THE VAPOR PRESSURES OF METALS; A NEW EXPERIMENTAL METHOD

By Worth H. Rodebush and Alfred L. Dixon[1]

Abstract

Quasi-static method of measuring vapor pressures.—The vessel A containing the liquid and surrounded by a furnace for maintaining a uniform temperature, is connected by one tube C to a manometer M and a reservoir containing a neutral gas such as nitrogen at a suitable pressure, and by another tube B to an intermittent pump. Outside the furnace the two tubes are connected to opposite sides of a differential manometer D. Successive portions of the nitrogen are pumped off through B until the manometer D begins to show a permanent difference of pressure; then the reading of M is the vapor pressure desired. The action depends on the fact that when the pressure in M is less than the vapor pressure, nitrogen can get from C to B to equalize any difference of pressure caused by the pump, only by diffusion against the up-streaming vapor in C, and inter-diffusion in the case of a tube 3 to 4 mm in diameter is slow. A test of the method gave values for the *vapor pressure of mercury 170° to 203°C* only .04 mm greater on the average than those of Smith and Menzies.

Vapor pressure of lead, 1118° to 1235°C was found to vary from 5.70 mm to 19.70 mm in good agreement with the equation $\log_{10} p(\text{mm}) = -10372/T - \log_{10} T - 11.35$, which also fits the best results of Egerton at lower temperatures. The *heat of vaporization of lead at its melting point* is calculated to be 46,300 cal. The chemical constant comes out -1.40 which is close to the value -1.59 computed from the quantum theory of monatomic gases.

THE accurate determination of the vapor pressures of the less volatile metals is a matter of very considerable experimental difficulty. Because of the very high temperatures the exact measurement of the boiling point is out of the question, while the measurement of the boiling point under reduced pressure is subject to large errors because of radiation losses from the thermocouple and the tendency of vapors to superheat. The fact that these two effects cause errors in opposite directions does not reduce the uncertainty.[2] The dynamical method[3] has been applied at high temperatures but it seems to be very unsatisfactory. The best results are to be expected from some form of static method since we can attain a much more uniform and exact temperature in our apparatus if

---

[1] Research Fellow of the Chas. A. Coffin Foundation.

[2] The authors (Jour. Am. Chem. Soc. **47,** 1036, 1925) have measured the vapor pressure of lead by this method. The mean of that series of observations is confirmed by our new measurements but the discrepancies between individual observations are very great.

[3] Haber and Zisch, Zeits. f. Physik **9,** 325 (1922).

we minimize the rate at which heat is carried away from it. This is especially important since we have no liquids suitable for baths in a high temperature thermostat. In the ordinary application of the static method a portion of a vapor is trapped off over its own liquid in a U-tube, the liquid serving as a manometer. Such a method has been used successfully, for instance, in measuring the vapor pressure of mercury. At higher temperatures there are two serious difficulties: (1) The quartz glass or other material becomes opaque so that we cannot read the level of the liquid, (2) because of the evolution of absorbed gases we cannot keep a pure vapor in the enclosed space. To avoid these difficulties the authors have evolved a method which approaches static conditions as a limit in operation.

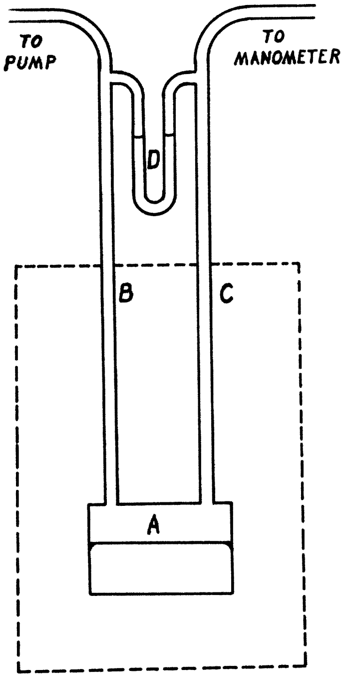

Fig. 1. Diagram of apparatus.

METHOD

The apparatus, constructed of Pyrex, quartz glass or other material suited to the working conditions, is shown diagrammatically in Fig. 1. The metal or other substance whose vapor pressure is to be obtained is contained in a shallow reservoir *A* not less than 2 cm internal diameter. The tubes *B* and *C* of 3 to 4 mm internal diameter are of sufficient length so that the upper part of the apparatus remains cool when immersed in a furnace to the depth shown by the dotted line. A differential manometer *D* is provided, containing a suitable liquid, such as paraffin oil. The temperature is measured by a thermocouple attached to the outre wall of *A*.

In operation the apparatus is filled with nitrogen to a pressure greater than the expected vapor pressure and the furnace is brought to constant temperature. Successive portions of nitrogen are pumped off through the tube *B*, sufficient time being allowed after each withdrawal for the liquid levels in the manometer *D* to stop moving. While the theory is somewhat involved the actual behavior of the apparatus is simple. So long as the pressure of the nitrogen in *C* is greater than the vapor pressure of the substance in *A* no permanent difference in level on the two sides of the differential manometer can be established. As soon as the pressure of the nitrogen drops below the vapor pressure, the vapor in A acts as a valve to prevent the passage of nitrogen through from C to B and a permanent difference in level can be set up in the manometer D, which is approximately equal to the difference between the vapor pressure of the substance and the pressure of the nitrogen in B. For reasons which will be elaborated below it is necessary to obtain the reading when the difference is as small as can be observed in order to fix the vapor pressure with accuracy.

THEORY OF THE METHOD

While the apparatus works in a very simple manner it is not obvious why this is so, since diffusion effects might be expected to play an important part at higher temperatures. The theory which applies to the case has been elaborated by Gaede[4] and the reader is referred to his papers for the fundamental considerations. We have a vapor rising in a tube and being totally condensed against an external pressure of a gas. Let us call the partial pressure of the vapor P and the partial pressure of the inert gas p, using the subscript 1 to denote pressures in the reservoir A and the subscript 2 to denote pressures in the tubes B,C above the condensation line of the vapor. In the hydrodynamic equation for the flow of gases in tubes of 3 to 4 mm bore at 10 mm pressure, the term containing the viscosity of the gas is large in comparison with the term containing the coefficient of friction against the walls of the tube. If there were no gas above the vapor in the apparatus then the equation for the upward flow of the vapor (in gram mols per second) would be

$$m=\frac{\pi r^4(P_1+P_2)}{16\ RTL\eta}(P_1-P_2)\ . \tag{1}$$

Here r is the radius and L the length of the tube, R the gas constant, η is the coefficient of viscosity and P_1 and P_2 are the vapor pressures at the two ends of the tube. If now there is a gas with pressure p_1 above the vapor, then we have the added resistance of diffusion which may be treated as a pressure drop $\Delta P=\Delta p$ equal in magnitude for gas and vapor but in opposite directions, Eq. (1) now becomes

$$m=\frac{\pi r^4(P_1+P_2)}{16\ RTL\eta}(P_1-P_2-\Delta P)\ . \tag{2}$$

A similar equation holds for the gas. The vapor is being continually condensed in the upper part of the tube so that $P_2=0$. The gas is diffusing

---

[4] Gaede, Ann. der Physik **41,** 289 (1913); **46,** 357 (1915).

into the closed chamber A so that p_1 must reach some limiting value and the gas flow become zero when the gas pressures on the two sides of the apparatus are equal.

Now if the gas flow is zero,

$$\Delta P = \Delta p = p_2 - p_1 \tag{3}$$

and Gaede obtains for the general conditions of equilibrium:

$$p_1 + P_1 = p_2 + \frac{16\eta D}{P_1 r^2} \log_e\left(\frac{p_2}{p_1}\right). \tag{4}$$

There are three cases to distinguish. For the case $P_1 < p_2$ it is apparent that if any inequality in the pressure p_2 is produced between the two sides of the apparatus, the gas must sweep through the vapor from one side of the apparatus to the other and equalize the pressure. It only remains to calculate the rate of reflux of the vapor up the tube since a too rapid escape of heat by this way would disturb the static condition desired. The equation for the rate of reflux is obtained by combining (2), (3) and (4), obtaining

$$m = \frac{\pi r^2 D}{RTL} \cdot \log_e\left(\frac{p_2}{p_1}\right). \tag{5}$$

Here R, the gas constant, should be expressed in c.g.s. units. So long as $p_2 > P_1$ the term log (p_2/p_1) must remain small and since the diffusion coefficient D is of the order of magnitude 10^6 at unit pressure, the rate of reflux will be very small indeed.

As the external pressure is lowered and we approach the condition $p_2 = P_1$ we find that p_1 at equilibrium is still appreciable and the term log (p_2/p_1) may be calculated from Eq. (4). The coefficient of viscosity η has been shown to be of the order of magnitude 10^{-3}. If we substitute rough values in c.g.s. units for the constants in (4), remembering that $p_2 = P_1$, we have

$$p_1 = \left[\frac{2.3 \times 16 \times 10^{-3} \times 10^6}{1.3 \times 10^4 + (0.3)^2}\right] \log_{10}\left(\frac{p_2}{p_1}\right).$$

The numerical coefficient is approximately 30. Hence if $p_2 = 10$ mm, p_1 is less than 0.1 mm, and Eq. (5) shows that the rate of flow of the vapor up the tubes remains small.

If the external pressure is reduced considerably below the vapor pressure in A, then the rate of flow of vapor up the tubes will become so large that the vapor in A will (because of rapid escape of heat, etc.) become unsaturated; i.e. P will be less than the true vapor pressure corresponding to the external temperature. This effect was always observed experimentally if the external pressure was lowered greatly. For this reason it is desirable that the reservoir A be of as large cross-section as possible. We can keep the unsaturation as small as we please by keeping the permanent difference of pressure which we set up small.

It remains to show that permanent difference of pressure can be maintained when the external pressure on one side is equal to the vapor pressure and on the other side is slightly less. Here it is a question of rate of diffusion. The equation for the rate of diffusion of the gas against the ascending vapor is given by the expression similar to Eq. (2).

$$m' = \frac{\pi r^4 (p_1 + p_2)}{16\, RTL\eta}(p_2 - p_1 - \Delta P) \tag{6}$$

where ΔP is the drop in pressure in the ascending vapor, which is to be ascribed to the "diffusion resistance." When $p_2 - p_1 = \Delta P$ we have zero gas flow and the condition of equilibrium given by Eq. (2).

Now if $p_2 = P_1$ on one side of the apparatus while p_2 is decreased slightly on the other side, p_1 will decrease and tend to remain in equilibrium with the lower value of p_2. For a first approximation let us assume that p_1 is decreased by 1 dyne per cm^2 but that the upward flow of vapor is undisturbed and hence unchanged in value. The net value of the last parenthesis in (6) will then be 1, and

$$m' = \frac{\pi \times (0.3)^4 \times 1.3 \times 10^4}{16 \times 8.3 \times 10^7 \times 10^3 \times 10 \times 10^{-3}} = 10^{-8} \text{ (approx.)}.$$

As a matter of fact the downward movement of gas against the ascending vapor means that ΔP, the pressure drop in the vapor due to diffusion, must be increased, since the vapor flow is retarded and less of its pressure drop is expended on external friction. We have therefore used too large a value for the parenthesis in (6), and the rate of flow calculated is too great. In actual operation of the apparatus it was demonstrated repeatedly that a considerable difference of pressure could be maintained indefinitely between the two sides of the apparatus when the gas pressure was equal to the vapor pressure.

Experimental Procedure

The difference in levels in the paraffin oil in D was read to 0.01 mm with a cathetometer. C was connected to one limb of a U-tube manometer, the other limb being connected to a pump capable of producing a high vacuum. Sulfuric acid was used as a liquid in this manometer and the difference in levels was likewise read with the cathetometer.

Sulfuric acid was used instead of mercury because of its smaller density and smaller surface tension. Not only is the absolute difference of level for a given pressure much greater but the percentage error from the capillary effects of dissimilarities in the sides of the manometer is greatly reduced.

Considerable experimentation was required to determine the exact size of the tubes *B* and *C* to give the most satisfactory operation. When *B* and *C* were too large, disturbing effects were produced by too rapid flow of the vapor up the tubes, while if they were too small they were clogged by the returning condensed liquid. A bore slightly in excess of 3 mm was found to be the most satisfactory.

VAPOR PRESSURE OF MERCURY

As a test of the method a number of determinations were made on mercury with a Pyrex apparatus. The apparatus was placed in an electrically heated oil bath and the temperatures were read with a copper-constantan thermocouple which had been calibrated at the boiling points of water and benzophenone. The results are shown in Table I together with values interpolated from the reliable measurements of Smith and Menzies.[5] The agreement is excellent. Any deviations are to be attributed to differences between the temperature scales used by Smith and Menzies and that of the authors.

TABLE I

Vapor pressure of mercury

T	*P*(obs)	*P* (Smith and Menzies)
170.4°C	6.29 mm Hg	6.22 mm Hg
178.1	8.30	8.22
180.1	8.80	8.82
183.9	10.13	10.08
189.6	12.33	12.24
197.2	15.78	15.77
202.8	18.90	18.90

VAPOR PRESSURE OF LEAD

In order to measure the vapor pressure of lead, the part of the apparatus which was to be heated was constructed of quartz glass. This part of the apparatus was placed in a Vitreosil test tube and this in turn inserted in an electric tube furnace mounted in a vertical position. The bulb *A* was placed about 10 cm from the bottom of the furnace and the lower part of the furnace was plugged with insulating material. The top of the furnace extended about 20 cm above the reservoir *A* and the

---

[5] Smith and Menzies, Jour. Am. Chem. Soc. **32,** 1434 (1910).

vitreosil test tube was filled in around the tubes B and C with quartz beads. The furnace was wound with chromel wire. The temperature was measured by a Pt-PtRh thermocouple which was tied to the outside of A with platinum wire. The temperature was regulated with a hand controlled rheostat and it was not difficult to avoid fluctuations of more than 0.2-0.3 degree at 1200°C. Since the apparatus was insulated above and below and separated from the heating coil by double insulating walls it is believed that the temperature was not only constant but nearly uniform for a considerable distance above the reservoir. The thermocouple was calibrated at the melting points of potassium chloride[6] and potassium sulfate and showed only small deviations from the standard table of Adams.[7] The lead was free from appreciable amounts of impurities.

The results are shown in Table II. These results agree with the other measurements by the authors previously referred to but are in marked disagreement with those of Ingold[8] who also used the boiling point method. The only other data of importance on the vapor pressure of lead are those of Egerton[9] who used the method of Knudsen at much lower temperatures.

TABLE II

Vapor pressure of lead

T	P (obs)	P (calc)
1391°K	5.70 mm Hg	5.63 mm Hg
1408	6.80	6.83
1424	8.25	8.18
1441	9.86	9.85
1458	11.82	11.81
1475	14.21	14.10
1491	16.70	16.58
1508	19.70	19.66

When our data for log p are plotted as a function of $1/T$, they lie on a straight line within very narrow limits. This would imply that C_p the atomic heat capacity at constant pressure was the same for molten lead as for lead vapor. The work of Iitaka[10] shows that C_p for liquid lead is apparently independent of temperature and equal to 7 calories. Since C_p for monatomic vapors is 5 calories, in setting up a vapor pressure equation we have assumed $C_p = 2$ and have obtained the equation

$$\log_{10}P(mm) = 10372/T - \log_{10}T + 11.3500. \tag{10}$$

---

[6] Roberts, Phys. Rev. **23**, 286 (1924).

[7] Adams, "Pyrometry," Am. Inst. Min. Metallurg. Engineers, N. Y. (1920).

[8] Ingold, J. Chem. Soc. **121**, 2419 (1922).

[9] Egerton, Proc. Roy. Soc. **103**, 496 (1923).

[10] Iitaka, Science Reports, Tokohu Imp. Univ. p. 899 (1919).

The values calculated from this equation are shown in the third column of Table II. This equation also fits very closely those data which Egerton has designated as his best at lower temperatures. The heat of vaporization of lead at its melting point may be calculated by the Clapeyron relation from this equation; the value found is 46,300 cal.

In an apparatus of the sort described above, thermal effusion effects may be expected to produce errors. Careful experiments showed that with tubes of 3 to 4 mm bore the effects due to thermal transpiration were of the order of magnitude of 0.01 mm.

Since pressures can be read with a precision of 0.001 mm the accuracy obtainable with this method depends upon the temperature control and the patience of the operator. The exact location of the highest pressure at which a readable pressure difference can be maintained is necessarily a time-consuming operation.

THE CHEMICAL CONSTANT

According to the quantum theory of monatomic gases[11] the constant C_0 in the following equation (in which M is the atomic weight)

$$\log_{10}p(\text{atm}) = -\frac{\Delta H}{2.3RT} + \frac{5}{2}\log_{10}T - \frac{1}{2.3R}\int_0^T \frac{C_p dT}{T} + \frac{2.5}{2.3} + \frac{3}{2}\log_{10}M + C_0 \qquad (11)$$

should be equal to -1.588. Using the best values obtainable for specific heats and heats of fusion[12] to evaluate the integral and the values for ΔH and log p obtained from Eq. (11) above, we find[13] $C_0 = -1.40$. While it is difficult to estimate the experimental error, there is little doubt that it is sufficient to account for the discrepancy. The greatest source of uncertainty is probably in the specific heat values used both above and below the melting point.

LABORATORY OF PHYSICAL CHEMISTRY,
UNIVERSITY OF ILLINOIS,
May 6, 1925.

---

[11] Tetrode, Ann. Physik (4) **38,** 434 (1912).
Einstein, Berl. Akad. p. 261 (1924).

[12] The data for specific heats were taken from the work of Eucken and Schwers (Verh. Deut. Physik. Ges. **15,** 582, 1913), Griffiths and Griffiths (Trans. Roy. Soc. London **214A,** 319, 1914) and Iitaka, loc. cit.[10] The heat of fusion was also determined by Iitaka.

[13] Cf Simon, Zeits. Physik. Chem. **110,** 572 (1924). Simon uses the data of Ingold in his calculation and gets a value $C_0 = -0.8$. His theory that C_0 is a function of the heat of vaporization appears to us to depend for experimental support upon Ingold's data.