

methods. The latter method is believed to give the most accurate value for the normal boiling temperature ($-33.20 \pm 0.05^\circ$).

A method for examining the consistency of vapor-pressure data is used whereby it is possible to obtain easily an accurate formula connecting pressure and temperature over any desired temperature range. The equation for the vapor pressure of ammonia from the freezing point (-77) to the critical temperature (132.9) is,

$$\log_{10} p = -1969.65/T + 16.19785 - 0.0423858 T + 5.4131 \cdot 10^{-5} T^2 - 3.2715 \cdot 10^{-8} T^3,$$

where the pressure units are mm. of mercury under normal conditions. The pressures given by this equation represent the experimental data within the limits of experimental error but they are the order of one per cent. higher than the values decided upon by Regnault.

An improved method of electrically determining the weight necessary to equilibrate the force due to the mercury column used in the absolute piston gage calibration is described. The electrical contact method decreases the time needed to make observations with the piston gage as well as enormously increasing the sensitiveness.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE VAPOR PRESSURES OF LIQUID METALS.

By JOEL H. HILDEBRAND.

Received November 14, 1917.

A valuable paper on the vapor pressures of metals was recently published by Johnston.¹ In addition to summarizing the existing data he has calculated for each metal the constants of the vapor-pressure equation, $\log p = -A/T + B$, and the heat of vaporization, which is 4.58A. In view of the inaccuracy of much of the data involved it has seemed to the writer that it would be useful to attempt to correct these calculations by applying the rule discovered by him² that the entropy of vaporization (*i. e.*, the heat of vaporization divided by the temperature of vaporization on the absolute scale) is the same for all normal liquids, provided that the comparison is made at temperatures where the saturated vapors have the same concentration. It is to be noted that this differs from the familiar Trouton's Rule in that the comparison is made at temperatures of equal concentration of saturated vapor instead of at temperatures of equal vapor pressure, such as the boiling points. It has been shown that this generalization makes it possible to superimpose the vapor-pressure curve for one substance upon that for another by the aid of a

¹ Johnston, *J. Ind. Eng. Chem.*, 9, 874 (1917).

² THIS JOURNAL, 37, 970 (1915).

single constant, a , which expresses the ratio of the absolute temperatures at which the two substances vaporize to give vapors of the same concentration. If the vapor pressure of the substance chosen as standard is given by the expression

$$\log p = -A_s/T + B_s,$$

then the vapor pressure of another normal substance is

$$\log p = -aA_s/T + B_s + \log a,$$

where $a = (T/T_s)_{\text{conc.}}$.

This relationship enables the vapor-pressure curve of a normal liquid to be constructed from a single point, such as the boiling point, provided we know the values of A and B for some substance we may select as standard. It seems, from the evidence in this and in the earlier paper, that the metals may be regarded as normal liquids.

Since the vapor pressure of mercury has been measured with great accuracy we will select this liquid as the standard. Using the values of Smith and Menzies,¹ and plotting $\log p$ against $1/T$ just as Johnston has done, we obtain the nearly straight line shown in the figure. The equation for this line we may take as

$$\log p = -3140/T + 7.85,$$

p being expressed in mm. of mercury. Vapor pressures of other substances, if our rule holds and the measurements are accurate, should then be given by the general equation

$$\log p = -3140 a/T + 7.85 + \log a,$$

and the measurements should coincide with those for mercury if $\log p - \log a$ is plotted against a/T . It is easiest to determine the value of a by successive approximations. The figures show the result of this process, using data for cadmium, zinc, thallium, lead and silver.

For cadmium and zinc we have vapor-pressure measurements by Barus² at higher pressures and by Egerton³ at very low pressures. These both agree with the theory, but not perfectly with each other, so that a slightly different value of a must be used in the two cases to conform with the mercury. The values for the boiling points given by Heycock and Lamplough⁴ indicate that the temperatures of Barus are too high by an amount very nearly corresponding to the higher values of a used in calculating his measurements. It is very striking that the same value of a applies to the figures of Heycock and Lamplough at 760 mm. and to those of Egerton at pressures of 10^{-4} mm.

¹ Smith and Menzies, *THIS JOURNAL*, **32**, 1447 (1910).

² Barus, *Phil. Mag.*, [5] **29**, 141 (1890).

³ Egerton, *Ibid.*, [5] **33**, 33 (1917).

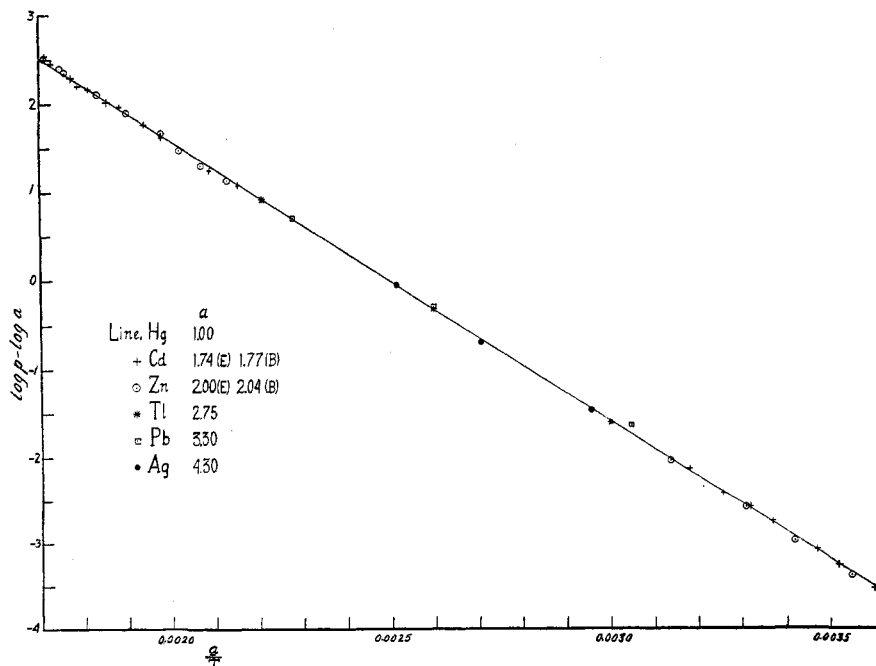
⁴ Heycock and Lamplough, *Proc. Chem. Soc.*, **28**, 4 (1914); *Chem. News*, **105**, 66 (1912).

The values used for thallium, lead and silver are those measured by von Wartenberg.¹

Table I gives the values of a for the above-mentioned elements, together with the source of the data used.

Metal.	a .	Data by
Mercury.....	1.00	Smith and Menzies
Cadmium.....	1.74	Egerton; Heycock and Lamplough
	1.77	Barus
Zinc.....	2.00	Egerton; Heycock and Lamplough
	2.04	Barus
Thallium.....	2.75	von Wartenberg
Lead.....	3.30	von Wartenberg
Silver.....	4.30	von Wartenberg

These constitute practically all of the data available for testing the theory. The values for arsenic, platinum, molybdenum and tungsten, cited in Jonston's paper, apply to solid metals, and could not be expected to agree very closely with the theory which is applicable only to the vapor pressures of liquids. It is true that we have, also, a number of figures for various metals by Greenwood,² but, as Johnston shows, they are often inconsistent with the measurements of others, and, furthermore, do not



¹ von Wartenberg, *Z. Elektrochem.*, **19**, 482 (1913).

² Greenwood, *Proc. Roy. Soc. London*, (A) **83**, 483 (1910).

lend themselves to the straight line plot to be expected in such cases. They appear, therefore, to be of little use in determining the slope of the line, and hence in fixing values of A and B. In other words, the values of A and B calculated from Greenwood's vapor pressures would vary widely, using different pairs of measurements. It seems to the writer that our theory gives a means of calculating these constants from the values of a necessary to bring the boiling points of these metals on to the general curve more accurately than they can be calculated by applying the Clapeyron equation to the measurements themselves. In Table II, accordingly, in addition to the values for the metals in Table I, are given values of a for a number of metals calculated from Greenwood's values of the boiling points at one atmosphere pressure, which may, perhaps, be considered more accurate than those at other pressures. Slightly different values would be obtained using his other points.

TABLE II.

Metal	a	—A.		B.		Heat of vaporization.	
		—3140 a .	Johnston.	7.85 + log a .	Johns- ton.	Hilde- brand.	Johns- ton.
Mercury.....	1.00	3140	...	7.85
Cadmium.....	1.74	5460	5460	8.09	8.04	25000	25000
Zinc.....	2.00	6280	6290	8.15	8.14	28800	28800
Magnesium.....	2.37	7450	7250	8.18	8.09	34100	33200
Thallium.....	2.75	8640	8850	8.29	8.50	39600	40500
Bismuth.....	2.93	9200	9010	8.32	8.12	42200	41300
Antimony.....	3.00	9430	9010	8.33	8.12	43200	41300
Lead.....	3.30	10370	9900	8.37	8.05	47500	45400
Aluminum.....	3.65	11450	11500	8.41	8.41	52500	52600
Manganese.....	3.85	12100	12300	8.44	8.55	55500	56300
Silver.....	4.30	13500	14300	8.48	8.97	61800	65500
Chromium.....	4.40	13800	14900	8.49	8.91	63200	68200
Tin.....	4.60	14450	15100	8.51	8.83	66200	69000
Copper.....	4.65	14600	16400	8.52	9.14	66900	75000
Nickel.....	4.80	15080	16700	8.53	9.12	69200	76500
Iron.....	4.90	15400	17000	8.54	9.10	70600	77800

The table gives also the values of A, of B, and of the heat of vaporization calculated from a , and, for comparison, the corresponding values calculated by Johnston. It will be noted that for the higher boiling metals there is a considerable difference between the two sets of values. This is due to the fact that the method of Johnston gives no certain guide as to the rate of increase of A and B, whereas the method herein described makes this a matter of linear extrapolation.

It must be emphasized that the foregoing material is in no wise to be construed as a criticism of Johnston's calculations. If the data were more accurate the well-recognized method employed by him would undoubtedly give results identical with our own. The only advantage of the new method employed herein is that it evidently furnishes a better means of criticising

inaccurate data, and of deducing the vapor-pressure temperature function from meager data.

In conclusion, it may be stated that the theoretical bearing of the rule regarding the entropy of vaporization will be the subject of a future communication.

Summary.

The rule concerning the entropy of vaporization, previously published by the author, is shown to apply to all liquid metals for which the experimental data are trustworthy, giving a general vapor-pressure equation,

$$\log p = -3140a/T + 7.85 + \log a,$$

where a is a constant characteristic of each substance, and p is expressed in millimeters of mercury.

Values of a for metals for which we have but meager or unsatisfactory vapor-pressure data have been calculated.

These values of a permit the calculation of the heat of vaporization, and of the volatility of metals at any temperature.

BERKELEY, CAL.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTE OF WASHINGTON.]

THE LAWS OF CHEMICAL EQUILIBRIUM.

BY ERSKINE D. WILLIAMSON AND GEORGE W. MORREY.

Received October 23, 1917.

In discussing the relations which exist among the variables in chemical systems, the safest guide is the paper, now a classic, due to the genius of Willard Gibbs. Chemists in general have fought shy of it, owing to the extremely mathematical setting with which he surrounds his arguments and the result of this is that much ink has been spilled in proving, by roundabout methods, theorems which are either explicitly stated by Gibbs or are so readily deducible from his equations as to be implicit in his work. In the following pages we have attempted to popularize, insofar as such a term can be used in such a connection, the derivation of the fundamental equations and to deduce from them such extra formulas as are required for the derivation of the theorems bearing on the chemical side of equilibrium. The actual applications of the theorems will be discussed in later papers.

The greatest importance of this form of attack lies in the fact that the relations apply equally to concentrated and dilute solutions. The approximate formulas used at present for dilute solutions necessarily break down and are worse than useless as qualitative guides when examining the complicated systems which must be dealt with in geophysical problems. These approximate formulas can, however, be derived from the general ones by means of the necessary simplifying assumptions and such