tiometer switches;[1] hence, it can be tested for by connecting the external line directly to the external shield, setting the switches on zero, and then noticing if any change of deflection occurs on connecting or disconnecting the battery. The connection to the external shield in this test may be omitted if it is certain that the insulation between that and the measuring system will be as good in later work as it is at the time of the test.

The effectiveness of the external shield is certain if the shield is complete and is intact. Furnace leakage through an incomplete shield can be detected by reversing the furnace current, and the resulting false deflection (usually) can be measured by interrupting it.

Summary.

1. An insulation resistance of 5,000 megohms or more is often necessary to prevent serious disturbance of thermoelectric measuring systems from stray portions of power or lighting currents, and the frequently more sensitive resistance measuring system is of course in greater danger still. All such trouble is absolutely prevented by an equipotential shield, which is merely a connected system of metal plates, wires, etc., which interposes itself at every point of solid contact between the measuring system and external bodies. This shield need not be, and preferably should not be, "earthed."

2. Slight modifications of this shield are also useful in electric furnaces, in measurements upon power circuits, and within the potentiometer circuit itself.

3. These arrangements are easy to instal; most of them require no subsequent attention, and all are easily tested.

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

THE VAPOR PRESSURES OF SILVER, GOLD AND BISMUTH AMALGAMS.

By Ermon Dwight Eastman and Joel H. Hildebrand.

Received August 10, 1914.

The measurements presented in this paper on the vapor pressure of amalgams of silver, gold and bismuth are a continuation of an extensive study, planned and begun by one of us, of the laws of concentrated solutions from the standpoint of metallic solutions. Measurements on the vapor pressures of zinc amalgams have already been published,[2] and measurements by others of the electromotive force of amalgam concen-

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[1] This statement is here intended to apply only to the case of thermoelectric work, where the maximum change of switch setting is only a few millivolts.

[2] Joel H. Hildebrand, *Orig. Com. 8th Internat. Congr. Appl. Chem.*, **22**, 147; *Trans. Am. Electrochem. Soc.*, **22**, 319 (1912).

tration cells have been considered,[1] along with the vapor pressure measurements, in the light of Raoult's law, taking account, following Dolezalek,[2] of chemical changes such as solvation and association. For the progress of the work up to this point, as well as references to the literature on the subject, we would refer the reader to the previous papers.

Experimental Method.

The procedure followed has been essentially that used in the measurements on zinc amalgams. The amalgams whose vapor pressures were to be measured were confined in U tubes of the type shown in Fig. 1, in volumes a little more than sufficient to fill the closed limb of the tubes. The tubes were filled by introducing mercury and the metal in the desired proportions, the amalgamation and mixing being accomplished by the subsequent heating and vigorous agitation of boiling out. The angles in the tubes prevented portions of amalgam being carried over by the vapor during the boiling out. For the oxidizable bismuth amalgams, tubes like that of Fig. 2 were used. In this case the amalgams were formed by heating known weights of the constituents in the arm *a*, in an atmosphere of hydrogen. When the amalgams were run through the capillary *b*, into the U, all dross remained behind. The tubes were then sealed off at *b*. Hydrogen being now the gas in the tubes and apparatus, there was no oxidation.

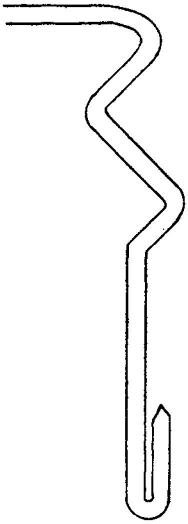

Fig. 1.

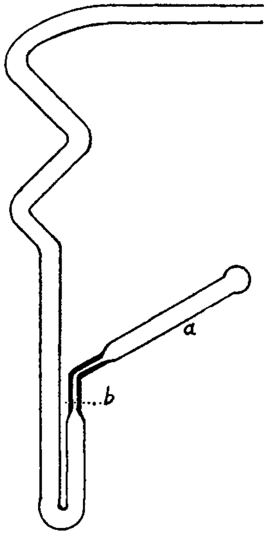

Fig. 2.

When filled, the tubes were placed in the thermostat, connected to a mercury manometer as shown in Fig. 3, and boiled out under reduced pressure to eliminate gas in the closed arms. Pressure in the open arm, sufficient to balance the pressure of mercury vapor in the closed arm, as indicated by the coincidence of the levels of the amalgam menisci, was then restored. After allowing time for thermal balance to be obtained, finer adjustments of pressure were made by means of the mercury reservoir shown, and the pressures read on the manometer. The relative pressure of solution and solvent being the quantity sought, a tube containing pure

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[1] *Orig. Com. 8th Internat. Congr. Appl. Chem.*, **22**, 139; *Trans. Am. Electrochem. Soc.*, **22**, 335 (1912).

[2] *Z. physik. Chem.*, **64**, 727 (1908); **71**, 191 (1910).

mercury was connected to a separate manometer of the same type, and observations made upon it immediately following and under the same conditions as the amalgam determinations. From these measurements, also, the temperature was given by the careful measurements of Smith and Menzies[1] on the vapor pressures of mercury.

The thermostat consisted of a tall beaker resting in a similar beaker one size larger, which served as a jacket. Fused sodium and potassium nitrate mixture, vigorously stirred, furnished the bath for the tubes, heated by the vapor of boiling phenanthrene in the outer beaker. The outer beaker was protected to the level of the inner bath by a glass cylinder cut from another beaker. The exposed portion acted as a condenser for the phenanthrene vapors. A Méker burner was the source of heat. In starting the thermostat, the nitrates were fused separately and poured into the inner beaker, which was already heated by the boiling phenan-

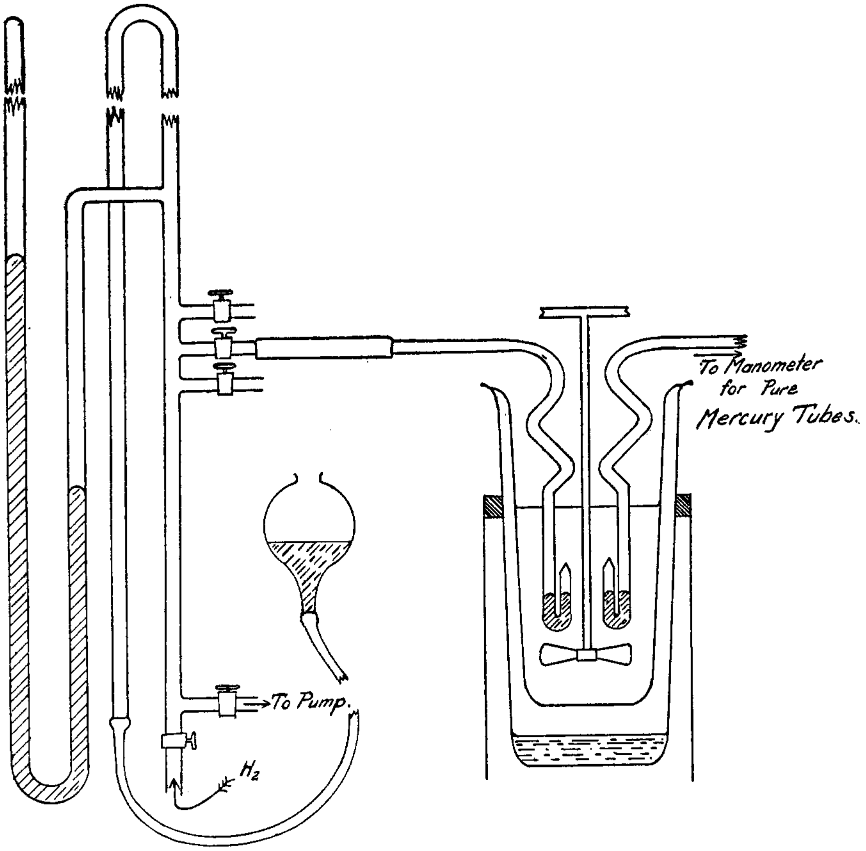

Fig. 3.

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[1] This Journal, 32, 1434 (1910).

threne. At the conclusion of a run both the nitrates and the phenanthrene were removed from the beakers. During observations the top of the thermostat was covered as well as possible with strips of mica. The constancy of temperature attainable may be seen in the tables of results.

Sources of Error.

The quantities to be determined were the relative vapor pressures and the atomic fractions of the amalgam constituents at constant temperatures.

The variation of relative pressure with the temperature is not large. The practically simultaneous determination of the pressures from amalgam and mercury, therefore, eliminate the observed variations in the temperature as serious sources of error, provided equilibrium was reached.

The error due to impurities in the materials would appear in the estimation of the atomic fraction. The mercury used was carefully purified by washing in dilute nitric acid[1] and distilling in a current of air.[2] The gold and silver were also purified in the laboratory by the usual methods. Kahlbaum's bismuth was used. Since there are no abnormally large effects due to traces of impurities, the error from this source was negligible. There were slight variations from the values of the concentrations, as had from the weights of the constituents, on account of the condensation of small amounts of mercury in the upper portions of the tubes. This, too, was negligible, except in the case of the extremely concentrated bismuth amalgams. Here a correction was made by weighing the condensed mercury. It was, of course, always possible, though seldom necessary, to analyze the amalgams after the experiment, if any doubt as to its composition existed.

The accuracy of the results was determined, it is seen, by the accuracy of the pressure determinations. This was preserved, as far as possible, by the elimination, by boiling out, of the gas which it was found was given off by the glass in varying amounts in the closed arm during determinations. Condensation of the vapor of mercury in the closed arm by increasing the pressure permitted very small amounts of gas to be detected at the point of the tube. The tubing was of large enough diameter to minimize any unequal effects of surface tension in the different arms of the tubes. An incandescent bulb placed behind the thermostat enabled the menisci to be easily observed. The error in adjustment and reading of the pressures, it is estimated, was not greater than a millimeter. This was greatly reduced by making a number of observations for each determination. The degree of agreement of these separate observations among themselves can be seen from the tabulated results. Due, probably, to increasing skill in manipulation, this was markedly better in the case of bismuth than of gold.

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[1] Hildebrand, THIS JOURNAL, **31**, 933 (1909).

[2] Hulett, *Phys. Rev.*, **33**, 307.

Experimental Results.

Silver Amalgam.—In Table I are given the results upon the vapor pressure of the single silver amalgam investigated. From a preliminary series of measurements it was found that silver is but slightly soluble in mercury, even at these temperatures. On that account but one accurate determination was made. In the table, P denotes the vapor pressure of the amalgam, P_0 that of mercury at the same temperature, t the corresponding temperature, according to the measurements of Smith and Menzies,[1] and N the number of atoms of mercury per atom of solute metal.

TABLE I.—SILVER AMALGAM.

	P.	P_0.	P/P_0.	t.
Wt. Ag 0.1783	318.2	325.3	0.978	313.1
Wt. Hg 14.013	318.2	325.7	0.977	313.2
$N = 42.27$	318.4	325.7	0.977	313.2
	315.4	324.7	0.972	313.0
	317.7	324.7	0.979	313.0
	318.1	325.7	0.977	313.1
		Mean,	0.9767	313.1
		$N/N + 1$	0.9769	

Gold Amalgams.—In order to save space we give the individual observations on but one amalgam, as a sample, in Table II. The results of the other series of observations are merely summarized in Table III, including the "probable error" of each set of observations of P/P_0, calculated by the usual formula. These results are represented graphically in Fig. 4, relative pressures, P/P_0, being plotted against the atomic fractions of gold, $1/N + 1$.

TABLE II.—GOLD AMALGAM.

	P.	P_0.	P/P_0.	t.
Expt. No. 27	344.9	350.1	0.986	316.7
Wt. Au 0.2018 g.	346.5	353.3	0.982	316.1
Wt. Hg 13.328 g.	345.3	351.5	0.983	316.7
$N = 65.0$	348.0	352.9	0.990	317.1
$N/N + 1 = 0.985$	351.5	355.2	0.990	317.4
	351.5	356.1	0.988	317.6
	351.0	355.5	0.988	317.4
	351.9	356.3	0.988	317.6
	351.3	356.5	0.987	317.4
	352.0	356.1	0.988	317.4
	352.7	356.1	0.991	317.4
		Mean,	0.987	317.3

Bismuth Amalgams.—Here again we will not burden the text with an extended series of tables of the separate series of observations, but summar-

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[1] *Loc. cit.*

Table III.—Gold Amalgams.

Wt. Au.	Wt. Hg.	No. of obs.	N.	$1/N + 1$.	P/P_0.	"Prob. error" ±.	t.
0.2018	13.328	11	65.0	0.0152	0.987	0.0006	317.3
0.5707	14.002	14	24.1	0.0398	0.979	0.0005	316.6
0.7436	12.541	13	18.14	0.0652	0.968	0.0006	315.4
0.997	13.125	10	12.96	0.0717	0.955	0.0006	317.5
1.269	12.666	8	9.84	0.0925	0.950	0.0014	313.0
1.354	11.796	6	8.81	0.1046	0.945	0.0005	319.8
1.636	12.441	12	7.48	0.1179	0.942	0.0006	317.5
2.363	13.125	3	5.56	0.153	0.931	0.0013	315.9
3.109	13.125	2	4.22	0.191	0.933	0.0013	316.2

ize the mean values, giving the calculated "probable error" of the observed ratios P/P_0. The summary is given in Table IV. The results are plotted in Fig. 4, the ordinates, as before, being the relative pressures P/P_0 and the abscissae the atomic fractions of bismuth $1/N + 1$.

Table IV.—Bismuth Amalgams.

Wt. Bi.	Wt. Hg.	No. of obs.	N.	$1/N + 1$	P/P_0 obs.	"Prob. error" ±.	t.	P/P_0 calc.	Difference.
0.4125	7.388	5	18.57	0.0510	0.961	0.0007	320.3	0.960	+0.001
2.504	20.690	4	8.31	0.1074	0.929	0.0004	320.3	0.927	+0.002
2.647	14.644	4	5.73	0.1486	0.908	0.0002	321.1	0.904	+0.004
3.669	10.757	4	3.05	0.247	0.840	0.0004	321.0	0.842	—0.002
7.865	14.274	3	1.88	0.347	0.765	0.0006	320.9	0.765	±0.000
7.582	8.485	4	1.16	0.463	0.650	0.0005	320.3	0.658	—0.008
11.201	8.383	5	0.777	0.563	0.542	0.0007	321.9	0.552	—0.010
12.576	6.334	5	0.522	0.670	0.432	0.0007	320.3	0.428	+0.004
19.598	4.980	4	0.262	0.793	0.278	0.0004	321.7	0.277	+0.001
9.328	0.618	2	0.0686	0.937	0.092	0.002	321.2	0.088	+0.004

Interpretation of the Results.

The expression most frequently used for calculating vapor pressures of binary mixtures is Raoult's law,

$$P/P_0 = N/N + 1.$$

It will be seen that the dilute silver amalgam investigated obeyed this law very closely, as all solutions undoubtedly would if sufficiently dilute. At this concentration, therefore, we may regard the atom and molecule of silver as identical, confirming the results of Ramsay.[1]

Turning next to bismuth amalgams, we see from Fig. 4 that the relative vapor pressures are greater than those calculated from the simple Raoult law, which would give a straight line, as indicated. There are two methods whereby such deviations have been accounted for. The first is to assume that Raoult's law is fundamentally correct, and that all apparent deviations are due to a change in the real mol-fraction, caused by a change in the molecular species present. For example, if the bismuth were completely associated to form Bi_2, then there would be not 1 mol of bismuth to N of

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[1] *J. Chem. Soc.*, **55**, 521 (1889).

mercury, but 0.5 mol, and the relative vapor pressure of the mercury would be given by the equation,

$$P/P_0 = N/N + 0.5.$$

Such a modification of Raoult's law gives values of P/P_0 for bismuth amalgams which are too great. The next step would be to assume a partial association according to the equation

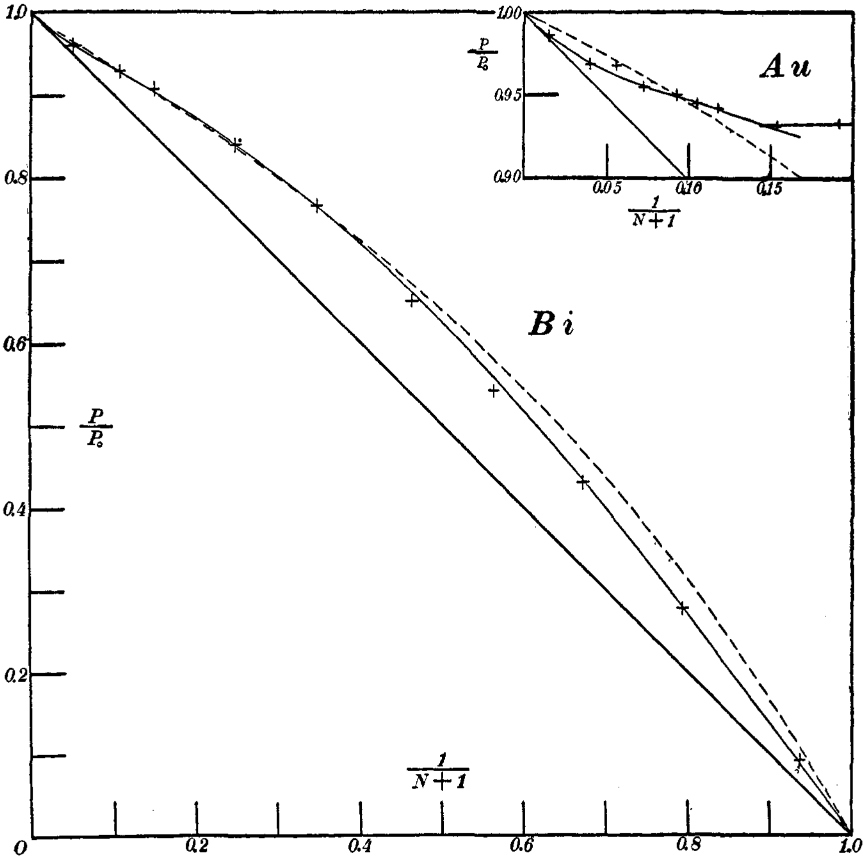

Fig. 4.

$$2Bi \rightleftarrows Bi_2.$$

Here, if α represents the mols of Bi_2 formed, and $1 - 2\alpha$ the mols of Bi present, then we would have for the mol-fraction of mercury

$$P/P_0 = N/N + 1 - \alpha, \qquad (1)$$

α and N being connected with the equilibrium constant K of the above equilibrium by the equation

$$K(1-2\alpha)^2/(N+1-\alpha)^2 = \alpha/(N+1-\alpha)$$

or

$$K(1-2\alpha)^2 = \alpha(N+1-\alpha) \qquad (2)$$

The elimination of α between Equations 1 and 2 gives the formula used successfully to calculate the relative vapor pressures of zinc amalgams[1] and the e. m. f. of concentration cells of zinc, lead and tin amalgams.[1] In the present case, however, we find that the observations will not fit this type of curve. If $K = 40$, P/P_0 is given by the broken curve in Fig. 4. It will be seen that the relative pressures are given fairly well up to a bismuth concentration of about 33 atom-per cent., but for more concentrated amalgams the observed values lie considerably below the curve. Nor is it possible to improve the agreement by altering the value of K. A smaller value of K would reduce the calculated values of P/P_0 chiefly at the left end of the curve in the figure, rather than at the right, where $1/N+1$ is large. The discrepancy could undoubtedly be removed by assuming a second equilibrium whereby there is partial formation of Bi_2Hg. This would introduce a second equilibrium constant into the equation for P/P_0, and give a very complicated expression, in spite of the fact that it would contain but two constants. The method for doing this is obvious, and it hardly deserves the space that it would require.

The second method for calculating such curves is in accordance with the theory published in an important paper by van Laar.[2] As has been pointed out by Washburn,[3] the law of Raoult cannot hold where two liquids are present which are not completely miscible. The vapor pressure of either component must be the same from each liquid phase, while by no assumption can its mol-fraction be the same in both. In other words, the escaping tendency of one component from the phase composed largely of the other is greater than its mol-fraction in that phase, due, we may imagine, to the inability of molecules of the first component, having a volume b, to penetrate as easily a liquid composed largely of molecules of the second, having a different volume, b'.[4] Now, if such a system were subjected to a change of temperature so that the two liquid phases became one, we can hardly imagine that Raoult's law would suddenly become valid, since the cause of the deviation when two liquids were present has been gradually diminished rather than suddenly removed. The idea underlying van Laar's treatment of the question is, therefore, undoubtedly correct, as he introduces the values of b, in the sense of the van der Waals equation, and also a factor, β, depending on the heat of mixing. Refer-

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[1] J. H. Hildebrand, *l. c.*

[2] *Z. physik. Chem.*, **72**, 723 (1910); **82**, 599 (1913).

[3] *Trans. Am. Electrochem. Soc.*, **22**, 330 (1912).

[4] The influence determining this difference between the relative escaping tendency and the mol-fraction have been termed by Washburn the "thermodynamic environment." In view of the kinetic explanation one is led to feel that the adjective might be omitted without any real sacrifice of meaning.

ence must be made to the original paper for the derivation of his equations and their theoretical consideration. We will merely give the equations there derived for each component.

$$P/P_0 = xe^{\frac{\beta(1-x)^2}{(1+r)(1+rx)^2}}, \quad \text{and} \quad P'/P_0' = (1-x)e^{\frac{\beta x^2}{(1+rx)^2}}$$

where

$$r = (b-b')/b', \text{ and } x = N/N+1.$$

In our notation the vapor pressure of mercury from amalgams may be expressed in the simplified form

$$P/P_0 = Ny/N+1$$

where $\log_{10}y = a/(1+cN)^2$. By making approximate solutions it was found that the measurements are given very closely by this formula when $a = 0.1425$ and $c = 0.234$. The curve corresponding to these values is drawn in the figure, the calculated values of P/P_0 corresponding to the measured values are given in the 9th column of Table IV, and the differences between the calculated and measured values are seen in the last column. The agreement is seen to be quite satisfactory. The values of a and c here used are quite empirical. Data upon the heat of mixing are not at hand, so that the value of a cannot be tested. However, c depends upon the ratio of b for mercury to that for bismuth. This would probably be not very different from the ratio of the molecular volumes at these temperatures, which is approximately 0.75. This would give to r the value -0.25, and to c, 0.75. This is quite different from the empirical value given above, so that the equation expressing the observations should hardly be considered, at least for the present, as having any theoretical significance.

The values of P/P_0 for gold amalgams, as will be seen from the curve, deviate strongly from the simple form of Raoult's law as the concentration increases. The small solubility of gold in mercury at this temperature prevents any considerable portion of the curve from being realized experimentally. The appearance of a solid phase at a concentration of about 15 atom-per cent. is evident from the curve, and was obvious during the experiment. The deviations are too great to be accounted for by the assumption of the presence of the compound Au_2Hg, the existence of which is reported by G. McP. Smith[1] from evidence gained by diffusion experiments. According to this assumption we should have

$$P/P_0 = (N-0.5)/N$$

The graph of this equation is given in the figure, and it is obvious that the measurements could be accounted for only by assuming a molecule containing more gold atoms and dissociating rather completely in dilute

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[1] THIS JOURNAL, 36, 847 (1914).

solution to give Au molecules. The construction of a curve on the basis of such assumptions would have very little theoretical justification, in view of the small range of concentration over which it might be tested. Turning to the equation in the form given by van Laar, we find that a satisfactory agreement with the observed values is obtained by taking

$$\log y = 0.23/(1 + 0.25N)^2$$

The curve drawn through the points is calculated from these constants in the equation

$$P/P_0 = Ny/N + 1$$

These two methods of accounting for vapor pressures of mixtures seem to be very different, and they have been the subject of some harsh polemic between van Laar[1] and Dolezalek.[2] It would seem that neither point of view should prevail to the exclusion of the other. Undoubtedly there exist cases where chemical changes should be regarded as the chief modifying factor, and the treatment used by Dolezalek is substantially correct. It is equally certain, however, that all deviations from the simple law cannot correctly be accounted for in this way, and that curves, as drawn in Fig. 4, may be strongly convex upwards where no essentially chemical changes are involved, and where the general principle underlying van Laar's treatment of the problem must be invoked. Some external evidence must be sought in many cases to decide in how far individual deviations from the simple law should be explained by one method or the other. For example, if we extrapolate from our measurements to find the condition of bismuth when $N = 0$, *i. e.*, when pure liquid bismuth is present, we find that according to the method of van Laar it might be monatomic, in spite of the convexity of the curve in Fig. 4, whereas, according to the method maintained by Dolezalek, it must be more or less associated. Now if we should find independent evidence as to the molecular weight of molten bismuth, we would be in a position to lend strong support to one or the other of these two points of view. A study of such evidence is being made, and will be the subject of a communication in the near future. We hope, also, that further light will be shed upon the subject by the vapor pressure measurements planned upon other amalgams. For the present, therefore, we will forego further discussion, and rest with the presentation of the above facts.

Summary.

Measurements have been made of the vapor pressures of silver, gold and bismuth amalgams, at approximately 318°. Silver being but slightly soluble at this temperature, one measurement only was made, with an

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[1] *L. c.*

[2] *Z. physik. Chem.*, **83**, 40 (1913).

amalgam containing 1.27% of silver. Raoult's law was found to be obeyed within the limit of experimental error.

Measurements with gold amalgams at concentrations up to 23.7% of gold showed the separation of a solid phase at an approximate composition of 16.5%. In the more dilute amalgams the vapor pressures were found to be greater than those calculated from the simple form of Raoult's law. The deviation is such that to explain it on the basis of Raoult's law one would have to assume a rather complex gold molecule. The observations are very well expressed by the equation:

$$\frac{P}{P_0} = \frac{N}{N+1}\, 10^{\frac{0.23}{(1 + 0.25\,N)^2}}$$

This equation corresponds in form to one derived by van Laar, but with values assigned to the constants which are purely empirical.

Bismuth amalgams of all concentrations are liquid at this temperature, and, like gold amalgams, gave vapor pressures higher than those calculated from Raoult's law. If the validity of that law is assumed the deviations from its simple form could be explained by assuming the two equilibria:

$$2\mathrm{Bi} \leftrightarrows \mathrm{Bi_2}, \text{ and } \mathrm{Bi_2} + \mathrm{Hg} \leftrightarrows \mathrm{Bi_2Hg}$$

This would give an equation containing but two constants, but complicated in form. The equation of van Laar, which permits deviations from Raoult's law without assuming association or other chemical changes, again expresses the observations very accurately when numerical values are chosen as follows:

$$\frac{P}{P} = \frac{N}{N+1}\, 10^{\frac{0.1425}{(1 + 0.234\,N)^2}}$$

It is pointed out, however, that too much stress should not be placed upon this agreement on account of the entirely empirical nature of the constants assumed.

To decide to what extent deviations from the simple Raoult's law should be accounted for by either of the two methods, it is shown that recourse must be had to other methods for distinguishing between normal and associated liquids.

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE MEASUREMENT OF OXIDATION POTENTIALS AT MERCURY ELECTRODES. I. THE STANNIC-STANNOUS POTENTIAL.

BY GEORGE SHANNON FORBES AND EDWARD PAYSON BARTLETT.

Received August 14, 1914.

The existing data on oxidation potentials are neither so abundant nor so concordant as the importance of the subject would warrant. This remains true of the stannic-stannous potential, for instance, in spite of