[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Activity of Potassium in Dilute Potassium Amalgams

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The primary purpose of this investigation was to determine the activity of potassium in amalgams as a function of concentration and temperature. The need for these data arose during the investigation of potassium triphenylmethyl as an electrolyte, and the study of equilibria involving organic free radicals,[1] and alkali metal amalgams.[2] Seven cells have been constructed. The electrolytes have been a water solution of potassium hydroxide, a solution in diethyl ether of the potassium addition compound of organic free radicals and a solution in ethylamine of potassium iodide.[1] We are greatly indebted to Mr. E. S. Fetcher, Jr., who constructed the first of the ethylamine cells used in this investigation. All seven cells gave very good agreement. However, the last two cells were so much superior that these alone were used in computing the final results. In the final section of this paper the bearing of these results on the nature of amalgams is discussed.

Experimental Method

Much of the experimental detail has been described elsewhere.[1]

The method of filling the cell is indicated in Fig. 1. The cell proper (A) has five fingers, permitting the use of amalgams of five different concentrations. At the bottom of each finger is sealed a platinum wire. This was sealed into ordinary Pyrex glass to give a gas-tight joint by using very fine ribbon. Number 40 wire was rolled into a ribbon about one-half millimeter wide. This was drawn through a small constriction and the glass worked in the flame until the joint was tight. Care must be exercised to avoid pulling, as the slightest tension will sever the wire. A safe method is to push the glass together at all times while making the seal. Contact was made outside the cell by pouring mercury into the leads (C).

A handle (B) served to support the cell after all other tubes had been sealed off.

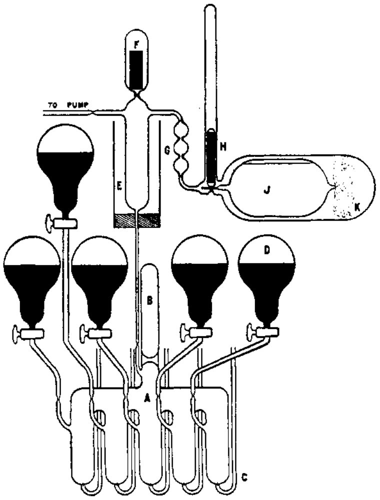

Fig. 1.—Method of filling the cell.

The amalgams were prepared and stored in the flasks (D). They were analyzed by drawing off samples in exactly the same way in which the amalgams were run into the cell. About 99.5% of the equivalent amount of half normal sulfuric acid was added to the amalgam from a weight buret, the flask heated on a steam-bath and air, free from carbon dioxide, slowly bubbled through the amalgam. When the solution became alkaline it was titrated with one-hundredth normal acid (diluted by weight from

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(1) Bent and Gilfillan, THIS JOURNAL, **55**, 247 (1933).

(2) Bent, Dorfman and Bruce, *ibid.*, **52**, 1498 (1930); **53**, 1786 (1931); **54**, 1393 (1932); **54**, 3250 (1932).

the half normal acid) using brom thymol blue as the indicator. With the help of a color standard the end-point could be determined within 0.04 mg. of potassium. Addition of the dilute acid was continued until the solution no longer became alkaline after three hours on the steam-bath. The stock half normal acid was standardized by comparison with constant boiling hydrochloric acid prepared according to the directions of Bonner and Titus.[3]

The capsule of ethylamine (J) was padded with glass wool (K) in order to prevent the rebound shattering the tube when the capsule was opened by means of the weight (H). The small bulbs (G) served to throttle the amine and prevent too rapid a rush of vapor into the cell. The amine was condensed in the cell by placing solid carbon dioxide in the tube (E). The potassium iodide was washed from the platinum boat (F) by cooling this tube with a little solid carbon dioxide.

The cell was then placed in a thermostat which consisted of a five-liter Dewar flask filled with water. This was easily controlled manually to 0.01°.

Experimental Results

The data recorded in the following tables were obtained from two cells. The first of these contained amalgams I, VI, VII, VIII and IX and the second contained amalgams II, III, IV, V and VI. The amalgam used by Lewis and Keyes in their cell containing metallic potassium had a composition of 0.2216 weight per cent. potassium, the same as that of amalgam VI. This amalgam was included in both cells in order to make the comparison of the different amalgams with each other and with metallic potassium more simple. These two cells had a resistance of a little more than 100,000 ohms. The composition of the amalgams is given in the first line of Table I.

The e. m. f. data recorded in Table I have already been corrected for three very small errors. The first of these is the calibration error of the potentiometer. These errors amounted to less than 0.016 mv. The second error is a small thermal e. m. f. observed in the potentiometer which was determined by short circuiting the leads. This amounted to 0.02 mv. A third correction was discovered by comparing the potential between amalgams *a* and *c* with the sum of the potentials for the pair *a* and *b* and for the pair *b* and *c*. It was found that the sum was almost invariably less than the single measurement by about 0.04 mv. This can be explained by assuming a contact potential in the switches of this amount. When this quantity was added to the observed readings there was no longer any consistent variation in these differences. The values obtained after making these three corrections are recorded in Table I.

The experimental or observed values are marked Obs. in the table. The difference between these values and those calculated by equation (1) are marked Diff. and will be discussed in the following section. Each recorded value is the mean of a great many readings, several hundred measurements having been made on each cell. Measurements involving an interval of time of but a few minutes did not differ by more than one hundredth of a millivolt. Measurements on different days or after the

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(3) Bonner and Titus, THIS JOURNAL, **52**, 637 (1930).

temperature had been varied usually differed by less than one tenth of a millivolt. The probable error will be discussed later.

Table II gives the data for amalgams containing a solid phase measured against amalgam VI as the reference electrode. These values were always obtained from both lower and higher temperatures and usually did not differ by as much as 0.1 mv. for a given cell. Equilibrium was established by gentle shaking for about an hour at a given temperature.

In order to apply a correction to the e. m. f. data on account of the change in the pressure of the ethylamine with temperature it is necessary to determine the partial molal volume of potassium in these amalgams. Two measurements of the density of the amalgams were made for this purpose. The pycnometer consisted of a 20-cc. Pyrex bulb to which was sealed a capillary of 0.5 mm. inside bore. The final volume was calculated from the position of the meniscus in this capillary as determined by means of a micrometer microscope. The pycnometer was carefully evacuated before filling with the amalgam. The density is given relative to that of mercury at 25°.

Weight fraction of potassium	0.002339	0.004730
Relative density at 25°	0.98275	0.96566

TABLE I

E. M. F. OF AMALGAMS REFERRED TO AMALGAM VI

		No. of amalgam			
		I	II	III	IV
T	Mole fraction[a]	0.026266	0.024438	0.021925	0.019437
50°	Obs.		0.04602	0.03839	0.03050
	Diff.		76	19	−18
35°	Obs.	0.05177	0.04499	0.03746	0.02968
	Diff.	−45	53	5	−23
25°	Obs.	0.05084	0.04418	0.03672	0.02908
	Diff.	−46	48	7	−21
15°	Obs.	0.05002	0.04336	0.03601	0.02850
	Diff.	−58	45	6	−21
0°	Obs.		0.04213		
	Diff.		39		

				No. of amalgam		
		V	VI	VII	VIII	IX
T	Mole fr.	0.015389	0.011267	0.006721	0.001924	0.0001950
50°	Obs.	0.01635				
	Diff.	−18				
35°	Obs.	0.01591		0.02155	0.06323	0.12742
	Diff.	−22		16	4	−38
25°	Obs.	0.01552		0.02099	0.06156	0.12373
	Diff.	−15		22	7	−29
15°	Obs.	0.01522		0.02051	0.05991	0.12003
	Diff.	−18		19	7	−27
0°	Obs.	0.01473		0.01967	0.05736	0.11450
	Diff.	−18		27	15	−22

[a] Each value given for the mole fraction is the average of at least two analyses. The average of the differences between pairs of analyses is 0.000006.

Table II

The E. m. f. of Saturated Amalgams Relative to Amalgam VI

Temp., °C.	Observed e. m. f.		Calcd.	Difference	
0.0	0.00540	0.00527[a]	0.00533	−0.00007	0.00006
5.0	.01330[a]		.01308	− .00022	
7.5	.01719	0.01712[a]	.01708	− .00011	−0.0004
15.0	.02965	0.02959[a]	.02962	− .00003	+0.00003
20.0	.03822		.03842	.00020	
25.0	.04755		.04755	.00000	

[a] These values were obtained from the second cell. All others were obtained from the first cell.

Interpretation of Results

In the discussion of the data the nomenclature of Lewis and Randall[4] and the physical constants of Birge are used.[5]

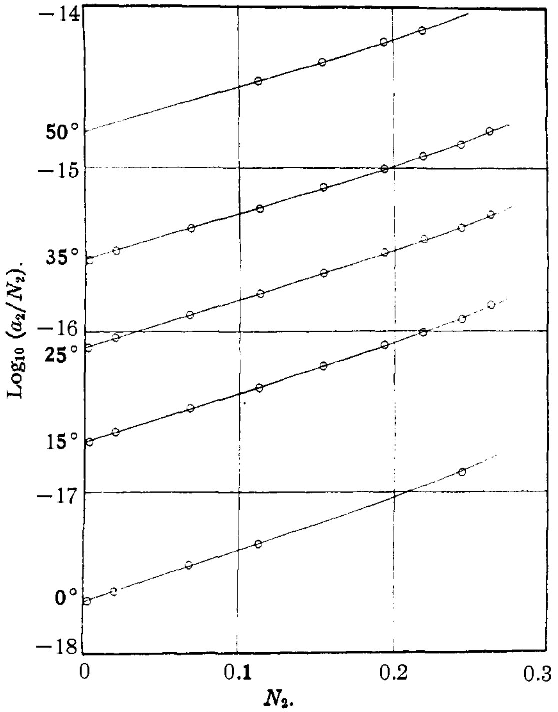

Fig. 2.—The deviation of potassium amalgam from Raoult's law.

The experimental data may be well represented by empirical equations, the use of which, however, is unfortunately time consuming. For convenience, therefore, the data have been represented graphically in Fig. 2

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(4) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York.

(5) Birge, *Phys. Rev. Supplement, Reviews of Modern Physics*, 1 (1929). These values are as follows: 0°C. = 273.18 abs.; 1 int. volt equ. = 23,065 calories. R = 1.98643. At. wt. Hg = 200.61. K = 39.096.

and the various computed thermodynamic quantities in Table III. Since four of the quantities given in this table are approximately linear functions of the concentration, rough values may be obtained, at concentrations not given, by interpolation. Only in the case of $\overline{F}_2$ and $\overline{S}_2$ is it not permitted to extrapolate to lower concentrations, as in these cases the partial molal quantity becomes infinite as the concentration becomes zero.

If we take the e. m. f. data of Table I and multiply each value by the faraday equivalent and divide by RT we obtain the difference in the natural logarithms of the activity of the potassium in the two amalgams. The values so obtained were found to be represented by the equation

$$\Delta\log_{10}a_2 = \log_{10}N_2 + (2446/T^{0.77700})\Delta\left\{N_2 + 3430N_2^4\right\} \qquad (1)$$

The difference between the experimental value and that calculated from equation (1) is given in the third line for each temperature. If one assumes that the form of the expression is correct, then the probable error can be computed to be 0.04 mv. This is perhaps too small an estimate. If we calculate the error by considering only a series of measurements at a given temperature, we obtain a more conservative estimate of 0.08 mv. We have taken this latter value as a measure of the accuracy of the data.

TABLE III

RELATIVE PARTIAL MOLAL DATA FOR POTASSIUM AMALGAMS

	Temp., °C.	Concn. (mole fraction) 0.001	0.005	0.01	0.02
$\Delta\overline{F}_2$	0	−26,048	−25,018	−24,446	−23,658
	25	−26,019	−24,906	−24,295	−23,465
	50	−25,989	−24,794	−24,145	−23,272
$\Delta\overline{S}_2$	0	−1.16	−4.49	−6.02	−7.73
	25	−1.18	−4.50	−6.02	−7.71
	50	−1.20	−4.51	−6.02	−7.70
$\Delta\overline{H}_2$	0	−26,355	−26,234	−26,081	−25,770
	25	−26,361	−26,237	−26,082	−25,765
	50	−26,367	−26,241	−26,083	−25,760
$\Delta\overline{F}_1$	0	−0.5618	−3.213	−7.432	−19.24
	25	− .6119	−3.471	−7.970	−20.41
	50	− .6618	−3.729	−8.505	−21.56
$\Delta\overline{S}_1$	0	.001999	0.01036	0.02158	0.04687
	25	.001999	.01034	.02147	.04643
	50	.001999	.01031	.02138	.04605
$\Delta\overline{H}_1$	0	− .01520	− .3813	−1.437	− 6.429
	25	− .01550	− .3888	−1.568	− 6.557
	50	− .01580	− .3956	−1.596	− 6.674

In equation (1) the exponent of T must be used to five significant figures in computations although the data are not accurate enough to determine this constant beyond the second significant figure.

A more useful way of expressing the data is to refer the activity of the potassium to the pure metal as standard state. This can be accomplished by combining these data with the measurements of Lewis and Keyes.[6] They have found the e. m. f. between metallic potassium and an amalgam in which the weight fraction of potassium is 0.2216 to be 1.0481 and the temperature coefficient to be −0.000272 volt per degree.

Before going farther with these data, however, it is necessary to consider the effect of pressure on the e. m. f. of the cell. During the course of our experiments the pressure of the ethylamine varied by as much as two atmospheres. The effect of this change in pressure may be computed providing we know the partial molal volume of the potassium in the amalgams. This we can compute from the density measurements recorded above. The apparent molal volume, that is, the change in volume when one mole of potassium is added to mercury to give an amalgam of the desired concentration, is found to be 24.57 cc. for the amalgam of weight fraction potassium 0.002339 and 24.61 for the amalgam of weight fraction potassium 0.004730. Since these figures differ so little from each other and the amalgams are very dilute, we may take these values to represent the partial molal volume of the potassium. Taking the volume of one gram atom of potassium as 45.5 cc., we find a change in volume for the cell reaction of 20.9 cc. Since the pressure of ethylamine is about 1.4 atmospheres at 25°, this introduces a correction of only 0.01 mv. in the e. m. f. of the Lewis and Keyes cell, which is much less than their experimental error. The correction in their temperature coefficient is relatively more important, giving a value of −0.000273. These calculations show that the correction becomes important only at the higher temperatures.

We can now combine equation (1) with the measurements of Lewis and Keyes to give the activity of the potassium referred to the solid metal as standard state

$$\log \frac{a_2}{N_2} = -\frac{5{,}695.6}{T} - \frac{27.69}{T^{0.77700}} + 3.3249 + \frac{2446}{T^{0.77700}} \left\{ N_2 + 3430 N_2^4 \right\} \pm 0.0017 \qquad (2)$$

Curves obtained with the aid of this equation are shown in Fig. 2. If Raoult's law were obeyed, $\log a_2/N_2$ would be independent of the concentration and would approach zero at the melting point of potassium.

With the aid of the above equation one may now obtain three relative partial molal quantities, namely, the free energy, entropy and heat content. The reference state for mercury is the pure liquid and for potassium is the solid metal. The relative partial molal free energy is obtained by adding $\log N_2$ and multiplying equation (2) by $RT \log_e 10$, giving

$$\begin{aligned} \overline{F}_2 = {} & -26{,}051 + 4.5739\ \{\log_{10} N_2 + 3.3249\}\ T + \\ & 4.5739\ \{2446(N_2 + 3430 N_2^4) - 27.69\}\ T^{0.22300} \pm 2 \qquad (3) \end{aligned}$$

By differentiating equation (3) with respect to the temperature the relative partial molal entropy is obtained

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(6) Lewis and Keyes, THIS JOURNAL, **34**, 119 (1912).

$$\bar{S}_2 = -15.21 - 4.5739\log_{10}N_2 - 1.0200\ \{2446(N_2 + 3430N_2^4) - 27.69\}\ T^{-0.77700} \pm 0.1 \qquad (4)$$

Finally from the relation $H = F + TS$ the relative partial molal heat content can be obtained

$$\overline{H}_2 = -26{,}051 + 3.5539\ \{2446(N_2 + 3430N_2^4) - 27.69\}\ T^{0.22300} \pm 20 \qquad (5)$$

Four equations may be obtained for the mercury analogous to equations 2–5. Substituting in the Duhem equation, d log $(a_1/N_1) = -(N_2/N_1)$ d log (a_2/N_2), the value of log (a_2/N_2) given by equation (2), and integrating we obtain the activity of the mercury as a function of N_2 and T. The integration constant is zero inasmuch as at zero concentration of potassium log a_1/N_1 equals zero. In this way equation (6) is obtained

$$\log\frac{a_1}{N_1} = -\frac{2446}{T^{0.77700}}\left\{\frac{N_2^2}{2} + \frac{N_2^3}{3} + \frac{N_2^4}{4} + 13{,}721\left(\frac{N_2^5}{5} + \frac{N_2^6}{6}\ldots\right)\right\} \qquad (6)$$

Following the method just employed for potassium three more equations may be derived for mercury.

$$\overline{F}_1 = 4.5739\left[T\log_{10}N_1 - 2446T^{0.22300}\left\{\frac{N_2^2}{2} + \frac{N_2^3}{3} + \frac{N_2^4}{4} + 13{,}721\left(\frac{N_2^5}{5} + \frac{N_2^6}{6}\ldots\right)\right\}\right] \qquad (7)$$

$$\overline{S}_1 = -4.5739\left[\log_{10}N_1 - 545T^{-0.77700}\left\{\frac{N_2^2}{2} + \frac{N_2^3}{3} + \frac{N_2^4}{4} + 13{,}721\left(\frac{N_2^5}{5} + \frac{N_2^6}{6}\ldots\right)\right\}\right] \qquad (8)$$

$$\overline{H}_1 = -8693T^{0.223}\left\{\frac{N_2^2}{2} + \frac{N_2^3}{3} + \frac{N_2^4}{4} + 13{,}721\left(\frac{N_2^5}{5} + \frac{N_2^6}{6}\ldots\right)\right\} \qquad (9)$$

The Solid Phase

We turn now to a discussion of the data involving amalgams in which a solid phase is present. These data are recorded in the second column of Table II. The plot of these measurements is shown by the steep curve in Fig. 3. The equation for this curve is

$$\Delta E = 0.00533 + 1.5153 \times 10^{-3}(T - 273.2) + 6.94 \times 10^{-6}(T - 273.2)^2 \qquad (10)$$

On the same plot are shown the curves for single-phase amalgams, points to the left of the curve of equation (10) representing supercooled amalgams. These five curves were drawn with the aid of equation (1). Each of the five curves thus represents an amalgam of known concentration. Each intersection with the two-phase amalgam curve gives a concentration and a temperature. Thus by simultaneous solution of equations (1) and (10) the data of Table IV for the solubility of potassium in mercury have been obtained. These data are shown graphically in Fig. 4. The equation for this curve is

$$x = 0.00252 + 8.12 \times 10^{-5}(T - 273.2) + 8.40 \times 10^{-7}(T - 273.2)^2$$

in which "x" is the weight fraction of potassium in the saturated amalgam.

Table IV

The Solubility of Potassium in Mercury

Values of the mole fraction are obtained by simultaneous solution of equations (1) and (10)

Temp., °C.	Mole fraction	Weight fraction	Temp., °C.	Mole fraction	Weight fraction
0	0.01271	0.00250	18.82	0.02191	0.00435
6.15	.01544	.00305	23.09	.02428	.00483
14.35	.01951	.00386	25.00	.02536	.00505
15.00	.01986	.00393	26.79	.02638	.00525

The free energy and heat of formation of the solid phase may also be calculated from these data. Smith and Bennett[7] have shown that the solid phase in equilibrium with dilute potassium amalgams has the composition represented by KHg_{12}. At equilibrium the free energy of solution of this compound in the liquid is zero. The free energy of formation of the compound is, therefore, just the sum of the relative partial molal free energies of the elements in the liquid. $\Delta F = 12\bar{F}_1 + \bar{F}_2$. $\bar{F}_1$ is found from equation (7) to be -29.43 calories and $\bar{F}_2$ is found from equation (3) to be $-23{,}077$ calories. Therefore ΔF for the formation of solid KHg_{12} from the elements is $-23{,}430$ calories.

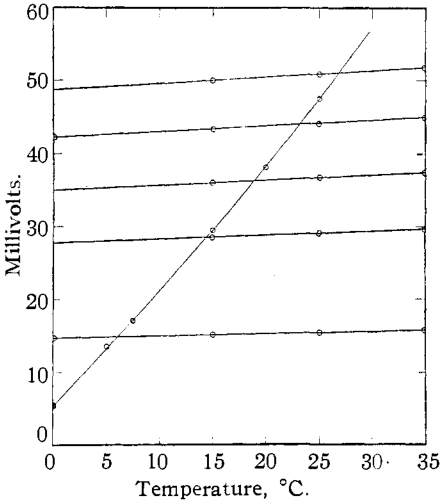

Fig. 3.—The e. m. f. of two-phase amalgams against amalgam VI. Also corresponding values for single phase amalgams against amalgam VI.

Under the restriction that the solution is to remain saturated F_1 and F_2 are functions of the temperature alone and

$$\frac{d\Delta F}{dT} = 12\frac{d\bar{F}_1}{dT} + \frac{d\bar{F}_2}{dT}, \text{ and}$$

$$\frac{d\bar{F}_1}{dT} = \frac{\partial \bar{F}_1}{\partial T} + \frac{\partial \bar{F}_1}{\partial N_2}\frac{dN_2}{dx}\frac{dx}{dT} = -\bar{S}_1 + \frac{\partial \bar{F}_1}{\partial N_2}\frac{dN_2}{dx}\frac{dx}{dT}$$

From equation (8) $\bar{S}_1$ is 0.6166, from equation (7) $\partial\bar{F}_1/\partial N_2$ is -1877 calories per mole per mole fraction unit. From the definition of the mole fraction dN_2/dx is 4.9235 when N_2 is 0.02536. From equation (11) dx/dT is 0.0001232 at 25°. Consequently $d\bar{F}_1/dT = -1.2002$ calories per mole.

The easiest way to obtain $d\bar{F}_2/dT$ is to go back to the e. m. f. data. We may write

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(7) Smith and Bennett, This Journal, **32**, 624 (1910).

$$\frac{d\bar{F}_2}{dT} = -23{,}065\left(\frac{dE_1}{dT} + \frac{dE_2}{dT}\right)$$

in which E_1 is the e. m. f. measured by Lewis and Keyes, potassium to our amalgam VI, and E_2 is the e. m. f. of the saturated amalgam to this same amalgam VI. After the slight correction for the pressure effect dE_1/dT is -0.000273. Equation (10) on differentiation gives dE_2/dT as -0.001862. Hence $d\bar{F}_2/dT$ is the sum of these two values multiplied by 23,065 or 49.24 calories. Hence $d\Delta F/dT = -\Delta S = 49.23 - 14.49 = 34.84$ calories per mole per degree. From the relation $\Delta H = \Delta F + T\Delta S$ one finds that $\Delta H = -33{,}819 \pm 30$ calories per mole.

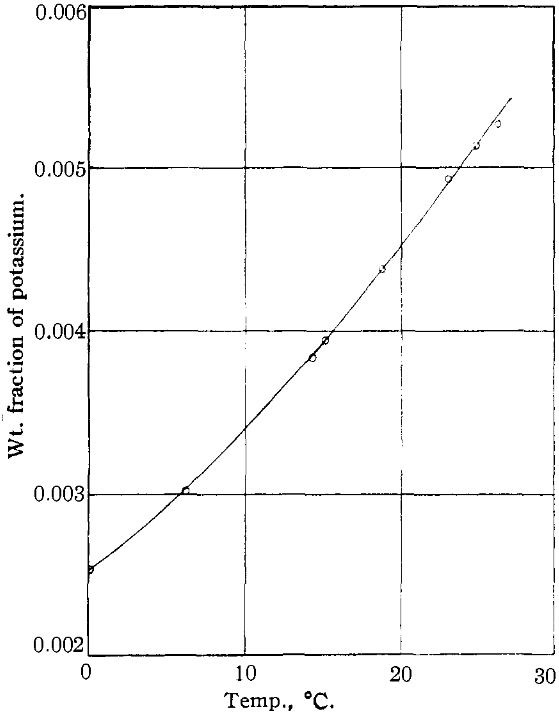

Fig. 4.—The solubility of potassium in mercury.

These figures enable one to calculate the heat of solution of the compound in the saturated solution. Equations (5) and (9) enable one to calculate the heat of formation of the compound in solution and give a value of $-25{,}705$ calories. Hence the heat of solution of the compound in saturated solution is 8114 calories per mole. Finally, equation (5) gives the heat of solution of potassium at infinite dilution as $-26{,}150$ calories. Hence the heat of solution of the compound in a large amount of mercury is 7669. Finally the relative partial molal heat content of the compound in the saturated solution referred to the infinitely dilute solution as the standard state is −445 calories.

Discussion of Results

In discussing the extreme deviations from Raoult's law exhibited by potassium amalgams we will approach the subject in two quite different ways. We will discuss first the significance of compound formation and later some inferences to be drawn from the thermodynamic data.

One may start by assuming that there are compounds in the liquid phase which have the same formulas as the solid phases indicated by the phase diagram. One may also assume that these compounds are only slightly dissociated in the liquid phase and that the various molecular species obey Raoult's law. This last assumption is only a first approximation. It has previously been shown that with the aid of these assumptions one may account for the vapor pressure of mercury and for the activity of sodium in dilute sodium amalgams.[8] The agreement of the calculated vapor pressures with the experimental values is not very good if one uses only the formulas of definitely established solid compounds. There is some uncertainty, however, as to just how many of these compounds exist and there is no proof that the same compounds exist in solution. By assuming additional compounds in solution one can obtain excellent agreement with the experimental data. This treatment does not prove that these compounds exist but indicates that the experimental facts are not incompatible with compound formation. The experimental data of Richards and Conant which were used in the above computation are not of sufficient accuracy in the most dilute range of concentration to enable one to say whether the hypothesis of compound formation accounted well for the data or not. On a plot such as that in Fig. 2 the data of Richards and Conant showed a decided dropping off in the range of low concentration. A curve obtained by assuming only one compound, $NaHg_{16}$, on the other hand, showed a slight flattening out in the range of small concentration. The data obtained in this research on potassium, on the other hand, show not the slightest deviation from a straight line in the range of small concentration. Our most dilute amalgam was about one-tenth the concentration of the most dilute amalgam of Richards and Conant. One could doubtless obtain a curve which would fit the experimental data by assuming a compound containing still a larger percentage of mercury. Such a procedure at present, however, seems quite useless. We have no reason for thinking that the various molecular species obey Raoult's law to anything more than a first approximation, and until we can calculate or determine these deviations it is impossible to push the hypothesis of compound formation farther. At present it is only possible to say that a large part of the deviation from Raoult's law exhibited by amalgams of the alkali

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[8] Bent and Hildebrand, THIS JOURNAL, **49**, 3011 (1927).

metals may be accounted for by assuming slightly dissociated compounds in the liquid phase.

Turning now to the partial molal quantities given in Table III we see some interesting facts. All of these partial molal quantities change very little with changing temperature. This result is perhaps due in part to the limited amount of data on cells containing potassium. Thus Lewis and Keyes made measurements at but two temperatures in order to obtain the temperature coefficient of the e. m. f. If we assume that d^2E/dT^2 is zero we are probably not introducing a very serious error in our computations since the first derivative is not large. However, it is just this assumption which causes the partial molal entropy and heat of potassium to be essentially constant. Since $\bar{F}_2$ is large it follows that it will not change much with the temperature but will change more than the heat or entropy as may be seen from the equation $\bar{F}_2 = \bar{H}_2 - T\bar{S}_2$. Multiplying $\bar{S}_2$ by T causes this product to change with the temperature even when $\bar{S}_2$ is constant. Turning now to the curves in Fig. 2 we note that their displacement with changing temperature is, therefore, due chiefly to the T coming into the equation $\bar{F}_2 = RT \ln a_2$.

The effect of temperature on deviations from Raoult's law has been discussed by Shibata and Oda[9] in a recent article in which they come to the conclusion that at 300–400° these amalgams become ideal solutions! This seems an extraordinary conclusion based on the extrapolation of an equation which is essentially empirical. Thus they find that the slope of their curves, when plotting data as in Fig. 2, is decreasing as the temperature rises. Assuming that the decrease in slope is a linear function of the temperature they arrive at a comparatively low temperature at which amalgams should become ideal solutions. In a similar manner if we take equation (2) which expresses our results within the error of our experiments we find that the coefficient of N_2 does not become zero until the temperature becomes infinite. Neither of these conclusions can be justified. In both cases empirical equations are being extrapolated far beyond the range of temperature for which they have been found to hold. This point will be discussed further in the next paragraph.

Another significant observation is that the partial molal entropy of the potassium is negative. For an ideal solution it would be positive and equal to $-R \ln N_2$. This rather large negative value more than offsets the small positive partial molal entropy for mercury with the result that there is actually a decrease in entropy in forming all but the most dilute amalgams from the elements. This clearly indicates that the amalgam does not have the random distribution of atoms that one would expect for an ideal solution but that some process, such as compound formation, has taken place to decrease the entropy.

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[9] Shibata and Oda, *J. Chem. Soc. Japan*, **52**, 352–364 (1931).

One must conclude from these facts that the various physical theories of binary mixtures are not applicable to potassium amalgams.[10] Not only is the entropy very much less than that which is assumed by the physical theories but there is a large contraction during the formation of the amalgam. This latter fact prevents one from calculating surface fractions or volume fractions as is done by Langmuir and Scatchard. However, these values would differ little from the mole fraction and could not be of significance in such dilute solutions. In view of the fact that potassium amalgams are so decidedly irregular, using the definition of regular given by Hildebrand, it is perhaps surprising that the data may be represented by the same equations as have been derived by the various physical theories. It is not apparent at first glance that this is so. However, equations (2) and (6) reduce to much simpler equations at constant temperature if one is not interested in an accuracy of more than a few tenths of a per cent. Equation (2) then assumes the familiar form $\log a_2/N_2 = \beta N_2$ and equation (6) becomes $\log a_1/N_1 = {}^1/_2\beta N_2^2$. At higher concentrations, which unfortunately cannot be secured at room temperature on account of the appearance of a solid phase, doubtless such simple equations could not be used. Perhaps the most significant inference which one may draw from these facts is that considerable caution is necessary in drawing any conclusion as to the correctness of a theory from the fact that the data agree with the results of the theory. Thus potassium amalgams very definitely do not conform to the assumptions of the theory of Heitler, yet they may be described quite well by the form of equation obtained by him.

In spite of the very "irregular" nature of potassium amalgams, a rather simple picture of the system is still possible. We may sum up the facts which we now have as follows. There are large forces acting between mercury and potassium atoms ($\overline{H}_2$ is large and negative). The forces as a first approximation are not affected by a rise in temperature. The organization or arrangement of atoms in the amalgam is also not affected, as a first approximation, by a change in temperature ($\overline{S}_1$ and $\overline{S}_2$ change little with temperature). The activity of potassium, however, is increased to a marked degree by increasing the temperature. This may be considered to be due to the fact that the heat of vaporization of potassium from an amalgam is much larger (due to $\overline{H}_2$ being large and negative) than from the pure metal and hence the vapor pressure increases much more rapidly from the amalgam than it does from the pure metal.

Finally, we might point out that some of the amalgams used in this investigation were kept for as much as six months. During this time there was apparently no change in the activity of the alkali metal. Some of the cells were studied for many weeks and also showed no change in e. m. f. with either variation in temperature or with the lapse of time. If these

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(10) Scatchard, *Chem. Rev.*, **8**, 321 (1931).

amalgams were colloidal, as suggested by Paranjpe and Joshi,[11] one would not expect such reproducibility.

Summary

1. Galvanic cells have been studied in which the reaction is the transfer of potassium from an amalgam of higher concentration to one of lower concentration. The e. m. f. of such cells has been determined as a function of temperature and concentration of the amalgam.
2. The partial molal free energy, heat and entropy of the potassium and mercury have been calculated.
3. The solubility of potassium in mercury has been determined from 0–50°.
4. The free energy and heat of formation of the compound KHg_{12} and the heat of solution of this compound have been determined.
5. The significance of these data is discussed.

[11] Paranjpe and Joshi, *J. Phys. Chem.*, **36**, 2474 (1932); Bent, *ibid.*, **37**, 431 (1933).

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Kinetics of Gas Explosions. IV. Ozone Explosions Induced by Hydrogen[1,2]

BY BERNARD LEWIS[3]

Introduction

The influence of hydrogen on the thermal decomposition of ozone was studied by Belton, Griffith and McKeown.[4] They found that two reactions occurred simultaneously, the decomposition of ozone and the formation of water. The addition of hydrogen to ozone increased the specific rate of ozone decomposition. For example, their bimolecular velocity constant of ozone decomposition increased sixfold when 156 mm. of hydrogen was added to a mixture of 70 mm. of ozone and 650 mm. of oxygen. The velocity constant for the formation of water by the assumed reaction $H_2 + O_3 = H_2O + O_2$ increased less rapidly, it being only threefold on increasing the hydrogen pressure from 33 mm. to 156 mm. in a similar mixture. The amount of hydrogen converted to water was small in comparison with the ozone decomposed. The available data published by these authors indicate that the percentage of hydrogen converted (measured when most of the ozone had decomposed) depends much more on the ozone concentration than on the hydrogen concentration. It increases

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[2] Parts I, II, III, with W. Feitknecht, THIS JOURNAL, **53**, 2910 (1931); **54**, 1784, 3185 (1932).

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[4] Belton, Griffith and McKeown, *J. Chem. Soc.*, **128**, 3153 (1926).