138. *The Determination of the Vapour Pressures of Amalgams by a Dynamic Method.*

By John S. Pedder and Sydney Barratt.

A characteristic of each of the alkali-metal amalgams is the formation of a series of compounds between the two component elements, some of which have a large positive heat of formation and are correspondingly stable. From the measured heat of formation of the compound represented by the formula Na_3Hg and by application of Nernst's heat theorem, Wartenberg (*Z. Elektrochem.*, 1914, **20**, 443) has shown that at 444° the conditions are favourable for the existence of a considerable proportion of this compound in the vapour above the amalgam. To test this conclusion experimentally, he distilled at 444° a quantity of sodium amalgam having a composition represented by Na_3Hg, and from the composition of the distillate deduced that the compound had distilled over unchanged. The accuracy of Wartenberg's conclusion has been questioned by Eucken and Neumann (*ibid.*, 1922, **28**, 322), who have shown, by distillation at constant pressure, that the compound Na_3Hg must be dissociated in the vapour state.

It is also known (Barratt, *Trans. Faraday Soc.*, 1929, **25**, 758) that the absorption spectra of the vapours of sodium, potassium, rubidium, and cæsium amalgams show well-defined bands which confirm the presence of compound molecules in the vapour state but give no information as to their concentration.

The most promising method for the further investigation of this problem is the determination of the partial vapour pressures of each of the constituents of various amalgams at a constant temperature. The dynamic gas-streaming method has therefore been adapted for the measurements at temperatures of 250—400°.

As far as can be ascertained, all previous measurements of this type above room temperature have been carried out with a static apparatus similar to that first used by Ramsay (J., 1889, **55**, 521). For purposes of comparison, measurements of the vapour pressures of cadmium and zinc amalgams have been carried out with the dynamic method.

Experimental.

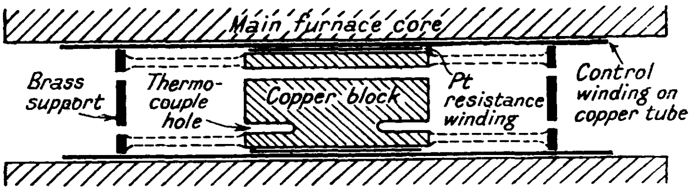
Principle of Method.—A measured vol. of inert gas (N or A) was passed slowly over the surface of the amalgam, which was maintained at a const. temp. in a furnace, so that the gas became fully saturated with the vapour from the amalgam; it was then passed through a cool tube, where the metal vapours condensed. The partial v. p. was calculated from the wt. and compn. of the metals thus distilled. An important check on the results was provided by passing the inert gas back over pure Hg contained in a tube alongside the amalgam tube in the furnace and through a second condenser tube where the pure Hg condensed. Thus, in each expt. the vapour pressure of pure Hg was determined. The mercury and amalgam tubes were arranged in position with the furnace cold, and a slow reverse stream of N was passed in through the condenser tubes to prevent metal being deposited in these tubes by diffusion while the furnace was being warmed to the required temp.

Furnace.—The form of furnace was decided upon only after many test expts. with both tubes containing pure Hg. It was considered important that the temp. along the whole length of the furnace should be as uniform as possible, and therefore a heavy Cu core was used. It consisted of a Cu tube, 21″ long and having an inside diam. of 3¾″ and walls ⅛″ thick, which was fitted with brass end-pieces to secure it in position inside a large furnace case. About 20 lb. of No. 12 S.W.G. Cu wire were wound in layers, and a thin coating of boiler compound was placed round this winding to prevent undue oxidation of the wire. Two layers of asbestos paper, to insulate the heating winding of nichrome ribbon, and two more layers of asbestos paper over the heating winding completed the core. This method of building up the core from wire is very much cheaper than the use of a solid Cu casting.

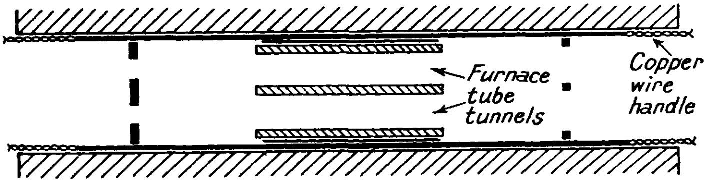
The greater loss of heat at the ends of the furnace than at the centre was compensated for by the addition of two more heating windings, wound on brass formers 2″ wide by 6″ in diam. placed one at each end of the Cu core. The space between the core and the furnace case was lightly packed with asbestos wool.

The currents through these heating windings were adjusted to maintain a temp. roughly 15° below that required. The extra heating was supplied by a current of about ½ amp. through a control winding on a thin Cu tube, 18″ long by 3¼″ in diameter, which was placed centrally inside the main furnace core. The current through this control winding was switched off and on automatically as the temp. inside the furnace rose or fell, by a device based on the change of resistance with temp. of a Pt wire. The Pt resistance wire (about 33 ohms) with stout Cu leads was inserted in the furnace and connected as one arm of a Wheatstone bridge. A mirror galvanometer was connected across the bridge, and an intense beam of light directed on to the mirror so that, when the bridge was balanced with the furnace at the required temp., the reflected light illuminated a photo-cell placed about 1½ m. away. With the photo-cell thus illuminated, a photoelectric current of about 1 micro-amp. was obtained. This was amplified by a thermionic valve, and the control heater current was switched on by means of a Hg contact relay operated by a Post Office relay in the anode circuit of the valve. The control heater current was arranged so that the furnace tended to overheat slightly, until the galvanometer beam moved off the photo-cell and the control heater circuit was broken by the relay.

FIG. 1.



Vertical section through centre of furnace.



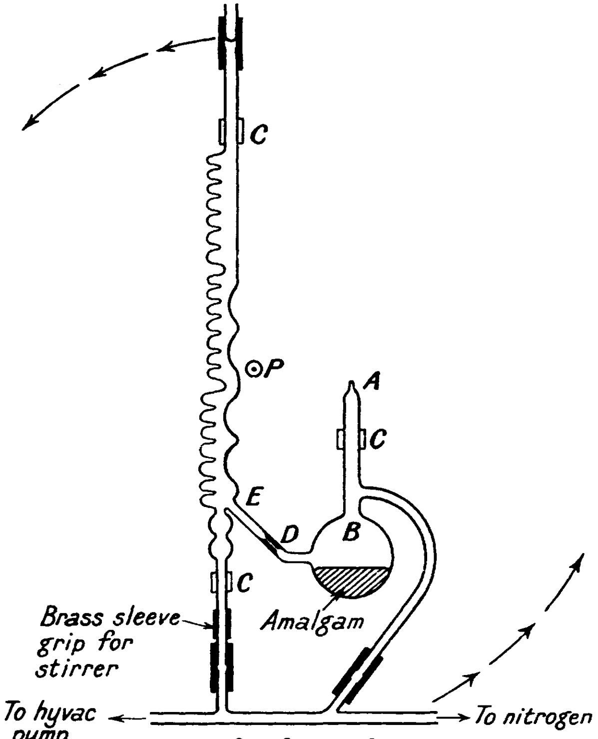
Horizontal section.

The Pt resistance, insulated by asbestos paper and alundum cement, was wound round a cylindrical Cu block, 2¾″ in diam. and 6″ long, which was placed centrally inside the control heater tube (Fig. 1).

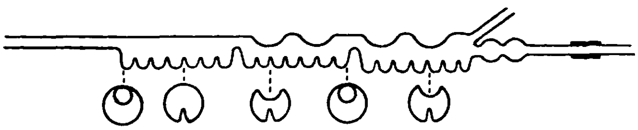
The tubes containing the amalgam and the Hg (subsequently referred to as the furnace tubes) were passed through two parallel tunnels, 1″ in diam., drilled through the Cu block. The temp. of the block was observed by two calibrated copper–constantan thermocouples, used in conjunction with a Leeds–Northrupp potentiometer. The thermocouples were insulated with thin silica tubes, and inserted in holes about 1½″ deep drilled into each end of the Cu block.

Considerable difficulty was encountered in the first expts. owing to the formation of a thin film of oxide on the surface of the amalgam, which greatly hindered the complete saturation of the N with the amalgam vapours. This was overcome by very complete elimination of O from the N, and by the use of two special furnace tubes. These were constructed from three lengths of 1″-diam. Pyrex tube joined eccentrically by short pieces of ½″-diam. tube, so that the Hg and amalgam were each divided into three separate pools. These tubes were improved later so that the amalgam could be stirred. The final design is shown in Fig. 2.

Fig. 2.



Apparatus for filling furnace tube.



Vertical and end-on sections of furnace tube.

For the v. p. measurement, the two tubes were arranged side by side in the furnace so that the middle bulbs accurately filled the tunnels provided in the Cu block, and the condenser tubes were inserted so as to project just into the first bulbs. A piece of rubber tubing placed half over the end of the furnace tube and half over the condenser tube provided a satisfactory gas-tight junction.

While the furnace was being warmed, the slow reverse stream of N was passed in through the Hg condenser tube, over the Hg in the three bulbs, back in a quill tube through the furnace to the amalgam condenser tube, over the three pools of amalgam, and so out. When the desired temp. had been reached, the condenser tubes were pushed in so as to project about ½″ into the middle bulbs and the measured vol. of N was passed through at an even rate. The condenser tubes were then stoppered and withdrawn, while N was passed slowly in at the other ends of the furnace tubes to exclude air. Thus, for the actual v. p. measurement the vapours from the middle bulbs, whose temp. was accurately known, were deposited in the condenser tubes. The contents of the middle bulbs were protected from oxidation by the pools on either side, and also the third bulb served as a pre-saturator for the N so that but little further evaporation occurred in the middle bulb and constancy of compn. of the amalgam therein was assured.

The control heater tube was fitted with Cu wire handles so that at the conclusion of the expt. it could be withdrawn from the furnace together with the furnace tubes, which then cooled much more rapidly than if left in the furnace.

Purification and Measurement of the Nitrogen.—For the expts. with the Cd amalgams, O was removed from the N by passing the cylinder gas over hot reduced Cu turnings, and through a train of tubes containing liquid Na–K alloy. Although very pure N was obtained, yet this arrangement was not satisfactory on account of the necessity for frequent replacement of the alloy tubes. The apparatus was therefore altered to permit the use of Wartenberg's method (*Z. Elektrochem.*, 1930, **36**, 259) of elimination of O, in which the impure N is enclosed in a steel bomb at a press. of 100—120 atm., together with (for a 300-c.c. bomb) 50 g. of bright Cu wire cut into short lengths, a piece of Sn, and about 70 c.c. of a solution prepared from 250 c.c. of satd. $(NH_4)_2CO_3$ aq., 250 c.c. of NH_3 aq. (*d* 0·880), 100 g. of NH_4Cl, and 500 c.c. of H_2O.

The bomb is rotated in an inclined position for about 1 hr. so that the Cu becomes exposed to both the gas and the solution. Under these conditions the Cu is readily oxidised, and the CuO dissolves to form a blue solution which slowly becomes colourless owing to the replacement of $Cu^{\cdot}$ by $Cu^{\cdot}$ ions. The colourless solution is very readily oxidised and the O content of the N is reduced to about 10^{-4}% (Wartenberg).

The N from the bomb was passed through two wash-bottles, the first containing dil. H_2SO_4 aq., and the second conc. H_2SO_4, to remove NH_3. As a further precaution for elimination of O, the N was passed over reduced Cu turnings in an electrically heated silica tube and also over liquid Na–K alloy.

Nitrogen required during the prepn. of the amalgams and when filling the furnace tube with amalgam was obtained from side tubes fitted with flexible-metal connexions (Tombac tubing). By suitable manipulation, it was possible to insert or withdraw the condenser tubes from the furnace tubes without admitting air into the latter.

For the v. p. determination, about 550 c.c. of N were measured at atm. press. in a carefully calibrated bulb in a thermostat. N was drawn in at slightly above atm. press. by means of a vacuum-controlled Hg piston until the bulb was almost full. The excess N was then bubbled out through a side tube which just dipped beneath the surface of conc. H_2SO_4 in a beaker. N was passed out to the furnace tubes by admitting air into the partial vac. above the Hg piston. The rate of flow was roughly indicated by a bubbler.

Preparation of the Amalgams.—The Hg used was purified by distillation in a still of the type described by Hulett (*Physical Rev.*, 1905, **21**, 388), and the amalgams were prepared by heating the roughly weighed quantities of the metals together in a Pyrex bulb. The amalgam was poured out through a short side tube on the bulb and into the furnace tube through the inlet tube provided for this purpose. The desired amount of amalgam was obtained in each bulb by suitably tilting the tube.

This procedure was satisfactory with the Cd amalgams, but slight oxidation sometimes occurred in pouring Zn amalgams into the furnace tube in this way. The improved method, illustrated in Fig. 2, was therefore used with Zn and K amalgams. The furnace tube was sealed on to a 6-cm. Pyrex bulb *B*, and the tubes were gripped at the points marked *C* by clamps mounted on a mild-steel bar, pivoted at *P* so that the whole assembly could be swung round. The amalgam was poured from the preparation bulb into the bulb *B*, and the inlet *A* sealed off. When the amalgam had cooled sufficiently, the apparatus was evacuated and refilled with N. The amalgam was then warmed, and the assembly tilted so that the amalgam flowed through the capillary *D* into the furnace tube, which was then drawn off at *E* and allowed to cool in a horizontal position.

As a further precaution, to ensure as thorough saturation of the N as possible, the Zn and K amalgams were stirred during the v. p. determination, by means of the special furnace tube shown in Fig. 2. The tube was rocked to and fro through an angle of 60°, and the sharp dents projecting upwards from the bottom of the tube stirred the amalgam. The large dents on the top of the tube served to force the flow of N nearer to the amalgam surface.

Analysis of the Amalgams.—With the Cd and the Zn amalgams, small weighed samples were dissolved in HNO_3, and the Hg determined volumetrically by titration with standardised NH_4NCS in presence of ferric solution.

In the analysis of the K amalgams the amounts of both constituents were determined. Amalgams containing up to 45 mols. % of K do not react vigorously with cold H_2O, and this was therefore poured on to the samples of the amalgams to obtain the K in solution. A slight excess of standard H_2SO_4 was then added, and after about 24 hr. CO_2 was boiled off and the excess acid titrated with standard KOH aq. with methyl-red as indicator. Amalgams containing 45—56 mols. % of K were cooled by a freezing mixture and treated with ice-cold H_2O before the above procedure was followed.

Amalgams containing larger propns. of K react vigorously even with cold H_2O. It is not satisfactory to obtain the K in solution by blowing moist air over the amalgam, since an appreciable amount of Hg is thereby oxidised. Small pieces of such amalgams, therefore, were dropped into cold abs. EtOH; when the reaction had subsided, H_2O and H_2SO_4 were added, and the analysis carried out as before.

The Hg remaining after the determination of the K was dissolved in HNO_3 and determined volumetrically as before.

Analysis of Distillates.—Since the expts. with Cd and Zn amalgam were performed mainly to test the accuracy of the exptl. method, and because of the comparatively small volatility of Cd and Zn, the distillates obtained in the v. p. measurements were not analysed for these two metals.

With the K amalgams, after each expt., the condenser tube containing the distilled Hg and K was weighed and then washed out with distilled H_2O and a measured vol. of standard approx. $N/1000$-H_2SO_4. The solution was kept for a few days in a Jena-glass flask, then CO_2 was boiled off, and the excess acid titrated with CO_2-free KOH, Sofnol No. 1 indicator being used.

Vapour-pressure Measurements.—Although it was possible, by means of the automatic control, to keep the temp. of the furnace const. to within about 0·1° during each expt., yet it was difficult to return to exactly the same temp. for every expt. To correct for such differences the average value of the v. p. of Hg throughout the series of expts. was determined. The ratio of the result of each expt. to this average value was noted, and the results for the amalgam were corrected proportionately. The amount of this correction was about 1—2%, and therefore, although the temp. coeff. of increase of press. of the amalgam is probably not the same as that for pure Hg, yet an error of the second order only will have been introduced by applying simple proportion to evaluate the correction.

Results.—*Cadmium amalgam.* For these expts., N from which the O had been removed by Na–K alloy was used, except in the last 5 expts., for which the N was purified by Wartenberg's method. The results are given in Table I, in which $a_1 = p_1/p_0$ is the activity of the Hg in the amalgam.

TABLE I.

Temp. = 283·5°. Average value for v. p. of Hg (p_0) = 168·7 mm. of Hg.

Expt. No.	Amalgam compn. (average).		Vapour press. (mm.).			a_1.
	Hg, % by wt.	Hg, mols. %.	Hg.	Amalgam.	Amalgam, corr. (p_1).	
1	90·95	84·93	169·2	134·8	134·4	0·796
2			158·6	125·9	133·9	
3			170·2	136·5	135·0	
4	76·55	64·6	171·8	92·9	91·2	0·547
5			170·4	94·3	93·3	
6	74·25	61·7	167·9	83·8	84·2	0·497
7			169·0	83·8	83·6	
8	67·8	54·3	154·5	56·7	61·9	0·352
9			166·3	63·2	64·1	
10			160·1	60·4	63·6	
11			168·5	62·6	62·7	
12			170·6	61·9	61·2	
13	49·7	35·7	164·3	30·3	31·1	0·184
14			169·0	31·2	31·1	
15	26·55	16·88	166·9	7·3	7·22	0·0428

Expts. 2, 8, and 10 show low values for the v. p.'s of both the Hg and the amalgam. The differences are too great to be due to a temp. error, and it is considered that some N was absorbed by the Na–K alloy, between the volume-measuring apparatus and the furnace tubes.

These activities of Hg have been plotted in Fig. **3**, together with the values obtained by Hildebrand (*J. Amer. Chem. Soc.*, **1920**, **42**, 545) using the Ramsay static method. The agreement between the two sets of results is as good as can be expected. The negative deviation of the activities of Hg from the ideal values (given by Raoult's law) may be explained if partial solvation be assumed : $Cd + Hg \rightleftharpoons CdHg$.

In view of the various disturbing factors, such as the change of vol. and heat on mixing the liquid metals and the different internal pressures of Hg and Cd, it is not possible to calculate accurately the degree of dissociation of such a compound from the v. p. data.

FIG. 3.

Activity of mercury in cadmium amalgams.

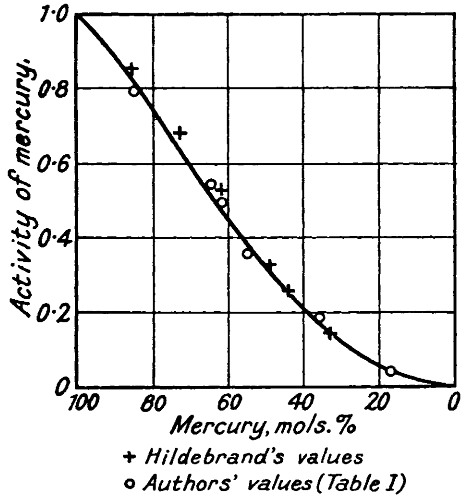
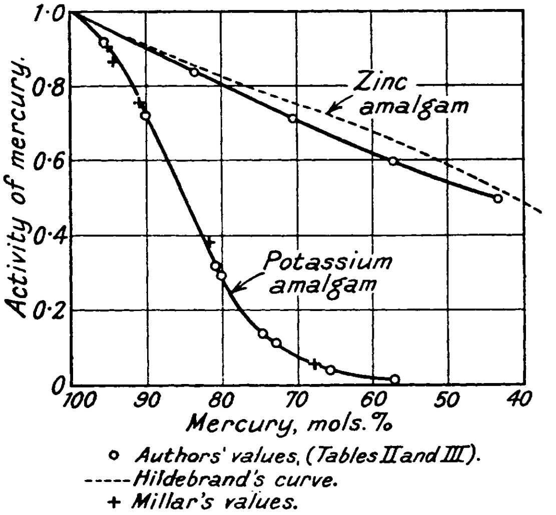


FIG. 4.



Zinc amalgams. In all the expts. on Zn amalgams, N from which O had been removed by Wartenberg's method was used, and the amalgams were stirred during the v. p. determinations. The results are given in Table II.

TABLE II.

Temp. = 284°. Average value for v. p. of Hg (p_0) = 169·6 mm. of Hg.

Expt. No.	Amalgam compn. (average).		Vapour press. (mm.).			
	Hg, % by wt.	Hg, mols. %.	Hg.	Amalgam.	Amalgam, corr. (p_1).	a_1.
1	70·25	43·5	165·0	81·8	84·1	0·498
2			171·4	85·8	84·9	
3	80·4	57·2	170·1	100·2	99·9	0·598
4			170·2	103·3	102·9	
5	88·0	70·6	168·7	119·5	120·1	0·710
6			170·2	121·1	120·7	
7	94·05	83·7	171·1	144·8	143·5	0·832
8			173·3	143·5	140·5	
9			166·7	137·1	139·5	

Amalgams containing less than 43·5 mols. % of Hg were not used owing to the difficulty of their preparation.

The values of a_1 in Table II have been plotted in Fig. 4, together with the results obtained by Hildebrand (*J. Amer. Electrochem. Soc.*, **1912**, **22**, 319) using Ramsay's static method.

It is considered that the slight positive deviation of a_1 may be due to the different internal pressures of the two metals.

The agreement between the static and the dynamic results is not good, but no decision can be reached as to which are more correct. The most likely cause of low results with the dynamic method is incomplete saturation of the N with the metal vapour, owing to the formation of an oxide film on the surface of the amalgam. This trouble should, however, be accentuated with K amalgams; but the results shown in Fig. 4 agree very well indeed with the values obtained by Millar (*J. Amer. Chem. Soc.*, **1927**, **49**, **3003**), who used the static method.

With the static apparatus, the accumulation of gases in the closed arm would cause positive errors. This effect would be less pronounced with K amalgams than with Zn amalgams, because the former can absorb gases to a greater extent than the latter.

Potassium amalgams. The results obtained with K amalgams containing up to **43** mols.% of K are given in Table III. The amounts of K distilled in these expts. at **300°** were too small for estimation with *N*/1000-solutions, and therefore the v. p. readings given represent the partial press. of the Hg.

TABLE III.

Temp. = 300°. Average value for v. p. of Hg (p_0) = 248·5 mm. of Hg.

Expt. No.	Amalgam compn. (average).		Vapour press. (mm.).			
	K, % by wt.	K, mols. %.	Hg.	Amalgam.	Amalgam, corr. (p_1).	a_1.
1			246·9	226·3	227·8	
2	0·869	4·3	247·7	228·4	229·1	0·919
3			250·5	230·1	228·3	
4			—	179·4	179·4	
5	1·98	9·39	—	178·9	178·9	0·722
6			248·1	179·9	180·2	
7	4·52	19·6	246·8	71·25	71·75	0·289
8	4·36	19·0	249·0	77·73	77·89	0·313
9	6·72	27·0	248·4	27·67	27·68	0·111
10	6·24	25·5	—	33·49	33·49	0·135
11	9·145	34·1	249·3	9·54	9·57	0·0385
12			249·1	9·58	9·56	
13	12·75	42·8	250·1	2·80	2·78	0·0112
14			248·0	2·78	2·79	

Readings for the v. p. of Hg were not obtained in Expts. 4, 5, and 10, owing to accident.

The activities of Hg (a_1) in K amalgams at 300° given in Table III have been plotted in Fig. 4, together with the values obtained by Millar (*loc. cit.*) by the static method.

Special experiments were performed to measure the partial v. p. at 300° of K over its 34·1 and 42·8 mols. % amalgams. About 10 times the normal vol. of N was passed over these amalgams. From the amount and compn. of the metal distilled and the known partial v. p. of the Hg, the partial pressures of K were calculated (see Table IV).

TABLE IV.

Amalgam. K, mols. %.	Hg and K distilled, g.	K distilled, g.	Hg distilled, g.	Partial v. p., mm.	
				Hg.	K.
34·1	0·6471	0·00008	0·6470	9·57	0·0061
42·8	0·1858	0·00066	0·1852	2·79	0·051

The very low partial pressures of K indicate the presence of almost undissociated compounds in the liquid amalgams. Little reliance can be placed on calculations of the compn. and degree of dissociation of such compounds from the v. p. data, unless the vol. and heat changes on mixing the liquid metals and the effect of their different internal pressures are taken into account.

To obtain a convenient amount of distilled metal for the measurement of the v. p. of amalgams containing more than 42 mols. % of K, it was necessary to heat the furnace to about **390°** and to abandon the check measurements with pure Hg. Particular attention was paid to the maintenance of a const. temp. throughout these expts. and the results are given in Table V.

Attempts were made to analyse the amalgams used in Expts. **9—12** by blowing moist air on to samples; since these were unsuccessful (see p. **541**), the compositions given in parentheses were obtained from the curve shown in Fig. 5, in which the partial pressures of Table V are plotted against compn.

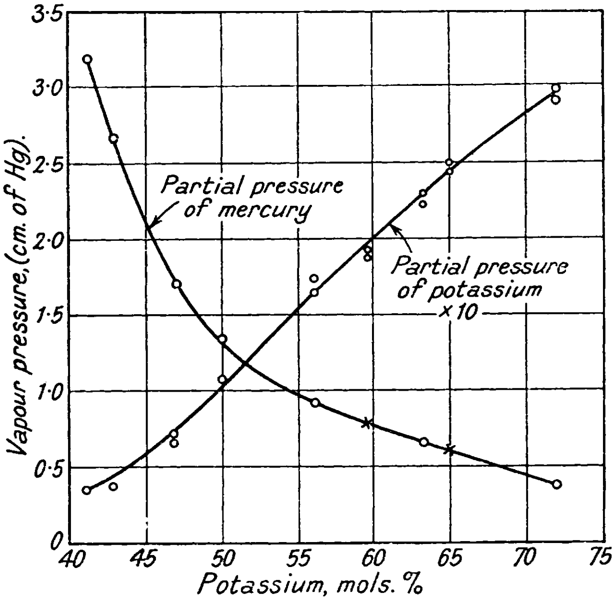
TABLE V.

Temp. = 387·5°.

Expt. No.	Amalgam comp.		Metal distilled, g.		Partial press., mm.	
	K, % by wt.	K, mols. %.	Hg.	K.	Hg.	K.
1	11·98	41·1	0·2076	0·000442	31·87	0·348
2	12·75	42·8	0·1724	0·000466	26·68	0·370
3	14·67	46·8	0·1106	0·000824	17·34	0·663
4			0·1103	0·000880	17·29	0·707
5	16·27	50·0	0·0828	0·00134	13·04	1·082
6			0·0824	0·00132	12·98	1·068
7	20·0	56·1	0·0577	0·00214	9·128	1·736
8			0·0575	0·00203	9·099	1·646
9		(59·6)	0·0495	0·00237	7·839	1·92
10			0·0491	0·00230	7·780	1·87
11		(65·0)	0·0370	0·00306	5·872	2·49
12			0·0372	0·00300	5·902	2·44
13	33·5	72·0	0·0234	0·00366	3·721	2·98
14			0·0231	0·00357	3·676	2·91
15	25·18	63·3	0·0412	0·00281	6·552	2·29
16			0·0410	0·00275	6·504	2·23

FIG. 5.

Vapour pressure of potassium amalgams at 387·5°.



If there is no appreciable amount of a compound of K and Hg in the vapour at 387·5°, then the slopes of the partial pressure curves should be connected by the following equation derived from Duhem's equation,

$$\frac{dp_2}{dN_2} = \frac{dp_1}{dN_1} \times \frac{p_2}{N_2} \times \frac{N_1}{p_1}$$

in which p_1 and p_2 are the partial v. p.'s of Hg and K respectively (in mm. of Hg), and N_1 and N_2 are the corresponding mol. percentages. Then, if the curve for the partial pressures of Hg is assumed correct, the slope of that for K may be calculated and compared with the exptl. curve. The partial v. p.'s of Hg and K above amalgams of various concns. at 387·5° have been obtained from a large-scale plot of Fig. 5 and are given in Table VI, together with the calc. and obs. values for the slopes of the partial pressure curve of K.

The obs. curve is considerably steeper than the calc. This is to be expected if there is a considerable amount of a compound of K and Hg present in the vapour; for then, amounts of Hg and K corresponding to the partial pressures of Hg, K, and the compound are distilled in

TABLE VI.

N_2.	p_2.	N_1.	p_1.	dp_1/dN_1.	dp_2/dN_2, calc.	obs.	N_2.	p_2.	N_1.	p_1.	dp_1/dN_1.	dp_2/dN_2, calc.	obs.
42	0·4	58	2·9	0·2/0·65	0·59	0·6	60	2·0	40	0·76	0·2/5·4	0·65	0·9
45	0·58	55	2·1	0·2/0·9	0·75	0·7	65	2·44	35	0·59	0·2/6·0	0·74	0·78
50	1·03	50	1·3	0·2/1·9	0·83	0·96	70	2·8	30	0·43	0·2/6·6	0·84	0·7
55	1·52	45	0·96	0·2/4·0	0·65	0·94							

the dynamic expts., and spuriously high values for the partial pressures of the two elements would be obtained.

From Janecke's f. p. curve for K amalgams (*Z. physikal. Chem.*, 1907, **58**, 246), the compound KHg seems likely to be the most volatile and stable. The small activities of K in amalgams containing less than 45 mols. % of K indicate that the more complex compounds are relatively non-volatile.

A similar conclusion confirming the presence of a compound in the vapour may be deduced from the activities of Hg and K (a_1 and a_2 respectively) in amalgams at 387·5° (Table VII). For the calcn. of the activities, the v. p. of K at 387·5° was obtained from Egerton's equation (see Sowerby and Barratt, *Proc. Roy. Soc.*, 1926, *A*, **110**, 190) $\log p_{\text{mm.}} = -4438/T + 7{\cdot}232$, and that of Hg from Menzies's equation (*Z. physikal. Chem.*, 1927, **130**, 90) $\log p_{\text{mm.}} = 9{\cdot}957094 - 3283{\cdot}92/T - 0{\cdot}665240 \log T$.

TABLE VII.

V. p. of K and Hg at 387·5° = 3·25 and 1280 mm. respectively.

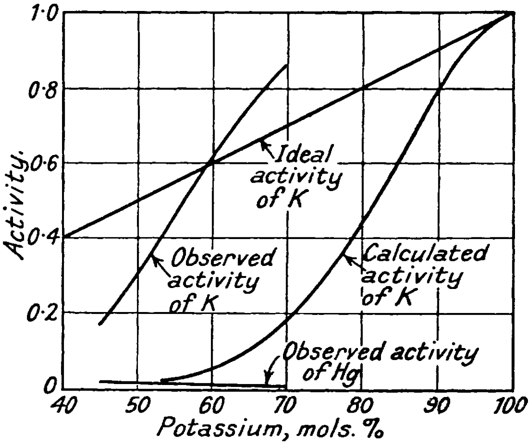
K, mols. %.	Partial press., mm. Hg.	K.	a_1.	a_2.	K, mols. %.	Partial press., mm. Hg.	K.	a_1.	a_2.
45	21·1	0·58	0·0165	0·178	60	7·6	2·00	0·0059	0·615
50	13·0	1·00	0·0102	0·308	65	5·9	2·45	0·0046	0·753
55	9·5	1·54	0·0074	0·473	70	4·2	2·82	0·0033	0·867

The activities are plotted against the compn. of the amalgams in Fig. 6.

The activities of K become greater than the ideal values required by Raoult's law. It is considered unlikely that its true activities reach such high values, since such deviations are invariably accompanied by correspondingly low solubility, and, in the extreme case, lead to the separation of two liquid layers.

FIG. 6.

Activities of potassium amalgams at 387·5°.



An estimation of the true activities of K has been made in the following way. From Millar's data (*loc. cit.*) for amalgams containing up to 32 mols. % of K, the following van Laar type equation for the activities of Hg in amalgams at 387·5° has been obtained :

$$\log a_1/N_1 = -7{\cdot}1/(1 + 0{\cdot}82N_1/N_2)^2.$$

By application of the Duhem equation, the activities of K are given by

$$\log a_2/N_2 = -7{\cdot}1 \times 0{\cdot}82/(0{\cdot}82 + N_2/N_1)^2.$$

The activities of K thus calc. have been plotted in Fig. 6. It is not to be expected that these values are accurate, but they indicate the order of the activities to be anticipated where there is no compound present in the vapour.

Since the calc. activities are considerably lower than the exptl. values, it again appears that the partial pressures, and therefore the activities, of K obtained in these expts. are higher than the true values owing to the presence of a compound in the vapour above the amalgam at 387·5°.

SUMMARY.

An apparatus for the measurement of the vapour pressures of amalgams or alloys by the dynamic gas-streaming method at temperatures between 250° and 400° is described.

The partial pressures of mercury above cadmium amalgams at 283·5°, above zinc amalgams containing up to 56·5 mols. % of zinc at 284°, and above potassium amalgams containing up to 42·8 mols. % of potassium at 300° have been measured.

The partial pressures of potassium and mercury above potassium amalgams containing 41·1—72 mols. % of potassium at 387·5° have been measured, and from the result it has been deduced that a considerable amount of a compound of mercury and potassium, probably KHg, is present in the vapour of these amalgams at that temperature.

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