The method is applicable to the study of any elastic medium that can be formed into a membrane.

The influence of chrome alum and formaldehyde on gelatin jellies is shown.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

THE VAPOR PRESSURES OF POTASSIUM AMALGAMS

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According to the freezing point-composition curves of the amalgams of the alkali and alkaline earth metals,[1] these solutions should possess properties far different from those of the ideal solution. This assumption is confirmed by the vapor-pressure and electromotive-force measurements of several investigators.[2]

On account of the ease of distillation and availability of metallic potassium, its amalgams were chosen for study as examples of extremely imperfect solutions.

The method was that of Ramsay, which has been used by practically all investigators in this field. A closed J-tube was filled with the amalgam and thoroughly boiled out *in vacuo*, so that the short, closed arm contained no gas. The amalgam was then brought to a constant temperature and the pressure of the mercury vapor in the closed arm was balanced by that of hydrogen in the long arm. The pressure of the hydrogen was measured by means of a manometer. The fine adjustment of the hydrogen pressure was accomplished by means of a narrow barometric column as used by Hildebrand in his measurements of the vapor pressures of zinc amalgams.[3]

Apparatus.—The J-tube was of heavy-walled Pyrex tubing of 0.70 cm. internal diameter. The short arm was 3–4 cm. in length. The temperature was maintained by means of a well-insulated air-bath in which the temperature was kept uniform by means of a fan. Windows permitted observation of the amalgam. The voltage of the lighting circuit by which the oven was heated varied considerably, but it was found that equilibrium was attained so rapidly that the readings obtained fell upon the same curve whether the temperature was rising or falling.

The temperature was measured by means of a nichrome-constantan thermocouple

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[1] (a) Jänecke, *Z. physik. Chem.*, **57**, 510 (1907). (b) Smits and Beck, *Proc. Acad. Sci. Amsterdam*, **23**, 975 (1921).

[2] (a) Ramsay, *J. Chem. Soc.*, **55**, 521 (1889). (b) Meyer, *Z. physik. Chem.*, **7**, 477 (1891). (c) Schoeller, *Z. Elektrochem.*, **5**, 259 (1898). (d) von Wartenberg, *ibid.*, **20**, 443 (1914). (e) Eucken and Neumann, *ibid.*, **28**, 322 (1922). (f) Fay and North, *Am. Chem. J.*, **25**, 216 (1901). (g) Beckmann and Liesche, *Z. anorg. Chem.*, **89**, 171 (1914). (h) Beck, *Rec. trav. chim.*, **41**, 353 (1922).

[3] Hildebrand, *Trans. Am. Electrochem. Soc.*, **32**, 319 (1913).

which was chosen because its e.m.f. varies almost linearly with the temperature and the coefficient is high. The e.m.f. was measured with a Leeds and Northrup "Type K" potentiometer and an unsaturated Weston standard cell which was checked against one calibrated by the Bureau of Standards. The thermocouple was calibrated against the boiling points of water and of naphthalene and the melting point of a sample of zinc furnished for the purpose by the Bureau of Standards. The e.m.f.'s observed were found to be represented accurately by the equation used by Eastman and Rodebush[4] for copper-constantan at low temperatures

$$E = E_0 + aT^n$$

where E = e.m.f., and in the present instance $E_0 = -6840$, $\log a = 0.05706$, $n = 1.5490$ and T = degrees Kelvin. From this formula a table was constructed and all readings were converted to temperatures by its aid. The temperature scale was checked against that used by Smith and Menzies[5] in their determination of the vapor pressure of pure mercury by a similar determination with the apparatus used for the amalgams. The results are shown in Table I, which gives the pressures found and those calculated from the formula of Smith and Menzies. The divergence indicates the order of the experimental error; for instance, the temperature was known only to about 0.5°.

The pressure of the hydrogen was measured with a closed mercury manometer of 1.5cm. internal diameter which was placed before an accurate steel scale. Readings were taken through a telescope placed about 2 meters distant.

Materials.—The mercury was washed three times by spraying through a column of dilute nitric acid 150 cm. high and twice distilled in a current of air under reduced pressure.

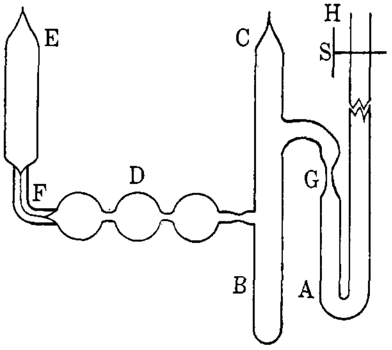

Fig. 1.

The amalgam was then made in a Pyrex glass apparatus represented by Fig. 1, which is one-third actual size. Having been well cleaned, the apparatus was first evacuated through the stopcock S by means of a mercury diffusion pump and heated almost to the softening point of the glass for about fifteen minutes. Air was then admitted, the tips of E and C were broken off and the desired amount of mercury was introduced through C, which was then sealed. The potassium, which had been kept under ether and dried beforehand, was placed in E, which was then sealed. The apparatus was evacuated for about two hours and strong heating of the parts which did not contain potassium or mercury was repeated at intervals. The potassium was warmed, but not melted, and the mercury was boiled gently. Finally, after a 500cc. McLeod gage connected to the line showed not more than 0.00005 mm. pressure of mercury when the apparatus was hot, the potassium was melted. It ran readily through the capillary F into the first bulb D, leaving the oxide shell in E, which was then sealed off at F and discarded.[6] The potassium was then distilled from one bulb D to the next and the residue in each case was sealed off. From the last bulb the potassium was distilled

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[4] Eastman and Rodebush, This Journal, **40,** 489 (1918).

[5] Smith and Menzies, *ibid.*, **32,** 1434 (1910).

[6] This method of cleaning the alkali metals was described by Lewis and Kraus, This Journal, **32,** 1459 (1910).

slowly into the mercury in B. The stopcock was then closed and the J-tube A with the stopcock and the attached tube B was broken off at H. The amalgam was then well mixed and the amount poured into A which was necessary to fill it from the point G slightly past the bend. The tube was then sealed to the vacuum line and B was sealed off at G. Hydrogen was next admitted. During all of these operations it was necessary to keep the tube and its contents warm in the cases of the more concentrated amalgams, for the frozen amalgams always broke the tube on melting. The three more dilute amalgams had the color of mercury, but the three more concentrated ones were gray to copper-colored. The remaining portions of the concentrated amalgams, which were examined in B, were fairly hard and of considerable mechanical strength. It is not thought that the color of the concentrated amalgams was due to impurity or to moisture in the glass, for it appeared as soon as the potassium and mercury came into contact and did not increase in the presence of hydrogen. Indeed, mercury vapor, which was always present near the top of B, turned the bright surface of the globules of potassium almost black.

The hydrogen was produced by the electrolysis of sodium hydroxide solution, passed over hot platinized asbestos and dried with phosphorus pentoxide. It had no visible effect upon the amalgams.

TABLE I

THE VAPOR PRESSURE OF MERCURY

T, °K.	$p_{\text{mm.}}$, obs.	Smith and Menzies
468.3	14.7	14.77
518.0	62.4	64.88
571.9	244.8	240.05
575.3	258.7	258.37
613.0	560.7	555.6
613.9	570.4	565.2

Analysis.—The tube containing the amalgam was sealed off, broken and dropped into an excess of 0.5000 *N* hydrochloric acid. A piece of platinum wire aided the solution of the metal, which was complete in about twelve hours. The excess of acid was then titrated and the mercury, after washing and drying at 40°, was weighed. Check results were obtained on the excess of amalgam remaining in B after the amount needed had been poured into A.

There were several sources of error on account of which the results can lay no claim to high accuracy. Even with pure mercury the error was about 2%, due largely to the leak of heat up the thermocouple leads. The use of a radiation shield around the thermocouple and the J-tube did not affect the readings except when it obscured the levels of the amalgam. The amalgams of low concentration did not affect the glass but those of the highest concentrations darkened it after a time and then showed a tendency to stick slightly.

Two serious sources of error were the evaporation of mercury into the open arm of the tube and the accumulation of hydrogen in the closed arm, the former causing low results, the latter high. The pressure of the hydrogen was removed frequently, so that the amalgam boiled into the open arm of the tube and at the same time the mercury which distilled and condensed on the upper part of the tube was shaken down by violent tapping. After this operation hydrogen could not be detected in the narrow tip at B where the tube had been sealed off and the mercury in the open arm was kept at a minimum. The tube, when taken for the analysis, was always drawn off at a point which had been inside of the furnace, so that mercury which had condensed in the open arm remained there. The errors in the steel scale and the reading of the manometer were less than those mentioned above.

TABLE II

VAPOR PRESSURES OF POTASSIUM AMALGAMS

T, °K.	$p_{\text{mm.}}$ of Hg
No .1, N_2 = 0.0492	
516.5	54.3
516.9	55.4
590.8	319.8
591.6	331.2
593.1	339.3
601.7	402.7
603.3	416.6
606.8	456.0
608.0	458.4
No. 2, N_2 = 0.0552	
513.5	49.2
513.8	49.8
514.4	50.6
515.9	53.0
516.4	54.0
516.9	54.0
615.1	508.1
615.3	510.0
615.6	511.3
625.7	593.2
626.1	595.2
627.2	595.6
628.2	602.6
629.0	609.9
No. 3, N_2 = 0.0877	
457.2	7.4
457.2	7.8
457.8	8.0
459.5	8.2
461.8	9.0
482.0	16.7
483.6	18.1
484.4	18.4
490.6	22.0
506.2	34.2
517.0	43.9
568.1	174.8
617.7	446.2
618.2	451.3
618.5	449.2
618.7	450.5
619.4	450.3
628.2	536.0
629.0	544.7
No. 4, N_2 = 0.180	
549.8	53.4
550.6	54.4
553.5	58.2
555.7	60.8
557.8	64.3
558.6	65.3
578.5	101.2
579.4	103.2
579.8	104.4
580.0	104.6
580.5	106.0
643.4	377.7
644.9	387.5
648.0	407.8
649.6	415.3
No. 5, N_2 = 0.321	
564.8	10.0
565.1	9.8
565.4	9.6
565.6	10.2
565.6	9.8
637.0	56.0
638.2	59.2
639.0	59.8
640.1	59.8
640.5	61.2
712.5	273.9
712.6	276.1
712.8	276.9
713.2	278.6

The data are given in Table II. The first column gives the temperature in degrees Kelvin and the second the pressure in millimeters of mercury at 0°. The mole fractions of mercury and of potassium are represented by N_1 and N_2, respectively.

These data, together with Smith and Menzies' data for pure mercury, are plotted in Fig. 2, and the equations for the straight lines which best fit the points for pure mercury and for each amalgam follow.

No.	N_2	Equation	
0	0	$\log p_1 = 7.841 - (3125/T)$	(1a)
1	0.0492	$\log p_1 = 7.799 - (3125/T)$	(1b)
2	0.0552	$\log p_1 = 7.779 - (3125/T)$	(1c)
3	0.0877	$\log p_1 = 7.717 - (3125/T)$	(1d)
4	0.180	$\log p_1 = 7.569 - (3212/T)$	(1e)
5	0.321	$\log p_1 = 7.968 - (3950/T)$	(1f)

These equations represent the individual pressures within 1–5%, usually 2–3%.

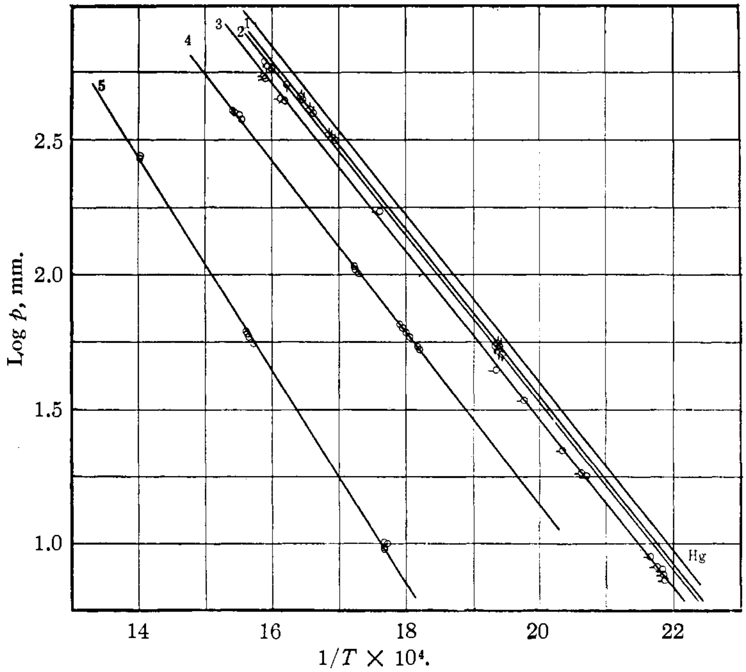

Fig. 2.—The vapor pressures of potassium amalgams.

In Table III are given the values of N_1 and of the activity, $a_1 = p_1/p_1^0$, of the mercury for each amalgam at 200, 250, 310 and 390°. The values of p_1 and p_1^0 were calculated from the equations for the vapor pressures of the amalgams and pure mercury.

Table III

The Activity of Mercury in Potassium Amalgams

	Temperature, °C.			
N_1	200	250	310	390
0.951	0.908	0.908	0.908	0.908
.945	.867	.867	.867	.867
.912	.752	.752	.752	.752
.819	.349	.364	.378	.394
.679	.0241[a]	.0355[a]	.0515	.0762

[a] Supercooled solution.

The equation of van Laar, which is discussed by Hildebrand,[7] was used to express the relation at each temperature between a_1/N_1 and the composition expressed as $r_1 = N_1/N_2$. The constants of the following equations were calculated from the data of Table III.

200° $\log a_1/N_1 = -64.71/(1 + 2.689r_1)^2$ (2a)
250° $\log a_1/N_1 = -28.94/(1 + 1.774r_1)^2$ (2b)
310° $\log a_1/N_1 = -14.16/(1 + 1.209r_1)^2$ (2c)
390° $\log a_1/N_1 = -7.041/(1 + 0.816r_1)^2$ (2d)

TABLE IV

COMPARISON OF PRESSURES CALCULATED FROM EQUATIONS 1 AND 2

Amal. no.	Eq. no.	Temperature, °C.			
		200	250	310	390
1	1b	15.56	66.70	275.0	1218
	2a–d	15.47	66.24	272.8	1206
2	1c	14.85	63.70	262.5	1164
	2a–d	15.16	64.92	267.3	1182
3	1d	12.88	53.95	227.6	1085
	2a–d	13.10	56.24	231.7	1025
4	1e	5.98	26.74	114.6	530.0
	2a–d	5.98	26.76	114.8	530.1
5	1g	0.41	2.61	15.57	102.4
	2a–d	0.41	2.60	15.60	102.6
Pure Hg	1a	17.15	73.52	303.0	1343
	Smith and Menzies	17.20	74.20	305.0	1336

Table IV gives the value of the vapor pressures calculated from the van Laar equation for each temperature and those calculated from the vapor pressure equations 1a–f. It will be noted that the agreement is about that of the agreement of equations 1a–f with the experimental data.

From the relation

$$\log \frac{a_2}{N_2} = \frac{\alpha_1 \beta_1}{(\beta_1 + r_2)^2} \qquad (3)$$

where a_2 is the activity of potassium and $r_2 = N_2/N_1$, which Hildebrand[7] has derived from the van Laar equation, the activities of the potassium can be calculated and an idea of the magnitude of the Henry's Law constant can be obtained by setting $r_2 = 0$, although the extrapolation is hardly to be recommended.

Fig. 3 is the plot of a_1 against N_1 for each of the four temperatures, the largest deviation from Raoult's law at each of the two highest concentrations being that corresponding to the lowest temperature.

Hildebrand has shown that $\log a_1/N_1$, for many systems, varies approximately linearly with N_2^2. In Fig. 4 these quantities are plotted for each temperature and the best curves, which are more nearly straight lines for the highest temperatures than for the lowest, are drawn.

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[7] (a) van Laar, *Z. physik. Chem.*, **72,** 723 (1910); (b) **83,** 599 (1913). (c) Hildebrand, "Solubility," The Chemical Catalog Co., New York, **1923,** p. 45.

In order to calculate the e.m.f. of the potassium electrode we should have to calculate from Equation 3 the activity of potassium in a dilute amalgam at each temperature for which the constants are given in Equations 2a–d, find the activity of potassium in that amalgam at 25° by extrapolation and then measure the potential of the amalgam against some standard electrode The last step has already been performed for a 0.2216%

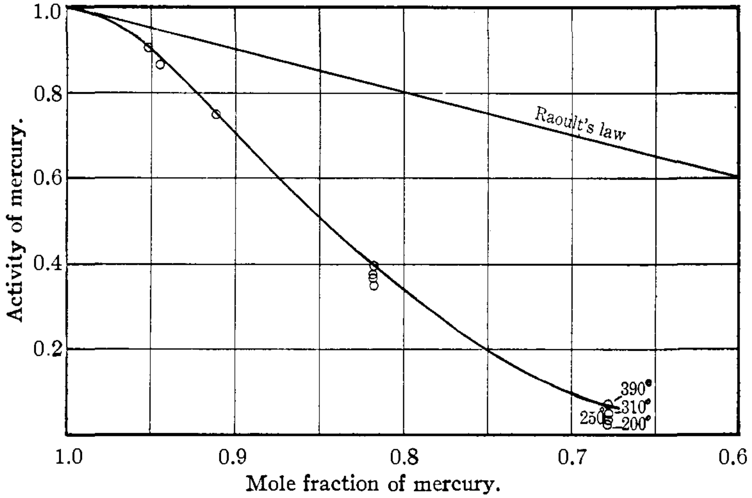

Fig. 3.—The activity of mercury in potassium amalgams.

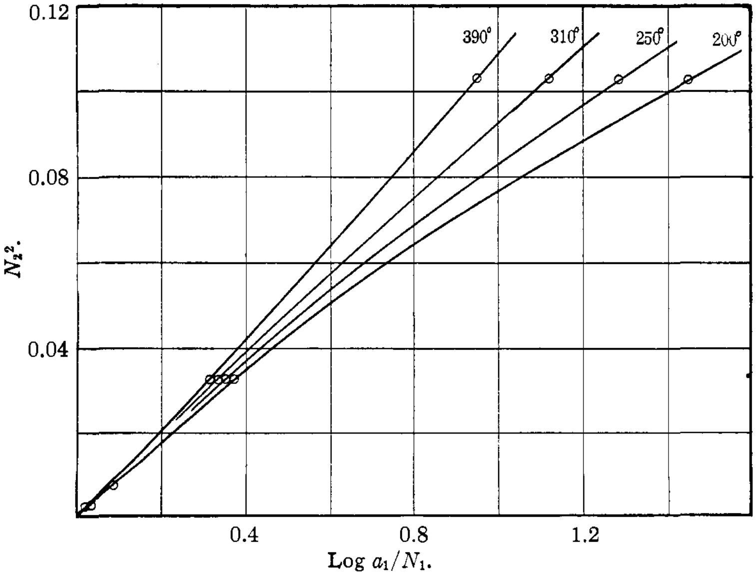

Fig. 4.—The variation of log a_1/N_1 with N_2^2.

potassium amalgam by Lewis and Keyes,[8] but due to the fact that a_2 changes rapidly with the temperature, which a_1 does not, the extrapolation of the calculated values to 25° does not appear feasible.

It is of interest to note that, within the accuracy of these data, the heat of vaporization of mercury from the amalgams in which the concentration of potassium is as high as 8 mole per cent. is equal to that of pure mercury. This may be explained if we assume that a mercuride exists in solution, and that, with respect to pure mercury as the solvent, it is a perfect solute. Such may easily be the fact if a large number of atoms of mercury are chemically combined with or attached to each atom of potassium. This average number, calculated from the vapor pressure lowering and the concentration of the solution, is 9.44 for No. 1, 10.6 for No. 2 and 7.36 for No. 3. Evidently the analysis for No. 2 is low, a fact which accounts for the position for this amalgam on Fig. 3.

At higher concentrations than 8 mole per cent. the partial molal heat content of the mercury becomes negative, as is to be expected in solutions in which the deviations from Raoult's Law are so greatly negative, and the more so the higher the concentration of potassium.

Summary

The vapor pressures of mercury in equilibrium with five potassium amalgams have been measured. The concentrations ranged from 5 to 32 mole per cent. of potassium and the temperatures from 184 to 445°.

The equation of van Laar, which expresses the vapor pressure as a function of the concentration, temperature being constant, has been found to agree with the experimental data within the limits of accuracy of the latter.

The relative partial molal heat content of solvent mercury in the amalgams not exceeding 8 mole per cent. of potassium was found to be zero.

The deviations from Raoult's Law are among the greatest yet noted in any solutions and, as is to be expected, they decrease with rising temperature.

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[8] Lewis and Keyes, THIS JOURNAL, **34**, 119 (1912).