $NaHg_6$ explain the vapor pressure of amalgams from an activity of 0.1 to 0.9, while in very dilute amalgams the compound $NaHg_{16}$ explains both vapor pressure and e.m.f. data.

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