

iodide solution are shown to give a constant e. m. f. when measured against an unpolarizable electrode. Freshly cast rods of cadmium are shown to attain this value with time.

4. The behavior of cadmium electrodes in concentration cells is explained as due to an allotropic change.

5. Crystalline electrolytic deposits of cadmium on cadmium rods or platinum are shown to give a reproducible e. m. f. when measured against an unpolarizable electrode. This e. m. f. is, however, slightly higher than that given by the gray cadmium electrodes. Amalgamated electrodes are not reproducible.

6. Photomicrographs indicate a change in crystalline form and confirm the conclusions drawn from the e. m. f. measurements.

7. Attempts to inoculate the surface of the freshly cast cadmium with the stable modification indicate that the action is extremely slow.

8. Photomicrographs indicate that in all cases the change is due to a deposit upon the surface instead of to a pitting of the surface.

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## THE ENTROPY OF VAPORIZATION AS A MEANS OF DISTINGUISHING NORMAL LIQUIDS.

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In a series of studies which we are making on the theory of solutions, it has become necessary to distinguish between deviations from Raoult's Law, whose cause may be considered physical, and those due to chemical changes. As has been pointed out in a previous paper,<sup>1</sup> the choice between the alternatives in a given case is possible if we know whether or not the pure liquids are associated. For example, the occurrence of vapor pressures greater than those calculated by Raoult's Law in a mixture of benzene and stannic chloride, is explained by Schulze and Hock<sup>2</sup> on the assumption that the stannic chloride is associated, to a degree depending on the concentration. A great many deviations from Raoult's Law may be explained in this way, as the writer himself has done in the case of a number of amalgams.<sup>3</sup> Such an assumption would be unjustifiable if we were sure that both liquids were themselves normal, that is, unassociated, for the presence of another component must tend to diminish such association rather than to increase it. In fact, in the case of benzene

<sup>1</sup> Ermon D. Eastman and Joel H. Hildebrand, "The Vapor Pressure of Gold, Silver and Bismuth Amalgams," THIS JOURNAL, 36, 2020 (1914).

<sup>2</sup> Z. physik. Chem., 86, 445 (1914).

<sup>3</sup> Trans. Am. Electrochem. Soc. 22, 319, 335 (1912); THIS JOURNAL, 35, 501 (1913); 36, 2020 (1914).

and stannic chloride, just mentioned, all of the criteria we are able to apply show stannic chloride to be a normal liquid, so that its failure to lower the vapor pressure of benzene to the extent demanded by Raoult's Law is to be explained, not by a reduction in the number of mols of stannic chloride added, but rather to a physical effect such as would result from a change in the internal pressure, tending to increase the escaping tendency of the benzene.

In order to judge similarly of the correctness of the assumptions made in the calculations with amalgams, it is necessary to know whether the liquid metals are normal or associated. Unfortunately, however, most of the relations used to distinguish between normal and associated liquids are applicable only to organic liquids; being additive properties depending upon atomic values determinable only for such elements as form a number of compounds in various proportions. The only relations that are applicable to liquid metals are the surface tension law of Eötvös,<sup>1</sup> and Trouton's rule,<sup>2</sup> either in its original form or in one of the various modifications that have been proposed.

The application of the former relation to liquid metals has led to the conclusion that they are more or less associated. The value of this testimony will be considered in a future communication, this one being reserved for a discussion of the evidence furnished by the heat of vaporization.

The original Trouton rule states that the heat of vaporization of a liquid, divided by its absolute boiling point, is a constant for all normal liquids. This relation holds very well for normal liquids boiling in the neighborhood of 100° to 300°. It has been derived theoretically from the theorem of corresponding states;<sup>3</sup> however, it must hold more closely than this theorem.<sup>4</sup> As an extreme instance, mercury, for which Trouton's rule holds very well, shows wide deviation from the "law" of corresponding states. Moreover, its critical temperature, though not known, is certainly above 1000°,<sup>5</sup> so that its boiling point, 632° A, is far from being 0.66 of its critical temperature on the absolute scale, as would be required to give any validity to this proof of Trouton's rule for mercury.

For associated liquids, such as water, alcohol, and liquid ammonia, the ratio is larger, which is explained by assuming that when a liquid is associated and its vapor is not associated, a certain amount of heat is required to dissociate the molecules of the liquid, hence the normal heat of vaporization is increased. The effect on the boiling point is doubtless

<sup>1</sup> *Wied. Ann.*, **27**, 448 (1886). See also Ramsay and Shields. *Z. physik chem.*, **12**, 431 (1893).

<sup>2</sup> *Phil. Mag.*, [5] **18**, 54 (1884).

<sup>3</sup> See for example Iterson, *Z. physik. Chem.*, **53**, 633 (1905).

<sup>4</sup> See Bingham, *THIS JOURNAL*, **28**, 717 (1906).

<sup>5</sup> Menzies, *THIS JOURNAL*, **35**, 1065 (1913).

not very large, so that when abnormally high values are obtained the evidence of dissociation seems fairly satisfactory. Since the quotient of the heat of vaporization by the absolute boiling point represents the increase in entropy of the substance during vaporization, and since we wish to refer to this ratio at temperatures other than the boiling point, we will use the less cumbersome term entropy of vaporization.

A rule essentially the same as that of Trouton has been given by Le-Chatelier and Forcrand<sup>1</sup> whereby the entropy of dissociation of certain solid compounds at one atmosphere pressure is approximately 33 calories per degree.

As Trouton's rule has become more completely tested, especially at extreme temperatures, it has become evident that the entropy of vaporization to one atmosphere is by no means constant for all normal substances, but that it increases with the boiling temperature. Various modifications have accordingly been suggested. Two of these have been proposed by Nernst,<sup>2</sup> *i. e.*,  $L/T_b = 8.5 \log T_b$ , and  $L/T_b = 9.5 \log T_b - 0.007T_b$ , where  $L$  is the molecular heat of vaporization at constant pressure, and  $T_b$  the absolute boiling point. It is impossible to determine from what Nernst says, whether they have any other than an empirical foundation. They seem to be intended chiefly to take into account the low boiling gases. Another formula has been proposed by Bingham,<sup>3</sup>  $L/T_b = 17 + 0.011 T_b$ . This formula is also empirical, and has been constructed without much reference to liquids boiling at very high or very low temperatures. More recently Forcrand<sup>4</sup> has published a formula, also empirical, but which has attempted to include liquids with very high, as well as those with very low boiling points:  $L/T_b = 10.1 \log T_b - 1.5 - 0.009T_b + 0.0000026T_b^2$ . The course of this equation at high temperatures was determined by using data for the boiling points of silver and copper. It should be mentioned that the values at high temperatures would be considerably different if the data for zinc, bismuth, lead and tin, apparently as trustworthy as those for silver and copper, had been taken into account. For this reason the use of the formula by Forcrand for extrapolation to still higher temperatures, to get the boiling point of carbon, cannot be regarded as very significant.

Except for zinc and cadmium, the only values for the vapor pressures of metals at high temperatures are those of Greenwood,<sup>5</sup> who determined the boiling points at three different pressures. Unfortunately, it is not possible to decide how much weight to give to these measurements. The

<sup>1</sup> *Ann. chim. phys.*, [7] 28, 384, 531 (1903).

<sup>2</sup> *Gött. Nachr.*, 1906.

<sup>3</sup> *THIS JOURNAL*, 28, 723 (1906). A recent paper by Sonaglia should be mentioned in this connection, *Nuovo Cimento*, 7, 321 (1914).

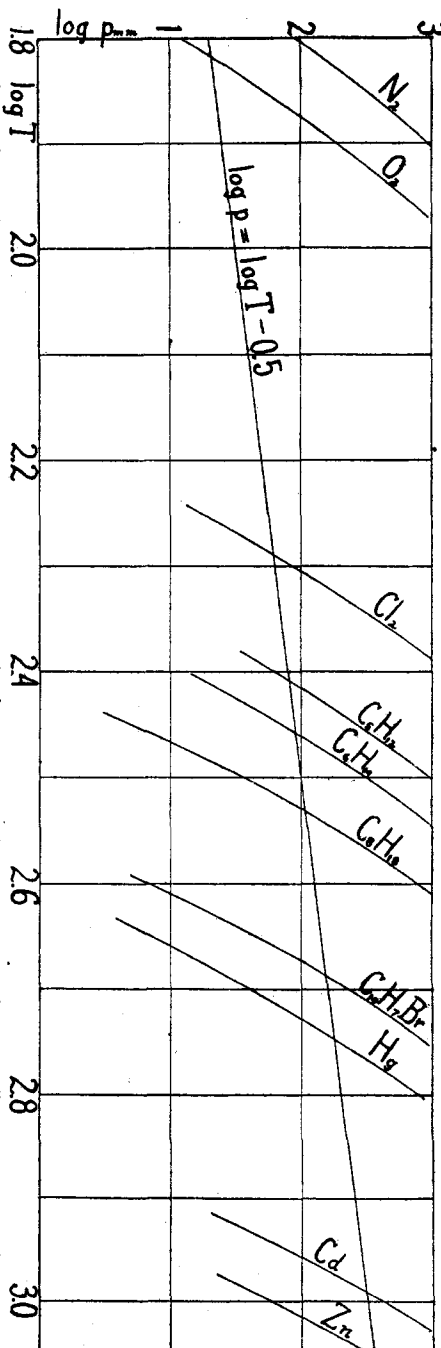
<sup>4</sup> *Compt. rend.*, 156, 1439, 1648, 1809 (1913).

<sup>5</sup> *Proc. Roy. Soc. [A]*, 83, 483 (1910).

heat of vaporization calculated from one pair of values is widely different from that calculated from another pair in the case of each element. The simplest way to test vapor pressure measurements is to plot  $\log p$  against  $1/T$ , which should give almost a straight line. The measurements of Barus<sup>1</sup> on cadmium and zinc when plotted in this way seem to be very satisfactory, a number of values being given in each case. On the same basis, however, the data of Greenwood for the other metals can hardly have much weight, either for or against any generalization on the entropy of vaporization. We hardly feel justified, therefore, in using the formula of Forcrand, gotten by using arbitrarily the data for two metals, to decide whether or not several others are normal or associated in the liquid state. It becomes necessary, therefore, to have some more justifiable basis for extrapolation from ordinary to high temperatures.

A formula has been published recently by Cederberg,<sup>2</sup> but it cannot be applied to the metals, as it requires a knowledge of the critical pressure and temperature.

It must be noted, first of all, that the boiling point at one atmosphere pressure has no special significance. We may, if it is desired, select any pressure or function of the pressure and temperature for comparing the entropy of vaporization of different substances. In order to represent the entropy of vaporization graph-



<sup>1</sup> *Phil. Mag.*, [5] 29, 141 (1890).

<sup>2</sup> *Z. physik. Chem.*, 77, 498 (1911).

ically we may put the Clapeyron-Clausius equation,  $d \ln p / dT = L_v / RT^2$ , into the form:  $d \log p / d \log T = L_v / RT$ . If, then,  $\log p$  is plotted against  $\log T$ , the tangent to the resulting curve at any point represents the entropy of vaporization at that temperature divided by  $R$ . The appearance of such curves is shown in the accompanying figure, the original scale being greatly reduced in order to represent a number on the same plot. Now, if Trouton's rule in the original form were true, then the tangents to all of these curves should have the same slope at a value of  $\log p$  corresponding to one atmosphere. It is evident, however, that this is not the case, but that the slope of the curves, at equal values of  $\log p$ , increases regularly with the logarithm of the temperature. Therefore, the entropy of vaporization for different substances cannot be the same at equal pressures, but rather at pressures that increase in some way, with the temperature. It was found that the tangents to the curves at points cut by any line of unit slope have the same slope, with a remarkable degree of precision. For accurate comparison the curves can be plotted on different sheets of transparent paper, and a line drawn on each whose equation is  $\log p = \log T + K$ , where  $K$  is a constant. By sliding one plot over the other, keeping this straight line superimposed on the two plots, it is possible to superimpose the curves with surprising accuracy, from the curves for nitrogen and oxygen up to those for cadmium and zinc.

The significance of the line of unit slope is this: since, for any vapor, at pressures low enough for it to obey the gas laws sufficiently accurately, we have the equation  $p = RTc$ , where  $c$  denotes concentration, and therefore  $\log p = \log T + \log Rc$ , the constant,  $K$ , in the above equation must equal  $\log Rc$ , and therefore along such a line  $c$  is constant. Our conclusion may be stated in words as follows: the entropy of vaporization for normal liquids is the same when evaporated to the same concentration, *i. e.*, when the final mean distance between the molecules of vapor is the same.

In Table I are given values of  $L_v / RT$  which make possible a numerical comparison of the new rule with that of Trouton, or its equivalent. The first column of figures contains the values of  $L_v / RT_c$  according to the new rule, the subscript denoting equal concentration of vapor. These values were obtained by plotting  $\log p$  (in mm. of mercury) against  $\log T$  very carefully on a large scale, and determining the slope of the tangents to the curves when  $\log p = \log T - 0.5$ , corresponding to a value of  $c$  of 0.00507 mols of vapor per liter. The selection of this concentration was entirely arbitrary, there being no apparent reason for choosing any particular concentration except the desirability of avoiding any extrapolation of the experimental data, that is, using a line that would cut all of the curves so plotted. In the second column are the values of  $L_v / RT_p$ , taken from the same curves but at equal values for the pressure, so as to correspond to Trouton's rule. However, instead of comparing the values when the

TABLE I.

Substance.	$L/RT_c$ $\text{Log } p = \text{log } T - 0.5$ .	$L/RT_p$ $\text{Log } p = 2$ .	$T_c$ .	$T_p$ .
Nitrogen.....	13.8	11.0	55	63
Oxygen.....	13.8	11.4	75	81
Chlorine.....	13.9	13.5	194	200
Pentane.....	13.5	13.2	256	260
Isopentane.....	13.7	13.5	258	262
Hexane.....	13.6	13.3	286	289
Carbon tetrachloride.....	13.5	13.4	294	295
Benzene.....	13.7	13.7	298	299
Fluorobenzene.....	13.7	13.7	303	304
Stannic chloride.....	13.6	13.6	329	328
Octane.....	13.8	13.9	338	339
Bromonaphthalene.....	13.8	14.1	486	472
Mercury.....	13.1	13.5	560	533
Cadmium.....	13.2	14.8	988	908
Zinc.....	13.2	15.1	1130	1030
Ammonia.....	16.2	..	200	..
Water.....	16.0	..	325	..
Ethyl alcohol.....	16.7	..	307	..

pressure of the vapor is one atmosphere, and when it may deviate considerably from the gas laws, it was thought fairer to choose a somewhat lower pressure. Accordingly the values in the table are for  $\text{log } p = 2.0$ , corresponding to a pressure of 100 mm. of mercury. If Trouton's rule holds for one pressure it must hold for any other pressure. In the third and fourth columns are the temperatures at which the values in the first two columns were determined, respectively.<sup>1</sup>

The values of  $L/RT_c$  are also given for ammonia, water and alcohol, typical associated liquids, in order that the magnitude of the deviation from that cause may be evident.

It will be seen that the deviation of  $L/RT_c$  from the mean is scarcely greater than the limit of error except for the metals, for which it is several per cent. less. There is no systematic change with the temperature. On the other hand, the values of  $L/RT_p$  at equal vapor pressures, corresponding to Trouton's rule, show a systematic increase from 11.0, for nitrogen, to 15.1, for zinc.

There are two principal deviations from the new relation that should be pointed out. The difference between  $L/RT_c$  for the metals and the values for the other substances in the table, while not great, is distinctly

<sup>1</sup> The sources of the vapor pressure data used were as follows: nitrogen, Fischer and Alt, *Ann. Phys.*, [4] 9, 1149 (1902); oxygen, Estreicher and Olszewski, *Phil. Mag.*, [5] 40, 454 (1895); chlorine, Johnson and McIntosh, *THIS JOURNAL*, 31, 1138 (1905); pentane to octane, Young, *Sci. Proc. Roy. Dublin Soc.*, 12, 374 (1910); bromonaphthalene Kahlbaum, *Z. physik. Chem.*, 26, 603 (1898); mercury, Smith and Menzies, *THIS JOURNAL*, 32, 1447 (1910); cadmium and zinc, Barus, *Loc. cit.*

more than the difference due to any uncertainty in the experimental data. It may be suggested that this deviation is due to a difference in molecular complexity. When a molecule escapes from the liquid to the vapor it is relieved of a very high internal pressure which exists in the liquid, and may, conceivably, expand with an absorption of energy. The amount of energy so absorbed we should expect to be greater in the case of molecules containing many atoms than with those containing but few. The expression for the entropy of vaporization might be written, therefore,  $(L + e) / RT$ , where  $e$  denotes the energy absorbed within the molecules on expansion from the high pressures existing within the liquid to the low pressure existing in the vapor. The quantity  $e$  is doubtless small compared with  $L$ , that is, most of the energy is required to overcome the attraction between the molecules, and but little in the expansion of the molecule itself. It is possibly safe to say, in the light of our rule, that in so far as it concerns the overcoming of attraction between the molecules, the entropy of vaporization to the same concentration is the same for all normal liquids. If a liquid is associated, a third, and much larger quantity of energy is involved in the dissociation of the complex molecules into simpler ones. In such cases the total entropy of vaporization is distinctly greater than the normal value for the given concentration, as is seen in the last three instances in the table.

Another deviation is found in the cases of hydrogen and helium. If the vapor pressure data<sup>1</sup> at these low temperatures can be trusted, then the entropy of vaporization is less than our rule would require, although the agreement is very much better than it is on the basis of the original Trouton rule. The values could not be included in Table I without a wide, and hence uncertain, extrapolation to lower pressures in order to use the same concentration as was used in the table. The direct comparison can be made however, at higher pressures. On putting  $\log p = \log T + 0.444$ , corresponding to a concentration of 1 mol in 22.4 liters, we obtain the values in the first row of Table II. In the second row are given for comparison the values of  $L/RT_p$ , when  $\log p = 2.00$ , as before.

TABLE II.

Substance.....	Helium	Hydrogen	Nitrogen	Oxygen
$L/RT_c$ .....	7.0	9.8	10.5	10.4
$L/RT_p$ .....	5.0	8.6	11.0	11.4

In view of the rapid change in the specific heats of solids, and presumably also of liquids, in the neighborhood of the absolute zero, and the consequent effect on the heat of vaporization, the deviation from our rule at these low temperatures might perhaps be expected. A further con-

<sup>1</sup> Data for hydrogen, Travers and Jacquerod, *Proc. Roy. Soc.*, **70**, 490 (1902); *Z. physik. Chem.*, **45**, 416 (1905); data for helium, Onnes, *Versl. K. Akad. Wet. Amst.*, **19**, 1194 (1911) *Comm. Physik. Lab. Leid.*, **119**.

sideration of the possibility of introducing the specific heats so as to make the necessary correction will be postponed till later.

It is possible to express the rule here given in the form of an equation which gives the vapor pressure of any normal liquid at any temperature in terms of some other such liquid chosen as standard. Let us consider the vapor pressures of two normal liquids, one of which we will take as a standard for the reference of all others. We may integrate the Clausius equation for each of these liquids, assuming, for the moment, for the sake of simplicity, that the heat of vaporization does not vary with the temperature. The resulting equations for the two substances are then:

$$\ln p = -L/RT + I \quad (1)$$

$$\ln p_s = -L_s/RT + I_s \quad (2)$$

the subscript referring to the one chosen as standard. Since  $p = RTc$ , we can write

$$\ln c + \ln R + \ln T = -L/RT + I \quad (3)$$

$$\ln c_s + \ln R + \ln T = -L_s/RT + I_s \quad (4)$$

Let us now select temperatures,  $T_c$  and  $T_{c,s}$ , at which the concentration of the vapor will be the same for the two substances, *i. e.*,  $c = c_s$ , when, according to our principle,

$$L/RT_c = L_s/RT_{c,s}. \quad (5)$$

We may then subtract Equation 4 from Equation 3, obtaining

$$\ln T_c - \ln T_{c,s} = I - I_s. \quad (6)$$

Let us call

$$T_c/T_{c,s} = a, \quad (7)$$

whence

$$L = aL_s \quad (8)$$

and

$$I - I_s = \ln a. \quad (9)$$

We are thus able to calculate  $L$  and  $I$  for any substance from the corresponding values for the standard substance using a single constant,  $a$ , so that this constant becomes the sole characteristic of a normal liquid necessary to define its vapor pressure with considerable accuracy. We may write, then, a universal vapor pressure law for such liquids by substituting for  $L$  and  $I$ , in Equation 1, the values given by Equations 8 and 9, obtaining the equation

$$\ln p = -aL_s/RT + I_s + \ln a. \quad (10)$$

It must be recognized, of course, that this equation does not take account of the change of the heat of vaporization with the temperature, and hence cannot be an exact equation. However, the change in the heat of vaporization depending on the difference between the specific heats of vapor and liquid, is not large, and is not very different for various liquids, so that Equation 10 becomes more exact if written



$$\ln p = -a/R \int L_s/T \, dT + I_s + \ln a, \quad (11)$$

where  $L_s$  is a function of the temperature.

This equation gives another method of plotting vapor pressure data so as to distinguish normal from associated liquids. Equation 11 may be put in the form

$$\frac{\log p/a}{T/a} = \frac{1}{2.3 R} \int L_s dT + I_s. \quad (12)$$

The right hand member of this equation is common to all normal liquids, so that the curves for all normal liquids can be superimposed by plotting  $\log bp$  against  $bT$ , where  $b = 1/a$ . These curves are nearly straight lines, so that they are convenient for testing the accuracy of the experimental data and for comparing different substances with each other. The curves for associated liquids cannot be made to coincide with those for unassociated liquids by this means, but will be steeper, due to higher values for the heat of vaporization.

It should be noted that Equation 9,  $I - I_s = \ln a$ , gives the relation between the integration constants of the Clausius equation for all normal liquids, the "chemical constants" of Nernst, which have received considerable attention from him and others.

The question mentioned at the beginning of this paper, and which suggested the present study, regarding the association of liquid metals, cannot be answered very fully from the experimental data at hand. Mercury appears in the light of a perfectly normal liquid, the slight deviation being opposite in direction to that which indicates association, and being explainable on the basis of a smaller latent heat of expansion of the molecules themselves. Zinc and cadmium likewise appear normal at the temperatures in question. They might, however, be associated at much lower temperatures, such as were used in the amalgam measurements. This possibility could be excluded only by careful measurements at very low vapor pressures.

#### Summary.

It has been found that the entropy of vaporization (*i. e.*, the molecular heat of vaporization divided by the absolute temperature at which vaporization takes place) is the same for all normal liquids, not, as in Trouton's rule, where the vaporization takes place at the same pressure (one atmosphere), but when it takes place at the same concentration of vapor.

This fact may be expressed in the form of a vapor pressure equation containing a single constant characteristic of the liquid, this constant being determined from the temperatures necessary to give the same concentration of vapor in the different cases.