

## THE VAPOR PRESSURE OF SOLID SODIUM AND SOLID POTASSIUM AMALGAMS

BY FRANKLIN E. POINDEXTER

## ABSTRACT

**The vapor pressure of solid sodium and potassium amalgams.**—A Buckley ionization gauge was used to measure the vapor pressure of eight sodium amalgams ranging in concentration from 1 : 1 to 15 : 1 mol ratio of Hg to Na and of 3 potassium amalgams whose concentrations were 5 : 1, 10 : 1 and 21 : 1, Hg : K. The vapor pressure of each amalgam was measured at a number of temperatures which were determined by means of a platinum resistance thermometer. The pressures measured varied from approximately  $10^{-8}$  mm to  $10^{-3}$  mm over a maximum temperature range of from  $-56^{\circ}$  to  $90^{\circ}\text{C}$ . *The log  $p$  vs  $1/T$  graphs for the different amalgams were found to be approximately straight lines.* The difference between the free energy calculated by R. H. Gerke and the internal energy change as calculated in this work shows that the log  $p$  vs  $1/T$  graphs can be expected to be straight within the experimental error. The heats of reaction were calculated by means of the Van't Hoff reaction isochore, the pressures at different temperatures for these calculations being taken from the log  $p$  vs  $1/T$  graphs. These heats of reaction for the sodium amalgams varied from 15,000 cal. in the case of the amalgams rich in Hg to 14,000 cal. for the 2 : 1 amalgam. This small heat difference over such a wide range of concentrations indicates that most of the heat of reaction between Na and Hg is liberated in the formation of the initial compounds. The heats of reaction for the potassium amalgams were calculated to be 25,500 cal.

**Duration of the efficiency of a sodium mercury vapor trap.**—The vapor pressure of 1 : 1 sodium amalgam was extrapolated to  $20^{\circ}\text{C}$  and found to be  $3 \times 10^{-8}$  mm. The time necessary for sufficient mercury to diffuse through 100 cm of tubing having an internal diameter of 1 cm to form a 1 : 1 amalgam with 10 g. of sodium was found to be 1554 days. That is, a sodium mercury vapor trap containing 10 g. of sodium should hold the mercury vapor beyond the trap down to  $10^{-8}$  mm for 1500 days under the prescribed conditions.

**The relation between the free and internal energy changes of potassium and sodium.**—The internal energy change of potassium as calculated from the log  $p$  vs  $1/T$  graphs are somewhat greater than the free energy change as calculated by R. H. Gerke. This indicates that the temperature gradient of the e.m.f. of concentration cells should be small and negative. There seems to be no experimental data with which to check this prediction. For sodium Richards and Conant found that the temperature gradient of the e.m.f. of concentration cells was comparatively large and positive, thus indicating that the free energy change is considerably greater than the internal energy change. R. H. Gerke calculated the free energy change from electrochemical data for a 5 : 1, Hg : Na sodium amalgam to be 18,300 cal. which is of the order of 3,000 cal. greater than the internal energy change as calculated from the log  $p$  vs  $1/T$  graphs. That is, the present work is in agreement with the above.

THE vapor pressure of each of a number of solid sodium and potassium amalgams has been measured at a series of temperatures and the heat of formation calculated by means of the Van't Hoff Reaction Isochore. Notwithstanding the fact that the literature is practically devoid of data on the heats of reaction between these alkalis and mercury, yet, in the case of sodium amalgams, agreement is found both with Cady's work on heat of dilution and with that of Richards and Conant<sup>1</sup> on the e.m.f. of concentration cells. That is, the present work indicates that the heat of dilution is small compared to the heat of reaction involved in the formation of the initial compounds, and also that the heat of reaction, or total internal energy change  $U$ , is considerably less than the change in free energy as indicated by the comparatively large temperature gradient of the e.m.f. of concentration cells. In the case of potassium, no work has been done on the heat of dilution or on the e.m.f. of concentration cells and, consequently, no comparisons can be made. The present work indicates, however, that the temperature gradient of the e.m.f. of concentration cells of potassium in mercury may be expected to be small and negative.

There is also a matter of very practical importance involved in the study of the vapor pressure of the amalgams rich in these alkalis. This has been brought about by the recent discovery<sup>2,3</sup> in this laboratory that a sodium or potassium trap is almost, if not quite, as effective as a liquid air trap for stopping mercury vapor. A knowledge of the vapor pressure of an amalgam enables one to calculate the time that must elapse for sufficient mercury to diffuse into the trap to form this amalgam. That is, the time it takes for the mercury vapor beyond the trap to reach a given value can be estimated with a fair degree of accuracy. Such a calculation has been made for a sodium trap.

#### APPARATUS

The apparatus used is shown diagrammatically in Fig. 1, the essential features consisting of a Buckley<sup>4</sup> ionization gauge  $B$ , an amalgam reservoir  $R$ , a potassium mercury vapor trap  $T$  and a McLeod gauge with a high vacuum mercury diffusion pump and a Cenco rotary fore-pump. The McLeod gauge and pumps are not shown

<sup>1</sup> A fairly complete bibliography on Na amalgams will be found in a paper by Richards and Conant, *J. Am. Chem. Soc.* **44**, 610 (1922).

<sup>2</sup> F. E. Poindexter, *J.O.S.A. & R.S.I.* **9**, 629 (1924).

<sup>3</sup> Hughes and Poindexter, *Phil. Mag.* **50**, 432 (1925).

<sup>4</sup> Buckley, *Proc. Nat. Acad. Sci.* **2**, 683 (1916).

in the diagram. The most important part of this set-up is the ionization gauge and its accessories. Since it was found desirable to modify the type of Buckley gauge as used by Dushman<sup>5</sup> and others, it is thought desirable to describe the gauge here used in some detail.

The action of the ionization gauge depends upon the ionization of the gas molecules by electrons which are driven from the filament *F*, to the plate *P*, the ions thus formed being collected by the grid *G*. Now Dushman,<sup>5</sup> in his extended research, finds that the straight line relation between the ionization and the electron current (within

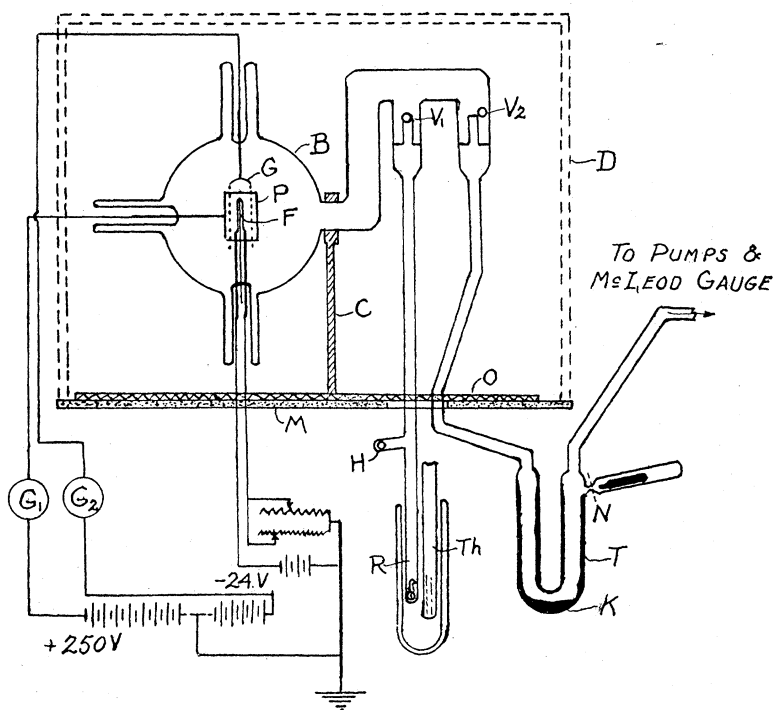


Fig. 1. Diagram of apparatus.

certain limits) holds only when the paths of all of the electrons are the same length. He also calls attention to the importance of separating the lead-in wires as much as possible in order to prevent electrical leakage over the glass. The present structure incorporates these features. However, the ion collecting grid *G*, is not a filament as Dushman<sup>5</sup> found necessary in his modification by reason of the outgassing difficulties. It was found in this and the three<sup>2,3,6</sup> pre-

<sup>5</sup> S. Dushman, Phys. Rev. **17**, 7 (1921).

<sup>6</sup> F. E. Poindexter, Phys. Rev. **26**, 859 (1925).

ceding researches that after a few days spent in alternately baking at 400°C, and bombarding the plate at red heat, the evolution of gas was below the limit of the gauge, i. e. less than  $4 \times 10^{-9}$  mm. The present design has the added, very important advantage that a filament may be replaced very easily without disturbing the remaining parts. In the writer's<sup>6</sup> work on mercury vapor pressure, an ionization gauge was described wherein protecting collars were used about the plate and grid stems in order to prevent electrical leakage. These collars are not necessary if mercury vapor is carefully excluded during the bombardment of the plate, sputtering being thus prevented.

The filament *F*, is a straight loop of 10 mil tungsten wire braced by means of a 20 mil tungsten wire thrust into the glass between the leads. The grid is a spiral of 7 mil tungsten wire carried by a 10 mil tungsten frame extending down each side, each end of the spiral being welded to the supporting frame. The plate *P* is of nickel and somewhat longer than the filament while the grid *G* is longer than the plate. This extra length in the plate and grid is a precaution against stray ions or electrons collecting upon the glass walls of the gauge which may give erratic results. The main part of the gauge is a one liter Pyrex flask. It is made large so that its temperature while the gauge is in use is considerably lower than the outgassing temperature.

The plate *P* was maintained at +250 volts relative to the filament *F*, by means of a storage battery. The galvanometer  $G_1$ , used to measure the electron current from filament to plate was a Leeds and Northrup type *P* galvanometer having a sensitivity of  $2.66 \times 10^{-8}$  amp. per scale division. A universal shunt was used with  $G_1$  which multiplied the electron current readings in steps of 10. The deflection of  $G_1$  was held at 100 scale divisions throughout the experiment, the shunt being set at 10 to 1, 100 to 1, and 1000 to 1. This eliminated any possibility of error due to non-uniformity of the galvanometer scale. The grid *G* was maintained at -25 volts with respect to the filament. The positive ions formed by the collision of electrons with the molecules of gas between *F* and *P* were collected on the grid *G*. The ion current from *G* was measured by the highly sensitive, critically damped, Leeds and Northrup type *R* galvanometer  $G_2$ , having a sensitivity of  $8 \times 10^{-10}$  amp per scale division. The sensitivity of this galvanometer was found to be constant over all parts of the scale.

The amalgam reservoir *R*, and the mercury vapor trap *T*, were connected to the ionization gauge through the steel ball valves  $V_1$  and  $V_2$ . The glass seats of these valves were repeatedly ground and polished with similar steel balls and the finest of emery flour—obtained by

means of fractional settling in water—to the point where the dry seats would hold the 1/2" ball in an inverted position for 5 minutes when partially exhausted by suction. The leakage of these valves was negligible at the pressures used in this work. The valves were opened and closed by means of an electromagnet.

A *U*-tube mercury vapor trap *T* was placed between the apparatus and the McLeod gauge. Clean potassium was driven into the trap and the empty container sealed off as indicated at *N*.

A platinum resistance thermometer of approximately 25 ohms resistance and carrying a current of .01 amperes was used to determine the temperatures. The potentiometer balance method against a standard resistance held at constant temperature was used, the balance being obtained through a Leeds and Northrup type *R* galvanometer. The platinum thermometer was calibrated three times at the ice, steam, and liquid oxygen points, at intervals of a few weeks. These calibrations checked. The constants and Pt differences found by Callender and others<sup>7</sup> were in close agreement with those of this thermometer, and it is thought that the temperatures are probably correct to 1/100°.

#### PREPARATION OF MATERIALS

The mercury used to prepare the amalgams was twice distilled in a current of air in a modified Hulett still. The purification of the alkali metal is more important than the redistillation of the mercury. In the first place, the oil in which sodium or potassium has been packed must be removed down to the last trace before introduction

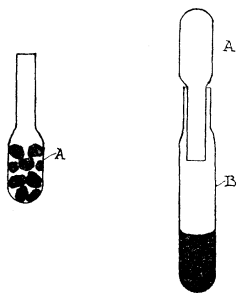


Fig. 2. Apparatus for cleaning the alkali metals.

into a high vacuum system. Secondly, these metals take up and retain gases in large quantities. While it seems that these gases can not be removed absolutely, yet much can be done by reflux distilla-

<sup>7</sup> E. Vanstone, *J. Chem. Soc. (London)* **105**, 2617 (1914).

tion. In order to remove the oil referred to above, the metal was washed and rinsed in benzol. Then it was placed in a large Pyrex test tube to which a smaller tube was sealed as shown at *A*, Fig. 2. This entire tube was heated in a bunsen flame till the oils were driven out and the alkali vapor began to burn at the mouth of the tube. The tube *A* was then permitted to cool and placed in juxtaposition with a second tube *B* into which the metal was driven by heating.

The outgassing and bottling arrangement for the alkali metals is shown in Fig. 3. The tube *B* of Fig. 3 was sealed on to the bottle system at *C*, through a thick walled capillary having an internal

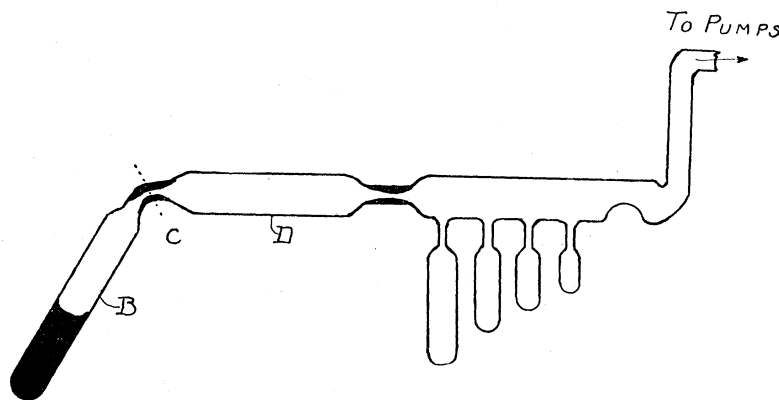


Fig. 3. Arrangement for bottling the alkali metals.

diameter of approximately 1 mm. After outgassing the glass parts of the system by heating with a hand burner, the lower end of the tube *B* was heated so that the alkali metal condensed in the upper part and ran back. This reflux condensation was continued for an hour or more, then the metal was evaporated into *D* and *B* sealed off at *C*. The clean metal was then driven through another capillary into the bottles which were sealed off with a hand blow torch. The weights of the empty bottles together with the weight per cm of the necks were recorded. In this way, the weight of the alkali metal in each bottle was determined to within .01 g.

#### PREPARATION OF THE AMALGAMS

It is a comparatively easy matter to prepare an amalgam of known composition by using one of the above described weighed bottles of alkali. Fig. 4 shows the necessary set up. A weighed quantity of mercury was run into the flask *A* and the bottle of alkali *B* sealed into the side neck *C*. The apparatus was exhausted through a flexible

connection *E* and the different parts outgassed by baking with a hand blow torch. The mercury was then run into the thin walled bottles *D* and the alkali metal run into *A*, the side neck *C*, being sealed off at *F* and the whole arrangement allowed to cool. The mercury was then run in on the sodium or potassium in small quantities by tilting *A*. As soon as all the mercury was mixed with the alkali, and still hot from the reaction, the flask *A* was sealed off at *G*. The whole was carefully heated in a large bunsen flame until the amalgam was entirely molten, care being taken not to heat it too much since it might have exploded from the mercury vapor pressure.\*

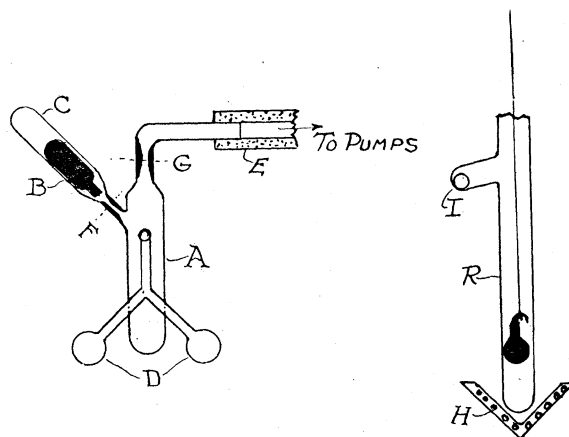


Fig. 4. Apparatus for preparations of the amalgams.

The molten amalgam was run into the thin walled bottles *D*, one of which was immediately sealed off and lowered into the electrically heated reservoir *R*, by means of a wire. In this way the amalgam was kept molten till the whole apparatus, Fig. 1, was outgassed and ready to run. When a concentrated amalgam solidifies, it usually breaks the bottle, hence the necessity of keeping the reservoir hot till the outgassing is completed. The glass bottle containing the amalgam was broken by dropping the steel ball *I* upon it, the ball being manipulated by means of an electromagnet.

#### EXPERIMENTAL METHOD

Probably the most important part of the experimental procedure was the outgassing. There were four sources of gas; the metal parts

\* All of the amalgams appear to be dissociated in the liquid state. In fact, the mercury begins to distill out before the melting point is reached in the case of concentrated amalgams. On this account it was necessary to seal off the mixing chamber at *G*, Fig. 4.

in the system, the glass walls, the bottle of amalgam, and the mercury vapor trap. The base of an electric oven is shown at *m*, Fig. 1, upon which a clamp *C* was mounted to support the apparatus. An asbestos lined, removable metal box, represented by the broken line *D*, served as the oven in which the ionization gauge and the steel ball valves were subjected to prolonged baking at 400°C. In this manner the gas was removed from the glass walls and partially removed from the metal parts. After from 6 to 12 hours baking, the oven was removed and the plate subjected to electron bombardment from the filament by means of a 1/2 k.w. 10,000 volt transformer. This outgassing by electron bombardment was continued for several hours until the gas pressure was less than  $10^{-5}$  mm while hot. Then the oven was placed in position and the baking at 400°C resumed and continued till the pressure was less than  $10^{-5}$  mm. During the baking, the other glass parts, including the McLeod gauge, were outgassed by means of a hand blow torch.

The outgassed alkali metal used in the mercury vapor trap *T* was prepared in the same manner as that used in preparing the amalgams. After a bottle of this metal (potassium in this case) was driven into the trap and the side neck sealed off, as indicated at *N*, Fig. 1, it was subjected to additional reflux distillation, the upper parts of the trap serving as the condenser. While it seems impossible to drive all of the gas out of the potassium yet in this way it was reduced to such an extent that it did not interfere with the work as long as the trap was at room temperature. Whenever it was necessary to let air into the apparatus, the reflux distillation was repeated. (However, the letting in of air does not impair the efficiency of the mercury vapor trap as a trap.<sup>3</sup>) The test which was used in conjunction with the ionization gauge readings to determine the thoroughness of the outgassing of the whole apparatus was that the mercury should stick in the top of the reading tube of the McLeod gauge after twelve hours standing with the pumps shut off, i. e.,  $p < 10^{-5}$  mm.

The temperatures were controlled by means of a thermos bottle bath about the amalgam reservoir. This bottle was cooled to such a temperature that the vapor pressure was below the limit of the gauge, and then warmed up in steps to 5° to 10° by the addition of small quantities of warmer liquid. Forty minutes were allowed for the equalization of the temperature, and twenty minutes for the equalization of pressure. That is, valve *V*<sub>1</sub>, Fig. 1, was closed and valve *V*<sub>2</sub> opened during the first 20 min. Then *V*<sub>1</sub> was opened and *V*<sub>2</sub> closed and the pressure allowed to build up for 20 min. In most cases, the pressure became steady in ten minutes.



It was necessary in some instances to correct for an initial gas effect. This correction was determined by cooling the amalgam to such a temperature that its vapor pressure was below the limit of the gauge and then allowing the pressure to build up for a period of 20 minutes at a time at consecutively increased temperatures. These pressures were approximately constant until the temperature was reached at which the vapor pressure of the amalgam began to play a part. This initial, constant pressure was subtracted from the pressure that built up in the subsequent periods. The correction was negligible in all of the amalgams with the exception of numbers 1, 2 and 3 (see col. 4 Table XII) and these will be discussed under Gas Effects.

The amalgams were analyzed for sodium or potassium by titrating the excess of dilute  $\text{H}_2\text{SO}_4$  used to acidify the amalgam, with  $\text{NaOH}$ , using phenolphthalein as indicator, the acid solution being boiled before neutralization.\* The mercury was weighed direct. In all cases the mercury broke up into fine permanent globules indicating the complete removal of the alkali as noted by Richards and Daniels.<sup>8</sup>

#### DATA AND RESULTS

The ionization gauge is particularly well adapted for pressures below  $10^{-2}$  mm. However, it is an indirect method and the ionization for a given electron current will be different for different gases. It is, therefore, necessary to calibrate the gauge at some one temperature for mercury vapor. Then the ratio of the ionization in that gas at any other temperature to that at the calibrating temperature is equal to the ratio of the respective pressures. That is, the vapor pressure,  $P'$ , in the ionization gauge  $G$ , is proportional to the ratio of the positive ion current  $I$ , to the electron current  $E$ , i. e.

$$P' = KI/E$$

Knudsen's<sup>9</sup> value of  $P = .0001846$  mm at  $0^\circ\text{C}$  was used to calibrate the gauge. When  $P'$  is in mm of mercury,  $I$  in scale divisions and  $E = 1000$  scale divisions, then

$$K = 3.38 \times 10^{-6} \text{ mm/1 scale division of ion current.}$$

The experimental data are given in Tables I to III. The values of  $P'$  in mm of mercury are given in column 3 of the tables as uncorrected pressures, because the pressures above the mercury in the amalgam reservoir are not directly in the ratio of the positive ion

\* The writer wishes to thank Prof. R. W. Pilcher of the Chemistry Department for making up the standard solutions used and for valuable suggestions as to the analysis.

<sup>8</sup> Richards and Daniels, *J. Am. Chem. Soc.* **41**, 1736 (1919).

<sup>9</sup> Knudsen, *Ann. d. Physik* **29**, 179 (1909).

current on account of the phenomenon of thermal effusion as pointed out by Knudsen,<sup>10</sup> West,<sup>11</sup> and others.

*Thermal effusion correction.* A correction of the pressure for thermal effusion between two regions of different temperature in a system is

TABLE I  
Vapor pressures of sodium-mercury amalgams.

Electron current scale divs.	Ion current scale divs.	Uncorrected pressure $P'$	True pressure $P$	Temp. of amalgams
(1) Hg:Na = .985:1				
100,000	12	$2.88 \times 10^{-7}$	$2.90 \times 10^{-7}$	44.6°C
"	17	$4.08 \times 10^{-7}$	$4.12 \times 10^{-7}$	47.5
"	33	$7.92 \times 10^{-7}$	$8.12 \times 10^{-7}$	57.1
"	78	$1.87 \times 10^{-6}$	$1.95 \times 10^{-6}$	67.3
"	118	$2.83 \times 10^{-6}$	$2.97 \times 10^{-6}$	72.2
"	230	$5.52 \times 10^{-6}$	$5.85 \times 10^{-6}$	79.9
"	513	$1.23 \times 10^{-5}$	$1.32 \times 10^{-5}$	90.8
(2) Hg:Na = 1.19:1				
100,000	11.0	$2.64 \times 10^{-7}$	$2.66 \times 10^{-7}$	46.3
"	23.7	$5.69 \times 10^{-7}$	$5.78 \times 10^{-7}$	51.4
"	38.5	$9.24 \times 10^{-7}$	$9.46 \times 10^{-7}$	56.4
"	71.3	$1.71 \times 10^{-6}$	$1.75 \times 10^{-6}$	61.4
"	104.7	$2.51 \times 10^{-6}$	$2.61 \times 10^{-6}$	66.0
"	188.0	$4.51 \times 10^{-6}$	$4.73 \times 10^{-6}$	72.0
"	295.0	$7.32 \times 10^{-6}$	$7.48 \times 10^{-6}$	77.0
"	707.0	$1.70 \times 10^{-5}$	$1.82 \times 10^{-5}$	84.3
(3) Hg:Na = 1.63:1				
100,000	2.5	$8.45 \times 10^{-8}$	$8.08 \times 10^{-8}$	9.58
"	7.0	$2.36 \times 10^{-7}$	$2.28 \times 10^{-7}$	14.46
"	12.0	$4.06 \times 10^{-7}$	$3.96 \times 10^{-7}$	21.39
"	25.5	$8.63 \times 10^{-7}$	$8.47 \times 10^{-7}$	25.86
"	41.0	$1.385 \times 10^{-6}$	$1.38 \times 10^{-6}$	31.08
"	65.5	$2.20 \times 10^{-6}$	$2.21 \times 10^{-6}$	36.31
"	101.5	$3.43 \times 10^{-6}$	$3.45 \times 10^{-6}$	40.85
"	157.0	$5.31 \times 10^{-6}$	$5.45 \times 10^{-6}$	48.45
"	389.5	$1.32 \times 10^{-5}$	$1.36 \times 10^{-5}$	59.75
(4) Hg:Na = 1.96:1				
100,000	23.0	$5.52 \times 10^{-7}$	$5.01 \times 10^{-7}$	-14.17
"	34.7	$8.33 \times 10^{-7}$	$7.62 \times 10^{-7}$	-10.36
"	36.0	$8.64 \times 10^{-7}$	$7.96 \times 10^{-7}$	-6.02
"	51.0	$1.22 \times 10^{-6}$	$1.13 \times 10^{-6}$	-3.67
"	75.5	$1.81 \times 10^{-6}$	$1.69 \times 10^{-6}$	-.08
"	90.8	$2.18 \times 10^{-6}$	$2.04 \times 10^{-6}$	+1.41
"	126.5	$3.07 \times 10^{-6}$	$2.86 \times 10^{-6}$	6.07
"	155.0	$3.72 \times 10^{-6}$	$3.52 \times 10^{-6}$	7.40
"	230.0	$5.52 \times 10^{-6}$	$5.24 \times 10^{-6}$	10.61
"	282.0	$6.77 \times 10^{-6}$	$6.47 \times 10^{-6}$	13.89
"	374.0	$8.98 \times 10^{-6}$	$8.58 \times 10^{-6}$	14.37
10,000	69.4	$1.67 \times 10^{-5}$	$1.70 \times 10^{-5}$	18.93
"	134.0	$3.23 \times 10^{-5}$	$3.31 \times 10^{-5}$	23.30
"	149.0	$3.58 \times 10^{-5}$	$3.69 \times 10^{-5}$	24.15
"	240.0	$5.76 \times 10^{-5}$	$5.98 \times 10^{-5}$	28.63
"	431.5	$1.03 \times 10^{-4}$	$1.08 \times 10^{-4}$	33.79
1,000	100.0	$2.40 \times 10^{-4}$	$2.57 \times 10^{-4}$	40.64
"	247.0	$5.93 \times 10^{-4}$	$6.41 \times 10^{-4}$	45.09
"	378.0	$9.07 \times 10^{-4}$	$9.91 \times 10^{-4}$	51.80

<sup>10</sup> M. Knudsen, Ann. d. Physik 31, 205 and 33, 1435 (1910).

<sup>11</sup> G. D. West, Proc. Phys. Soc. 31, 278 (1919).

TABLE I (continued)

Electron current scale divs.	Ion current scale divs.	Uncorrected pressure $P'$	True pressure $P$	Temp. of amalgams
		(5) Hg:Na = 3.41:1		
10,000	43.5	$1.04 \times 10^{-6}$	$1.02 \times 10^{-5}$	- 8.83°C
"	55.5	$1.33 \times 10^{-6}$	$1.30 \times 10^{-5}$	- 3.72
"	99.5	$2.39 \times 10^{-6}$	$2.38 \times 10^{-5}$	4.38
"	168.0	$4.03 \times 10^{-6}$	$4.04 \times 10^{-5}$	7.59
"	280.0	$6.72 \times 10^{-6}$	$6.80 \times 10^{-5}$	14.10
1,000	85.0	$2.04 \times 10^{-4}$	$2.13 \times 10^{-4}$	23.68
"	185.5	$4.44 \times 10^{-4}$	$4.68 \times 10^{-4}$	28.63
"	253.5	$6.07 \times 10^{-4}$	$6.48 \times 10^{-4}$	35.74
		(6) Hg:Na = 5.86:1		
100,000	16.0	$3.84 \times 10^{-7}$	$3.25 \times 10^{-7}$	-47.68
"	64.0	$1.54 \times 10^{-6}$	$1.33 \times 10^{-6}$	-36.74
"	168.0	$4.06 \times 10^{-6}$	$3.56 \times 10^{-6}$	-27.72
"	419.0	$1.01 \times 10^{-5}$	$9.02 \times 10^{-6}$	-19.26
10,000	156.0	$3.74 \times 10^{-5}$	$3.63 \times 10^{-5}$	-10.09
"	173.0	$4.15 \times 10^{-5}$	$4.02 \times 10^{-5}$	- 9.67
"	363.0	$8.72 \times 10^{-5}$	$8.58 \times 10^{-5}$	- 1.71
1,000	77.0	$1.85 \times 10^{-4}$	$1.86 \times 10^{-4}$	4.14
"	234.0	$5.62 \times 10^{-4}$	$5.75 \times 10^{-4}$	12.16
"	312.0	$7.49 \times 10^{-4}$	$7.69 \times 10^{-4}$	14.15
		(7) Hg:Na = 5.78:1		
100,000	8.5	$2.04 \times 10^{-7}$	$1.72 \times 10^{-7}$	-49.77
"	32.0	$7.68 \times 10^{-7}$	$6.58 \times 10^{-7}$	-42.43
"	133.5	$3.20 \times 10^{-6}$	$2.81 \times 10^{-6}$	-31.82
"	383.5	$9.21 \times 10^{-6}$	$8.22 \times 10^{-6}$	-22.64
10,000	103.5	$2.48 \times 10^{-5}$	$2.38 \times 10^{-5}$	-15.14
"	172.0	$4.13 \times 10^{-5}$	$4.02 \times 10^{-5}$	- 7.42
"	374.0	$8.98 \times 10^{-5}$	$8.86 \times 10^{-5}$	- .51
1,000	77.0	$1.85 \times 10^{-4}$	$1.87 \times 10^{-4}$	4.83
"	187.0	$4.49 \times 10^{-4}$	$4.57 \times 10^{-4}$	9.20
"	289.0	$6.94 \times 10^{-4}$	$7.12 \times 10^{-4}$	13.72
"	385.0	$9.24 \times 10^{-4}$	$9.53 \times 10^{-4}$	16.98
		(8) Hg:Na = 15.71:1		
100,000	1.5	$3.60 \times 10^{-8}$	$2.99 \times 10^{-8}$	-56.68
"	13.0	$3.12 \times 10^{-7}$	$2.66 \times 10^{-7}$	-45.29
"	59.5	$1.43 \times 10^{-6}$	$1.24 \times 10^{-6}$	-35.43
"	76.0	$1.82 \times 10^{-6}$	$1.55 \times 10^{-6}$	-34.94
"	173.5	$4.17 \times 10^{-6}$	$3.69 \times 10^{-6}$	-26.55
"	365.0	$8.76 \times 10^{-6}$	$7.85 \times 10^{-6}$	-21.20
"	410.0	$9.84 \times 10^{-6}$	$8.84 \times 10^{-6}$	-19.08
10,000	92.5	$2.22 \times 10^{-5}$	$2.13 \times 10^{-5}$	-14.58
"	144.0	$3.46 \times 10^{-5}$	$3.35 \times 10^{-5}$	-10.48
"	168.5	$4.05 \times 10^{-5}$	$3.93 \times 10^{-5}$	- 8.72
"	268.5	$6.46 \times 10^{-5}$	$6.32 \times 10^{-5}$	- 4.22
"	309.0	$7.42 \times 10^{-5}$	$7.30 \times 10^{-5}$	- 2.86
"	395.0	$9.48 \times 10^{-5}$	$9.36 \times 10^{-5}$	- .04
1,000	56.5	$1.36 \times 10^{-4}$	$1.36 \times 10^{-4}$	2.62
"	56.0	$1.34 \times 10^{-4}$	$1.35 \times 10^{-4}$	2.65
"	73.0	$1.75 \times 10^{-4}$	$1.77 \times 10^{-4}$	4.88
"	158.0	$3.79 \times 10^{-4}$	$3.85 \times 10^{-4}$	7.27
"	159.0	$3.82 \times 10^{-4}$	$3.87 \times 10^{-4}$	7.40
"	189.0	$4.54 \times 10^{-4}$	$4.62 \times 10^{-4}$	9.41
"	221.0	$5.30 \times 10^{-4}$	$5.42 \times 10^{-4}$	11.34
"	256.5	$6.16 \times 10^{-4}$	$6.31 \times 10^{-4}$	12.90
"	317.0	$7.61 \times 10^{-4}$	$7.83 \times 10^{-4}$	15.27
"	407.0	$9.77 \times 10^{-4}$	$1.01 \times 10^{-3}$	18.26

necessary when the mean free path is great compared to the dimensions of the parts connecting the two regions. In this research the tube

connecting the amalgam reservoir to the ionization gauge was approximately 1 cm in diameter and since the mean free path at the highest pressures measured ( $1.2 \times 10^{-3}$  mm) was of the order of 2 cm, it was necessary to make this correction. This correction for a similar gauge was discussed in detail in a recent paper<sup>6</sup> and the reader is referred to that discussion for the details.

TABLE II  
*Vapor pressures of potassium-mercury amalgams.*

Electron current scale divs.	Ion current scale divs.	Uncorrected pressure $P'$	True pressure $P$	Temp. of amalgams
		(9) Hg:K=5.226:1		
100,000	258.0	$8.72 \times 10^{-6}$	$7.96 \times 10^{-6}$	-13.61
"	425.0	$1.436 \times 10^{-5}$	$1.33 \times 10^{-5}$	- 7.16
10,000	94.5	$3.19 \times 10^{-5}$	$3.16 \times 10^{-5}$	- 2.95
"	161.0	$5.42 \times 10^{-5}$	$5.42 \times 10^{-5}$	2.11
"	282.0	$9.54 \times 10^{-5}$	$9.59 \times 10^{-5}$	7.15
"	475.5	$1.61 \times 10^{-4}$	$1.65 \times 10^{-4}$	11.46
1,000	86.0	$2.92 \times 10^{-4}$	$3.01 \times 10^{-4}$	15.70
		(10) Hg:K=10.667:1		
100,000	377.5	$1.28 \times 10^{-6}$	$1.15 \times 10^{-6}$	-19.51
10,000	60.0	$2.03 \times 10^{-5}$	$2.00 \times 10^{-5}$	- 2.45
"	111.5	$3.77 \times 10^{-5}$	$3.76 \times 10^{-5}$	1.88
"	181.5	$6.13 \times 10^{-5}$	$6.14 \times 10^{-5}$	6.43
"	283.5	$9.58 \times 10^{-5}$	$9.69 \times 10^{-5}$	10.72
"	457.0	$1.545 \times 10^{-4}$	$1.57 \times 10^{-4}$	14.20
1,000	76.0	$2.57 \times 10^{-4}$	$2.67 \times 10^{-4}$	18.15
"	114.6	$3.87 \times 10^{-4}$	$4.05 \times 10^{-4}$	21.93
		(11) Hg:K=20.833:1		
100,000	207.0	$6.96 \times 10^{-6}$	$6.26 \times 10^{-6}$	-24.03
10,000	89.0	$3.01 \times 10^{-5}$	$2.90 \times 10^{-5}$	-14.43
"	161.0	$5.44 \times 10^{-5}$	$5.31 \times 10^{-5}$	- 9.05
"	297.0	$1.005 \times 10^{-4}$	$9.89 \times 10^{-4}$	- 3.25
1,000	54.0	$1.825 \times 10^{-4}$	$1.84 \times 10^{-4}$	1.28
"	87.5	$2.96 \times 10^{-4}$	$3.01 \times 10^{-4}$	5.77
"	150.0	$5.07 \times 10^{-4}$	$5.20 \times 10^{-4}$	10.86

The experimental data and results are displayed in Tables I, II, III, and in the  $\log p$  vs  $1/T$  graphs of Figs. 5 and 6. In Tables I and II the electron and ion currents, columns 1 and 2, are given in scale divisions. These may be converted to amperes by multiplying by the sensitivities of the electron and ion current galvanometers,  $2.66 \times 10^{-8}$  and  $8 \times 10^{-10}$  respectively. The uncorrected pressures  $P'$ , in column 3, are the pressures in the ionization gauge. To get the true pressure,  $P$  in column 4 of the tables, in the amalgam reservoir, it was necessary to correct for thermal effusion as mentioned above. These corrected pressures are found in column 4. The molecular ratio of mercury to alkali, the heat for formation  $U$ , and the initial gas effect are shown in Table III, in which the amalgam numbers correspond to those of Tables I and II. The  $\log p$  vs  $1/T$  graphs in

Figs. 5 and 6 for pure mercury were plotted from data previously published by the writer.<sup>6</sup>

#### DISCUSSION OF RESULTS

*Gas effects.* There were three sources of gas back of the valve  $V_2$ , Fig. 1; the ionization gauge, the walls of the amalgam reservoir or amalgam bottle and the amalgam. These effects are made manifest in a striking manner in some of the graphs. Let us first examine the graphs of amalgams numbered 1 and 2, Fig. 5. The initial gas effects (col. 4 Table III) in the case of numbers 1 and 2 were 22 and 26 scale

TABLE III

The internal energy change,  $U$ , and the initial gas effect for Hg, Na and Hg,K amalgams.

Amalgam No.	Mol Ratio Hg:Alkali	Internal energy change $U$	Initial gas effect in scale divs.
Sodium amalgams			
1	.985:1	19,000	22
2	1.19 :1	21,500	26
3	1.63 :1	15,800	11
4	1.96 :1	14,000	0
5	3.41 :1	14,300	2
6	5.86 :1	upper curve	0
7	5.78 :1	14,500	0
8	15.71 :1	lower curve 15,500	1.5
Potassium amalgams			
9	5.226:1	25,500	0
10	10.667:1	25,500	0
11	20.833:1	.....	0

divisions of ion current respectively.\* The graphs of these two amalgams have slopes that are too steep (as indicated by the high\*\* heat values) and the one with the greater slope gave the greater initial gas correction. The slope of the graph number 3 is but slightly steeper than it should be (judging from the slopes of the graphs of the amalgams whose heats gradually increase with dilution and whose initial gas effects were negligible) yet its initial gas effects were approximately half that of number 1 and 2. This is accounted for by the fact that it became necessary to install a new filament in the ionization gauge just prior to the run on number 3. A new filament will continue to give off small quantities of gas in diminishing quantities for a number of days. Since we have no reason to believe that the evolution of gas from the filament would increase with a rise in temperature of the

\* See section on "Experimental method" for initial gas effect correction.

\*\* Since there is a positive heat of dilution for the amalgams, the total heat of reaction should be greater the greater the dilution.

amalgam, the slope of the graph should not be affected. It is not surprising that there was a slight evolution of gas in the case of these three amalgams since their mercury vapor pressure became readable at temperatures considerably above that of the room.

The break in the graph of amalgam number 4 near room temperature is an example of the extreme care necessary in outgassing. This

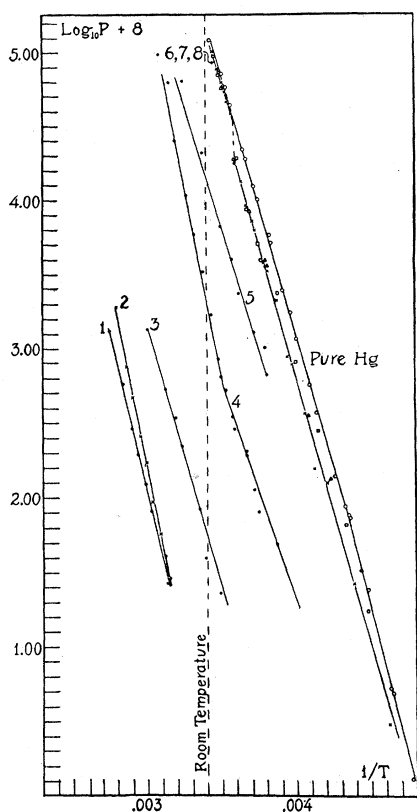


Fig. 5. Graphs for the sodium amalgams.

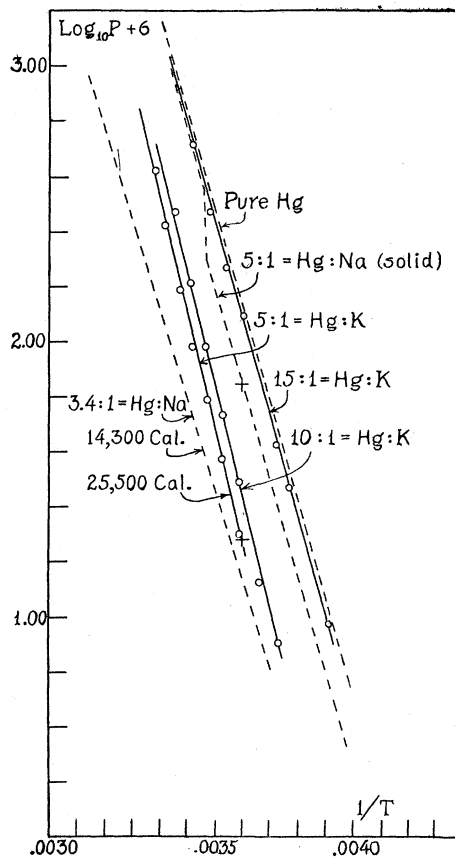


Fig. 6. Graphs for the potassium amalgams. (Some sodium amalgams are shown for comparison.)

bottle of amalgam was introduced cold. When the amalgam reservoir was warmed up the bottle broke and consequently neither the reservoir nor the outside of the bottle could be properly outgassed. There was no initial gas correction and the lower part of this graph gives a heat of reaction that is thought to be reliable.

Graphs of amalgams numbered 6, 7 and 8. The fact that the graphs of these three amalgams coincide is explainable on the basis of a saturated

solution in mercury of an amalgam whose formula is  $\text{NaHg}_5$ . A number of experimenters<sup>8</sup> have identified this well defined crystalline amalgam at ordinary temperatures. Between  $4^\circ$  and  $5^\circ\text{C}$ , however, the whole mass of amalgam and mother liquor solidifies, even in the case of amalgam number 8 which had a mol ratio  $15.7 : 1 = \text{Hg} : \text{Na}$ , and the vapor pressure suddenly drops. Evidently an amalgam can exist below say  $4^\circ\text{C}$  which has a formula of  $\text{NaHg}_x$  where  $x > 15.7$ . This behavior together with the two facts, first, that mercury is easily driven out of a solid amalgam far below its melting point, and second, that cooling curves have shown such a large number of compounds between mercury and sodium<sup>7,12,13</sup> inclines one to the thought that the role played by the greater part of the mercury in these amalgams is of the nature of that played by water in a large number of our common crystalline compounds. (See especially Roozeboom's work on ferric chloride.<sup>14</sup>) That is, we may well call this excess of mercury, above, say,  $\text{Na}_2\text{Hg}$ , mercury of crystallization.

It is also worthy of note that the vapor pressure of the partially liquid amalgam is but little below that of pure mercury. R. H. Gerke,<sup>15</sup> in a very interesting paper based upon the electrochemical measurements of a number of different observers, made the surprising prediction that this could be expected. He deduced that in the formation of a gram mol. of  $\text{NaHg}_5$  the reduction in the free energy of the gram atom of sodium amounted to 18,046 cal. while the reduction in free energy of a gram atom of the mercury was only 61 cal. His words on this point are:

"The most striking and unexpected conclusion which can be drawn from these data, is that the mercury does not greatly change in free energy when it enters into chemical combination with a more electro-positive metal. In other words, the vapor pressure of a pure liquid mercury is only very slightly greater than the partial pressure of mercury from an amalgam saturated with a mercuride."

This, also, adds weight to the theory that liquid amalgams are dissociated and that the greater part of the mercury even in  $\text{NaHg}_5$  is held as mercury of crystallization. Vanstone<sup>7</sup> concluded from electrical conductivity and specific volume measurements that all liquid amalgams are probably completely dissociated. From Smith and Bennett's work<sup>16</sup> we see that at  $5^\circ\text{C}$  the mercury and sodium in a saturated

<sup>12</sup> E. Vanstone, *Chem. News* **103**, 182 (1921).

<sup>13</sup> A. Schüller, *Zeits. Anorg. Chem.* **40**, 385 (1904).

<sup>14</sup> B. Roozeboom, *Zeits. Phys. Chem.* **10**, 477 (1892).

<sup>15</sup> R. H. Gerke, *J. Am. Chem. Soc.* **45**, 2508 (1923).

<sup>16</sup> G. McP. Smith and H. C. Bennett, *J. Am. Chem. Soc.* **32**, 622 (1910).

solution of  $\text{NaHg}_5$  is approximately in the mol ratio of 20 : 1. If these molecules are dissolved in mercury then the mol ratio of solvent to solute is 15 : 1 and consequently the vapor pressure should be lowered some 6 percent. Suppose, however, that the solute is  $\text{Na}_2\text{Hg}$ ,  $\text{Na}_3\text{Hg}$  or  $\text{Na}_4\text{Hg}$ , then it is readily seen that the vapor pressure would be lowered by a very small amount; i. e., it would be approximately 1 percent in the case of  $\text{Na}_4\text{Hg}$ .

*The graphs of 9, 10 and 11.* These are potassium amalgams. It will be observed that 9 and 10, Fig. 6, have a greater slope than the corresponding sodium amalgams which are plotted for the sake of comparison. This, of course, means that the heat of reaction between potassium and mercury is greater than that for sodium and mercury (the ratio is approximately 5 to 3). In the case, however, of number 11, we have a striking departure from the behavior of the sodium amalgams. This amalgam was partially liquid at the lowest temperature used and its vapor pressure differs but slightly from that of pure mercury. There is a well defined potassium amalgam whose formula according to Smith and Bennett<sup>16</sup> and others is  $\text{KHg}_{12}$ . Number 11 was evidently a saturated solution of these crystals in mercury.

*Heats of reaction.* The heats shown in column 3 of Table XII were calculated by applying the integrated Van't Hoff isochore<sup>17</sup> to large scale graphs similar to those shown in Figs. 5 and 6, that is

$$\text{Ln} \frac{p_2}{T_2} - \text{Ln} \frac{p_1}{T_1} = \frac{U}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (1)$$

where  $p_1$  and  $p_2$  are the saturated mercury vapor pressure of the amalgams,  $T_1$  and  $T_2$  are the respective temperatures on absolute scale,  $R$  is the gas constant and  $U$  is the total change of internal energy when a gram molecule of the amalgam is formed, i. e.,  $U$  is the heat of reaction at constant volume and is assumed constant over the range of temperature  $T_1$  to  $T_2$ . The vapor at these low vapor pressures can not depart appreciably from an ideal gas and, since the gas law is the only other simplified assumption involved in these calculations it is thought that the heats thus obtained are accurate to within say  $\pm 200$  cal.\*

<sup>17</sup> W. Nernst, Theoretical Chemistry, p. 747 (1923 edition).

\* The heats could not be calculated from the  $\log p$  vs  $1/T$  graphs with a greater accuracy than  $\pm 200$  cal. It is thought that the pressures as obtained from the smooth graphs of the amalgams of low or zero gas effect are accurate to within one percent. This error in the pressures introduces an additional error of approximately  $\pm 200$  cal. in the heats.



It will be noticed in Table III that the difference in the internal energy changes  $U$ , involved in the formation of the different amalgams is comparatively small. This means that the greater part of the heat of reaction is evolved in the initial compounds formed, i. e.,  $\text{Na}_3\text{Hg}$ ,  $\text{Na}_2\text{Hg}$ , etc. It also follows that the heat of dilution is comparatively small. Unfortunately the literature is practically devoid of data on the heats of dilution or reaction of sodium and potassium amalgams. There is considerable electrochemical data on the subject, which, however, cannot be directly applied<sup>18</sup> to the calculation of the heats of dilution as pointed out by Richards and Conant<sup>1</sup> p. 609 in their paper on the Electrochemical Behavior of Liquid Sodium Amalgams, in which they have this to say:

“Aside from a few rough experiments by Berthelot<sup>19</sup> and a few more of Cady<sup>20</sup> on heats of dilution, there has been no thermochemical study of sodium amalgams. It has been shown that these data are not directly applicable to the thermodynamic considerations of the electrochemical results, because the latter involve not dilution but rather transfer of sodium from a more concentrated to a more dilute amalgam.”

The heat of reaction between sodium and mercury in the formation of a 10 percent by weight amalgam ( $\text{NaHg}_2$ ) was found by Berthelot to be 10,300 cal. per gram molecule of amalgam. For a 7 percent by weight potassium amalgam (approximately  $\text{HKg}_3$ ) the same author found the heat of reaction per gram molecule of amalgam to be 20,800 cal. The method used by Berthelot was an indirect calorimetric process in which little confidence can be placed, yet, apparently, it is all we have with which to compare the heats calculated in the present work. In the case of the sodium amalgam, the heat of reaction as herein calculated is 140 percent of that found by Berthelot and for the potassium amalgam it is 125 percent. Notwithstanding the fact that the heats calculated in the present paper are a maximum (an increasing evolution of gas would increase the slope of the  $\log p$  vs  $1/T$  graph) it is thought that, with the exception of amalgams number 1, 2 and 3, the heats given in Table III are correct to  $\pm 400$  cal.

The heats given in Table III also indicate that the internal energy change is considerable less than the free energy change as calculated by Gerke.<sup>15</sup> This is in agreement with the work of Richards and Co-

<sup>18</sup> See Richards and Daniels<sup>8</sup> p. 1761, for a complete discussion of this point in connection with their work on Thallium Amalgams.

<sup>19</sup> Berthelot, *Am. Chem. Phys.* **5**, 18, 442 (1879).

<sup>20</sup> Cady, J., *Phys. Chem.* **2**, 560 (1898).

nant<sup>1</sup> on the temperature gradient of concentration cells of sodium amalgams. They found that the temperature gradient of the e.m.f. was positive and comparatively large giving a considerable difference between the free and internal energy change.

The change in internal energy for the potassium amalgams was calculated from the  $\log p$  vs  $1/T$  graphs to be 25,500 cal. According to Gerke,<sup>15</sup> the free energy change in the formation of a  $\text{KHg}_{12}$  amalgam should be 24,200 cal., assuming that the free energy change of the mercury is the same ( $-61$  cal.) as in the formation of sodium amalgams. Accordingly, then, we may expect the temperature gradient of the e.m.f. of potassium amalgam concentration cells to be small and negative. Unfortunately the writer has not been able to find experimental data with which to check this conclusion.

*Straight line graphs.* The integrated Van't Hoff relation, Eq. (1), may be written in the form

$$U = \frac{R(\ln p_2 - \ln p_1)}{1/T_1 - 1/T_2} - \frac{R(\ln T_2 - \ln T_1)}{1/T_1 - 1/T_2}. \quad (2)$$

Taking  $10^\circ$  intervals, the variation with the temperature of the last term of this equation from  $10^\circ\text{C}$  to  $-30^\circ\text{C}$  is but 81 cal. i. e., this term amounts to 405 cal. at  $10^\circ$  and 486 cal. at  $-30^\circ$ . This variation is well within the experimental error and, therefore, may be neglected. It follows then, from the fact that the best possible graph in all cases was a straight line, that the heat of reaction was constant within the experimental error ( $\pm 400$  cal.).

The heat of reaction,  $U$ , may be expressed as a function of the temperature as,

$$U = U_0 + \alpha T + \beta T^2 + \gamma T^3 + \dots \quad (3)$$

where  $U_0$  is the heat of reaction at  $0^\circ\text{K}$  and  $\alpha, \beta, \gamma$ , etc., are constants. This gives

$$dU/dT = \alpha + 2\beta T + 3\gamma T^2 + \dots \quad (4)$$

The integration of the Gibbs-Helmholtz relation

$$A - U = TdA/dT \quad (5)$$

and the substitution of the value of  $U$  as given in equation (3) gives,

$$A = U_0 + aT - \alpha T \ln T - \beta T^2 - \frac{1}{2}\gamma T^3 - \dots \quad (6)$$

where  $a$  is the constant of integration and  $A$  is the free energy change. Differentiating this last equation with respect to  $T$  we get,

$$dA/dT = a - \alpha - \alpha \ln T - 2\beta T - 3/2\gamma T^2 \dots \quad (7)$$

According to the Nernst theorem,

$$dA/dT = dU/dT = 0 \quad (8)$$

at 0°K. For this to be true both  $a$  and  $\alpha$  must be zero. Therefore we have

$$U = U_0 + \beta T^2 + \gamma T^3 + \dots \quad (9)$$

and

$$A = U_0 - \beta T^2 - \frac{1}{2}\gamma T^3 \dots \quad (10)$$

Neglecting terms in  $\gamma$  and beyond, we get upon subtracting (9) from (10).

$$A - U = -2\beta T^2 \quad (11)$$

Substituting 18,300 cal. for  $A$  as calculated by Gerke, and 14,500 for  $U$  as calculated from the  $\log p$  vs  $1/T$  graph, we get the value of  $\beta$  at 280°C to be  $-.024$ . From Eq. (4) we have  $dU/dT = 2\beta T = -13.44$  cal. per degree. According to the Nernst hypothesis,  $dU/dT$  diminishes in our case with decreasing temperature, but if it were constant over a range of say 40°, the variation in  $U$  would be approximately  $-500$  cal. But the effect of the last term in Van't Hoff relation discussed in the preceding paragraph was to diminish the value of  $U$  by 80 cal. over this range. Therefore the variation of slope was of the order of 400 cal. which is still within our error of  $\pm 400$  cal. Thus we can expect the  $\log p$  vs  $1/T$  graphs to be straight lines.

*Parallelism of graphs.* Since the slope of the  $\log p$  vs  $1/T$  graphs determine the heat of reaction, the parallelism means that the heat of dilution is comparatively small. This is in agreement with the work of Cady<sup>20</sup> who found the average heat of dilution of a 20:1 mol ratio of Hg:Na amalgam when diluted to 86.7:1 to be 136 cal. per gram mol. of mercury added. That is, the greater part of the heat of reaction is liberated in the initial compounds of mercury with sodium or potassium. In making up the amalgams, it was necessary to add the mercury very cautiously since the initial mercury always reacted with explosive violence, the heat liberated being sufficient to vaporize the alkali and mercury and scatter the whole over the walls of the mixing chamber.

*Duration of efficiency of sodium trap.* When mercury is first added to an alkali, it reacts violently. The violence of this reaction diminishes rapidly as the mercury content increases, the point being soon reached, at approximately a 1:1 mol ratio, at which the additional mercury is quietly soaked up. A drop of mercury on the wall of a vessel containing an amalgam whose mol ratio of Hg:Na is less than 5:1, i. e.,

solid amalgam, will disappear in a short time. A sodium or potassium trap between an apparatus and a source of mercury vapor will gradually turn black on the side next to the source of mercury vapor. This discoloration creeps but slowly along the trap, the farthestmost parts remaining perfectly bright for weeks. These facts indicate that the action between the mercury and the sodium is not a surface effect but is rather a mass action. That is, that the mercury is distributed more or less evenly throughout the mass of the amalgam formed. We will assume that it is a mass action in the following calculation.

Two facts are necessary to such a calculation. First, we must know the vapor pressure of a limiting amalgam. In this instance, we will take an amalgam whose molecular ratio of Hg to Na is 1:1. By drawing the best mean straight line through the three lowest points for amalgam number 1 parallel to the graph of amalgam 3 (gas effect in number 3 being small) the vapor pressure of a 1:1 amalgam was extrapolated to be  $3 \times 10^{-8}$  mm at  $20^\circ\text{C}$ . Then if we place 10 g. of sodium in a trap, 87 g. of mercury must diffuse into this trap in order for the mercury vapor pressure in the trap to be as much as  $3 \times 10^{-8}$  mm.

Secondly, we must know the rate of flow of mercury vapor through the connecting tubes under working conditions. The flow of gases at low pressures has been worked out both theoretically and experimentally by M. Smoluchowshky, M. Knudsen and W. Gaede who have published a large number of papers on this subject since 1908. The following treatment is from S. Dushman's book on High Vacuum.<sup>21</sup> When the mean free path of the molecule is large compared to the diameter  $D$ , of the tube through which the gas is flowing, then the quantity,  $Q$ , (measured in pressure volume units) which flows through the tube of length,  $l$ , in 1 sec. is related to the driving pressure,  $P_2 - P_1$ , by the equation

$$Q = \frac{P_2 - P_1}{(W_1 + W_2)\sqrt{\rho_1}},$$

where  $w_1 = 6l/\sqrt{2\pi}D^3 = 2.394l/D^3$ ;  $w_2 = \sqrt{2\pi}/A$  ( $A$  = Area of cross-section of tube); and  $\rho_1 = m/83.15 \times 10^6 T$  is the density at 1 bar pressure and at the temperature of the tube.

Let us assume a room temperature of  $20^\circ\text{C}$  and that the trap is separated from the source of mercury vapor by 100 cm of tubing whose diameter is 1 cm i. e.,  $l=100$  and  $D=1$ . Then we have  $w_1 + w_2 = 242.6$ . For mercury  $\rho_1 = 82 \times 10^{-10}$  at  $20^\circ\text{C}$ . The vapor pressure of

<sup>21</sup> Production and Measurements of High Vacuum by S. Dushman, General Electric Review (1922).

mercury at 20°C is .00121 mm and the back pressure of  $3 \times 10^{-8}$  mm is negligible compared to it. Therefore, we have, finally  $Q = 73.4$  cc/sec. That is, there are 73.4 cc of mercury vapor at a pressure of 1 bar entering the trap each sec. This amounts to .056 g. per day. This means that it would require  $87/.056$  or 1554 days for the pressure from the trap to reach  $3 \times 10^{-8}$  mm. During the first 2 years of this time the formula for the amalgam would be richer in sodium than  $\text{Na}_2\text{Hg}$ , and since it appears that the greater part of the energy of reaction is liberated in the formation of these initial amalgams, there is no telling how low the pressure really is.

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PHYSICS LABORATORIES,  
WASHINGTON UNIVERSITY,  
ST. LOUIS, MISSOURI.  
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