The Vapor Pressures of Monatomic Vapors

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SECTION 1. INTRODUCTION

THE accurate measurement of the vapor pressures of the elements is of considerable interest both from the point of view of theoretical calculations based on the Nernst heat theorem, and because a knowledge of vapor pressures is a necessary factor in interpreting the results of other experiments on vapors, e.g., determinations of f values from experiments on absorption or dispersion. The actual determination of vapor pressures presents technical problems of quite unusual difficulty, and with the methods available before 1925 there were very wide discrepancies (up to a factor of ten or more) in the values of vapor pressures obtained by different workers, each of whom appeared to have taken all necessary precautions. Usually there was more agreement between the results of different experimenters on the law of variation of vapor pressure with temperature than upon the absolute value at any one temperature, but even in this matter the agreement was by no means universal. For many elements the experiments covered only a comparatively narrow range of temperature, and this range was not always the one of greatest interest. Some experimenters have published tables of vapor pressures which have been derived by extrapolating empirical formulae far beyond the range covered by the experiments. There is no necessity to stress the uncertainty involved in extrapolating a formula whose constants are not well determined, especially when the formula is of the logarithmic type given in Eq. (4) (see Section 3).

Since 1925 a great deal of work has been done on vapor pressures, and for a considerable number of the elements reasonably consistent results have been obtained by independent methods. Moreover, as a result of this work it is now possible to see how far the methods used in the earlier period were reliable. Hence by assembling all the data for a number of elements it is possible to construct vapor pressure-temperature curves which probably give the vapor pressure at a given temperature to within 10 percent over a considerable range of temperature.

Most of the books and tables of constants do not include much of this more recent knowledge on vapor pressures, and the chief object of the present review is to present a summary of this knowledge in a form which, it is hoped, will be useful to both experimentalists and theoretical workers. This review is limited to monatomic vapors and no data are given for the vapor pressures of elements such as sulfur and iodine which are mainly polyatomic over most of the range of experiment. Also no data are given for ranges of pressure above 10^4 mm for any element since at high pressures interaction of the. atoms and consequent deviations from Boyle's law become important even for the rare gases. Subject to these restrictions the list of references given at the end of this paper is as complete as we have been able to make it in relation to work published after 1925 and includes some references to the more important earlier work. Further references to earlier work will be found in *International Critical Tables* and in *Tables Annuelles Internationales de Constantes et Données Numériques.* * From the point of view of general interest and as an introduction to the tables given in Section 4, we give in Section 2 a description of the principal experimental methods, and in Section 3 a very brief outline of the theoretical interest of vapor pressures of the elements. The concluding Section 5 gives a brief general summary of the present position and indicates those fields which should next be explored.

SECTION 2. EXPERIMENTAL METHODS

It is obviously not possible to give a detailed account of each of the many methods which have been used and we shall therefore classify the methods into groups and deal as far as possible with technical difficulties which are common to each group.

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* For work earlier than 1917 a review by Johnston, reference 11, may be consulted.

We may regard all the experiments on the vapor pressures of the rare gases as forming one set. These gases are monatomic over the whole range of investigation, and since they are permanent gases at room temperature their pressures may be measured without difficulty by any of the standard methods. The only serious difficulty is in the establishment of a satisfactory temperature scale at low temperatures. The discussion of the general problem of low temperature measurements lies outside the scope of this review and it is sufficient to state that a suitable series of fixed points has now been drawn up and temperatures may be measured without great difficulty down to about 5°A. Below this temperature the vapor pressures of all gases except helium are too low to be measured. For some time temperatures below 1.5°A were measured by extrapolating the helium vapor pressure curve determined at higher temperatures. Insofar as later work has provided alternative methods of fixing the temperature scale it may be regarded as confirming and correcting the previously assumed vapor pressure formula for helium.

The remaining elements which give monatomic or nearly monatomic vapors are all metallic. At room temperatures nearly all the vapor pressures are too low to measure, and for most elements the effective range of the measurements lies considerably above room temperature. The range of

FIG. 1b. Nomograph showing the range of pressure for which different methods have been used.

vapor pressures which have been investigated for the different elements is shown in Fig. 1a, and the useful range of the different methods is shown in Fig. 1b. From these graphs we see that measurements extend from 10^3 mm to 10^{-8} mm but that an approximately complete investigation has been made for only a very few elements. The experimental difficulties arising at high temperatures form a serious obstacle preventing the measurement of the higher vapor pressures of many elements, but there appears to be no reason why measurements in the lower ranges should not, in time, be made for nearly all metallic elements.

One curious feature shown by Fig. 1b is the small number of methods effective in the range 10^{-2} mm to 10 mm. There is definitely one group of methods suitable for pressures below 10^{-2} mm and another for pressures above 10 mm. Some experimenters have endeavored to extend either a high pressure method or a low pressure method into the intermediate range but not usually with complete success, and our knowledge of vapor pressures in this range is mainly derived from interpolation. It is convenient to accept this division of the methods into low pressure and high pressure methods, but before discussing these separately it is desirable to mention one or two difficulties common to all methods.

We have already mentioned the difficulty of establishing a temperature scale at low temperatures. In the range 300°A to 1500°A there are sufficient well-determined fixed points to enable

FIG. 1a. Nomograph showing the range of pressures for which the vapor pressures of different elements have been measured. Results of doubtful reliability are indicated by thinner lines.

thermocouples to be calibrated accurately. As our knowledge of vapor pressures is extended above 1500°A, temperature measurements will again become a serious difficulty, but since 'at present only a few not very accurate measurements have been made above 1500°A this difficulty is not at present a limiting factor.

Another difficulty in the temperature measurement is much more important. It is desired to measure the pressure of the vapor when it is in equilibrium with the solid or liquid at a known temperature. The natural arrangement is to have the solid or liquid at the bottom of the vessel, to make this the region of lowest temperature and to measure this temperature with a thermocouple. If, however, owing to unsatisfactory distribution of heating power or insufficient thermal insulation, a region of lower temperature should form elsewhere, condensation will occur at this "cold spot" and the pressure of the vapor may fall by a factor of 10 or more. This error is particularly insidious because as the measured temperature is raised the temperature of the "cold spot" also increases, and remains an approximately constant distance below the measured temperature. Thus the series of readings obtained may show an approximately correct variation with temperature although all pressures are too low by a considerable factor.

Another important problem is the purification of materials. The presence of a small amount of impurity, whose vapor pressure is higher than that of the element under experiment, may seriously affect the results. When vapor pressures in the higher ranges are being measured such an impurity will usually distil away fairly quickly, but when a vapor pressure of say 10^{-5} mm is being measured the vapor may, for a long time, consist almost entirely of the impurity and a spuriously high result may be obtained. The presence of a non-volatile impurity which dissolves in the metal may lower the vapor pressure appreciably. The only check on errors due to impure materials consists in successive purification by fractional distillation and by chemical methods. If possible it is desirable to prepare the element by two or more independent methods.

We shall now proceed to discuss the low pressure and high pressure methods separately.

Low pressure methods

We may conveniently divide the low pressure methods into two groups: Group I: Effusion methods; Group II: Direct manometric methods and electrical methods.

Group I. Effusion methods.—In these methods the vapor flows from a space where it is in equilibrium with the solid or liquid at a known temperature into a high vacuum through a fine hole or tube. Formulae derived by Knudsen[2] enable the vapor pressure to be calculated when the size of the orifice and the rate of flow have been measured. These formulae, which do not involve the viscosity of the vapor, are valid only when the mean free path of the atoms is much larger than the smallest linear dimension of the orifice. This consideration sets an upper limit of 10^{-2} mm to the pressure range in which these methods may be used. A lower limit of about 10^{-5} mm is reached when the rate of flow becomes too small for accurate measurement. The chief difference between the members of this group is in the method of measuring the rate of flow.

In Method Ia[20, 30, 43, 59, 77] the element is enclosed in a crucible of the shape shown in Fig. 2. The
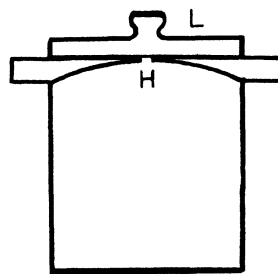

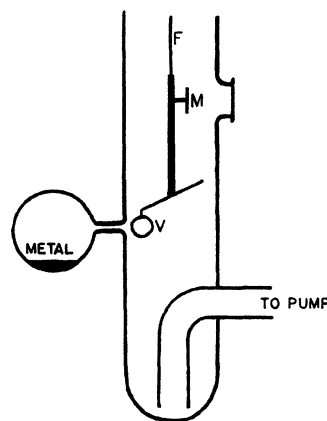Fig. 2. Crucible used in effusion experiments (Methods Ia and Ib).

Fig. 3. Apparatus for Method Ic.

crucible is placed in an apparatus which is evacuated and its temperature is adjusted to a desired value. By means of a vacuum winch the lid L may be raised and the vapor allowed to escape through the hole H for a measured time. The rate of flow is determined by weighing the crucible before and after the experiment.

In Method Ib[2, 10, 39, 61, 70, 78, 88, 92] the amount of material escaping from the crucible is measured by allowing a known fraction of the atomic beam to fall upon a suitable target and be condensed. The quantity is obtained by micro-titration.

In Method Ic[52] the strength of the atomic beam is measured by allowing it to fall upon a vane, which is suspended from a quartz fiber, and so to exert a couple. This couple is measured by twisting the fiber until the vane returns to its equilibrium position (see Fig. 3). By theoretical arguments and by subsidiary experiments, it is shown that the force on the vane depends only on the pressure and not on the molecular weight or viscosity of the vapor. In Method Id[65] it is also the momentum of the escaping vapor which is measured but the experimental arrangement is somewhat different.

Methods Ia and Ib have been widely used and appear to give very satisfactory results when all the necessary precautions are taken. Methods Ic and Id have each been used by only one experimenter. In both of these methods it is very difficult to avoid some error due to the absolute manometer effect.[72] By comparison with the results of other workers it appears that the values obtained for potassium by Method Ic are considerably too high, especially at very low pressures, and that those obtained by Method Id are a little too low.

The last method (Ie) of this group represents a first, and so far the only, attack on the very difficult problem of obtaining some measurements for the vapor pressures of very high boiling point elements like iron, nickel and even molybdenum and tungsten. The rate of evaporation of material from a heated wire is measured.[37, 85, 93] Thermodynamic arguments show that the vapor pressure may be determined from the rate of evaporation by regarding the surface of the wire as the effusion aperture, provided that it be assumed that the reflection coefficient for atoms
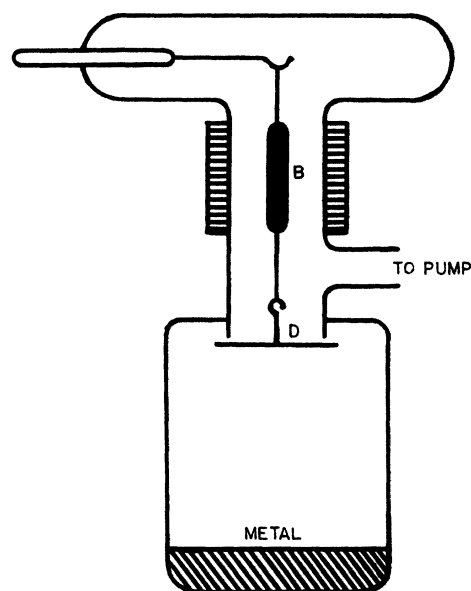
FIG. 4. Apparatus for Method IIe.

of the element falling on the wire at the working temperature is zero. If this assumption is not correct the measured vapor pressures are too low in the ratio $1 - r : 1$ where r is the reflection coefficient. There is some indirect evidence that, for elements of high atomic number and for clean surfaces, r is near zero, but it has also been shown that for an "ordinary" mercury surface the vapor pressure obtained from the rate of evaporation is only 0.0005 of the true value. Wilkins[56] has further suggested that owing to small scale surface irregularities the effective area of the surface may be many times the assumed area. This will tend to make the values obtained by this method too high, though it is very doubtful whether the error is as large as suggested by Wilkins. In view of the above considerations it is not possible to place confidence in vapor pressures deduced from these observations though the experiments are very valuable in relation to the purpose for which they were originally intended.

Group II. Direct manometric methods and electrical methods.—In most of the methods of this group the vapor pressure is measured by means of one of the standard low pressure vacuum gauges. There is no need to describe here the ionization gauge (Method IIa)[27] or the vibration gauge (Method IIb).[23] These gauges, in their usual forms, are not suitable for measurements

much above room temperature and their use is therefore restricted to a few elements. The difficulties of calibrating these gauges for absolute measurements are not unimportant, and it should be remembered that the ionization gauge must be calibrated by reference to a known vapor pressure and thus really gives only the variation of vapor pressure with temperature.

The lower limits of pressure for the more sensitive gauges are given by the release of gases from the walls (and other high vacuum difficulties) and also by the possible chemical or physical adsorption of the vapor on the walls. The first of these difficulties is largely avoided in Method IIc[28, 32, 84] in which the pressure measuring device is selective and measures only atoms of the vapor. Unfortunately the very property which makes it selective renders it applicable only to the higher alkali metals. In this method a tungsten filament at about 1500°A is suspended in the vapor. It has been shown that every alkali metal atom striking the filament comes off as a positive ion. The number of atoms striking the filament per second and hence the vapor pressure is obtained by measuring the positive ion current.

In Method IId[58] the detector of Method IIc is used to measure an atomic beam emerging from an effusion aperture as used in Method Ia or Ib. The method gives moderately good absolute

FIG. 5. Boiling point apparatus (Method IIIa).

measurements of vapor pressures, but is chiefly useful for detecting the presence of a small number of molecules in the beam. This is done by allowing the beam to pass between the poles of a magnet as in the Gerlach and Stern experiment. The atoms are nearly all deflected away from the detector by the powerful magnet used, but the molecules are undeflected and the fraction of molecules can thus be measured.

In Method IIe[41, 55] the pressure exerted by the vapor is measured in a very direct way. The manometer is shown in Fig. 4. D is a disk of graphite or quartz which is ground to seat on the end of the glass tube. The force exerted by the pressure of the vapor is balanced against that due to an electromagnet acting on the small piece of iron B. The manometer may be calibrated by means of a permanent gas. The method has given very satisfactory results in the range 10^{-3} mm to 10^{-1} mm and would appear to be suitable for extension to cover the intermediate pressure range (10^{-1} mm to 10 mm).

High pressure methods

These methods may be divided into two groups: Group III: Boiling point and partial pressure methods; Group IV: Direct manometric methods. In connection with the high pressure methods it is important to note that some methods measure the density (or a function of pressure and density) rather than the pressure. This consideration is not important in the lower pressure range where the vapors are certainly effectively monatomic.

Group III. Boiling point and partial pressure methods.—In the group of experiments which we are now considering, the vapor is supposed to be in equilibrium with its liquid in the presence of a "filling" gas which does not react with the vapor. In these experiments it is really the partial pressure of the vapor which is measured, and this partial pressure is, of course, equal to the vapor pressure of the liquid provided that a true equilibrium has been established. In the boiling point methods the vapor is allowed to drive out the filling gas from the space immediately above the liquid, but it is able to do this only when its own pressure becomes equal to that of the filling gas.
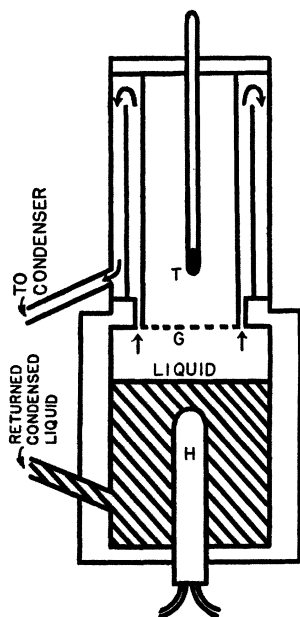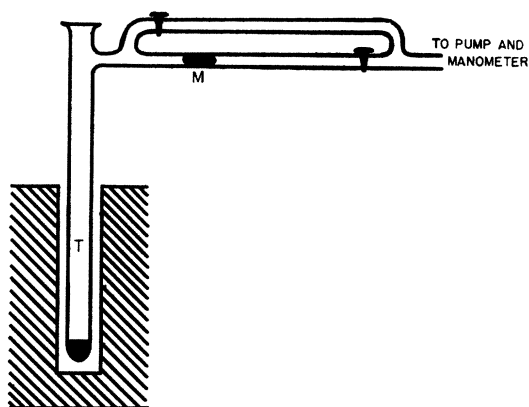
FIG. 6. Apparatus for Method IIIc.

The methods of this group usually yield accurate results for pressures above 50 mm, but serious difficulties arise at lower pressures.

Method IIIa is an elaboration of the ordinary hypsometer experiment. The determination of the standard boiling point (i.e., the temperature at which the vapor pressure becomes equal to 760 mm) has been studied in great detail, partly for the purpose of establishing temperature standards such as the sulfur point.[4] The standard apparatus is shown in Fig. 5. A thermocouple is suspended a short distance above the boiling liquid, and is suitably protected from (a) chemical attack by the vapor, (b) heating or cooling due to ebullition of the liquid, and (c) heating or cooling due to convection or radiation from the walls of the outer vessel. Provided that the dimensions of the apparatus have been carefully studied, this method is capable of giving an accuracy of 0.02°C in the boiling point corresponding to an accuracy of 0.02 percent in the determination of the vapor pressure (for sulfur). This boiling point method leads to the most accurate determinations of vapor pressures which have ever been made, and the accuracy is, in fact, chiefly limited by the difficulties of obtaining pure substances. It is usual to study the variation of boiling point for a few centimeters difference of pressure on either side of the standard pressure, and this presents no difficulty. There is also comparatively little difficulty in extending the method to measure vapor pressures down to about 100 mm of mercury. When, however, the vapor pressure becomes much lower than this,

the transfer of heat from the vapor to the thermocouple becomes slow, and conduction, convection, and radiation are able to maintain the thermocouple at a temperature appreciably different from that of the vapor, and so to cause an error which becomes proportionately large as the pressure becomes lower.

In Method IIIb[24, 68, 69] the element is contained in a crucible with a hole of moderate size, and it is heated in the presence of an inert gas at a known pressure. It is assumed that when the vapor pressure above the liquid reaches the pressure of the inert gas, there will be a sharp increase in the rate at which the material escapes from the crucible. This assumption does not appear to be entirely justified, and the results obtained by this method do not show satisfactory agreement with those obtained by other methods.

The apparatus used in Method IIIc[71] is shown in Fig. 6. As the tube T is heated, the element vaporizes, and when its vapor pressure becomes equal to the pressure of the inert gas, it is able to drive the latter out from most of the tube T. This is detected by a sudden movement of the mercury bead M. The temperature of the vapor can be measured by a suitably placed thermocouple or by an optical pyrometer for high temperatures. This method gives fairly reliable results for pressures from 10 to 50 mm of mercury, and has been used for the investigation of vapor pressures for a considerable number of elements.

In Method IIId (streaming method)[9, 17, 63] a stream of inert gas passes slowly over the surface of the metal. If M molecules of the metal evaporate, while G molecules of gas flow past, then the vapor pressure of the metal is given by

$$p = [M/(M+G)] \cdot P,$$

where P is the total pressure in the space where evaporation is taking place. The method measures the density and not the pressure of the vapor. G may be measured with any standard gas flow meter. Von Wartenberg[9] obtained pressures which appear to be too high; he estimated M from the loss in weight of the metal used. Haber and Zisch,[17] and more recently Thiele[63] have obtained results which are in much better accord with those of other workers. They measured the quantity M from the weight of metal condensed

from the gas stream in a cold part of the tube: the estimation being made in the form of a titration.

The apparatus used in Method IIIe[8, 54] is shown diagrammatically in Fig. 7. The lower volume (V_1) contains the metal to be investigated and can be maintained at a steady temperature. The upper volume (V_2) is attached to a manometer. Inert gas is allowed into the apparatus and the temperature and pressure are noted. V_1 is then heated and from the new value of the pressure in V_2, by applying Dalton's law of partial pressures and the gas equation, the pressure in V_1 due to the metal vapor may be calculated. It is normally assumed there is a sharp line of condensation in the connecting tube AB. An error is introduced if this is not so, but if the connecting tube is of narrow bore this error should not be very large. Kröner's[8] results by this method are not very accurate, especially in the lower half of the range covered, where deviations up to 25 percent exist. Recent experiments by Rodebush and Walters[54] show irregularities of about 10 percent over the whole range covered and appear to give the best results possible by this method.

The apparatus used in Method IIIf (quasi-statical method)[25] is shown diagrammatically in Fig. 8. The apparatus is filled with an inert gas to a pressure greater than the expected vapor pressure, and the furnace is brought to constant temperature; successive portions of the inert gas are pumped off from the tube B, sufficient time being allowed after each withdrawal for the manometer D to adjust itself. So long as the pressure of the inert gas in C is greater than the vapor pressure of the substance in A, no permanent difference in level can be established in D, but when the vapor pressure slightly exceeds the pressure of the inert gas a pressure difference is shown by D. Provided that the manometer D is reasonably sensitive, and that sufficient care is taken, accurate results may be obtained by this method in the range of pressure 10 to 50 mm of mercury.

Group IV. Direct manometric methods.—In this group of methods the vapor pressure is measured more directly than in the other three groups. A manometer is used to measure the gaseous pressure on one side of a septum, the other side of

which is supported by the metallic vapor pressure. The septum may be either solid or liquid. In view of their greater simplicity and directness, methods of this group are less likely than those of the other groups to suffer from large systematic errors.

In Method IVa[3, 33, 38] the liquid is made to act as the manometric fluid. The apparatus is shown in Fig. 9. The pressure of an inert gas in the tube T
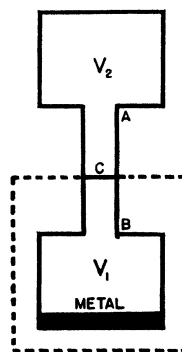

FIG. 7. Apparatus for Method IIIe.

is adjusted until the levels of the liquid in the two limbs are equal, and this pressure is assumed to be the vapor pressure. This method is especially suitable for measuring high vapor pressures, including those above atmospheric pressure, since the error, which is nearly constant in absolute magnitude, becomes proportionately smaller under these conditions.

In Method IVb[62] the vapor pressure of the element acts on one side of a glass membrane manometer; a permanent gas acts on the other. The pressure of the permanent gas is adjusted until the manometer indicates no difference of pressure. The permanent gas pressure is then measured on any standard gauge.

In the above description of methods we have excluded certain experiments[15, 46, 73, 79] in which the variation of vapor pressure with temperature is investigated by observations of some other property which is assumed to vary linearly with vapor pressure. (e.g. optical absorption or magneto-rotation). Where there are strong theoretical reasons for accepting this assumption, these experiments do help to confirm the slope of the vapor pressure-temperature curve, but in our view they should, in principle, be regarded as proving that the property in question does vary

linearly with vapor pressure rather than as determinations of vapor pressure.

SECTION 3. THEORY OF THE VAPOR PRESSURE EQUATION

The study of the vapor pressure equation has two objectives. The first is to suggest a suitable two- or three-constant formula to which we may attempt to fit the experimental results. The second, and more important, is to enable us to derive values of the chemical constants and so to provide some of the data for testing the validity of the Nernst heat theorem.

The Clausius-Clapeyron equation, in a simplified form applicable to perfect vapors of specific volume large compared with that of the condensed phase, may be written:

$$d \log p/dT = \lambda/RT^2, \qquad (1)$$

where p is the vapor pressure and λ the latent heat of vaporization at temperature T. Since we do not usually know λ as a function of T it is convenient to use the relation:

$$\lambda = \lambda_1 - \lambda_m - \int_{T_1}^{T} (C_c - C_g)dT, \qquad (2)$$

where λ_1 is the latent heat of vaporization at T_1 and C_g and C_c are, respectively, the specific heats at constant pressure of the vapor and of the con-
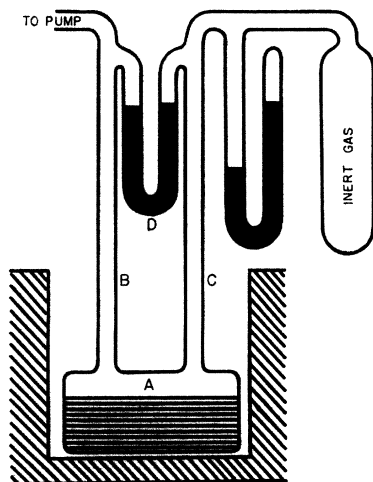

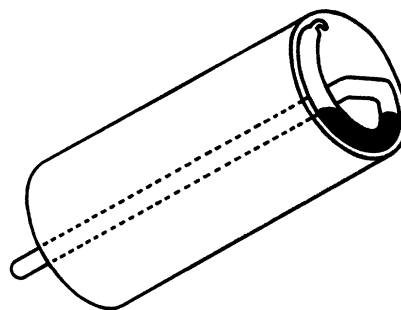FIG. 8. Apparatus for Method IIIf.

FIG. 9. Apparatus for Method IVa.

densed phase. λ_m is the latent heat of transition or fusion corresponding to any transition point (or melting point) lying between T_1 and T. T is greater than T_1.

Kirchhoff's equation

Kirchhoff's vapor pressure equation may now be deduced by inserting (2) into (1) and integrating with the assumption that $(C_c - C_g)$ may be regarded as constant in the range T_1 to T and that no transition point lies in the range. We then have

$$\log p = -\frac{\lambda_1 + (C_c - C_g)T_1}{RT} - \frac{C_c - C_g}{R} \log T + \alpha, \qquad (3)$$

where α is a constant of integration. This equation justifies the empirical form:[*]

$$\log_{10} p_{mm} = -(A/T) - B \log_{10} T + C. \qquad (4)$$

Other considerations show that A and C are essentially positive and B usually so. Many experimentalists have attempted to fit their results to an expression of this type by assuming a value of B from the specific heat data and then determining A and C by least-square methods. In relation to solids this procedure may be criticized on the ground that the logarithmic term in (4) is small and its variation is very small over a range short enough to justify the assumption that $(C_c - C_g)$ is constant. For a longer range it is necessary to use the more accurate integration of (1).

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[*] Some confusion is caused in the literature by failure to state whether pressures are in dynes, bars, atmospheres or millimeters of mercury. In this review pressures are in dynes/cm² and logarithms to base e unless otherwise stated. All temperatures are on the absolute centigrade scale (ice point = 273.14°A).

$$\log p = -\frac{\lambda_0}{RT}+\frac{5}{2}\log T$$

$$-\int_0^T \frac{dT'}{RT'^2}\int_0^{T'}(C_c-C_i)dT''+i. \quad (5)$$

Here λ_0 is the heat of vaporization at $T=0$ and C_g is put equal to $[(5/2)R+C_i]$. The term C_i stands for the part of the specific heat of the vapor which is due to molecular rotations, vibrations or excitations. In this expression the integral with respect to T'' must be understood to increase by λ_m when a transition point is passed. Using this form and integrating graphically Egerton has shown that for a number of metals the simple two-constant formula

$$\log_{10} p_{mm}= -(A/T)+C \quad (6)$$

represents the results with sufficient accuracy from the lowest temperature at which the vapor pressure is measurable up to the melting point. If any correction is needed it may probably be made more conveniently by means of a term directly proportional to T rather than by a logarithmic term. If the solid has a transition point the constants will change as this point is passed.

The Kirchhoff formula is theoretically unsuitable for calculations on vapor pressures at very low temperatures (i.e., for the rare gas group of elements). At temperatures below 100°A it is necessary to take account of the variation of specific heats. Born[19] has made calculations on argon using the Debye formula for the specific heat of the solid and similar calculations have been made for other elements. A formula for the vapor pressure containing four constants (of which two are adjustable) is derived and found to fit the results very accurately. A somewhat less accurate fit, which is yet good enough for most practical purposes, is given by purely empirical formulae of the Kirchhoff type.

In order to deduce the latent heat of vaporization at absolute zero it is necessary to return to Eqs. (1) and (2). Hence we derive

$$Rd \log p/d(1/T) = -\lambda = -\lambda_0+\lambda_m$$

$$+\int_0^T (C_c-C_g)dT. \quad (7)$$

From this equation λ_0 may be derived from the gradient of a graph of $\log p$ against $1/T$ provided that data for computing the integral are available. Fortunately it is not necessary to have accurate knowledge of specific heats at low temperatures because the corresponding portion of the integral is a small fraction of λ_0. Equation (7) requires that $d \log p/d(1/T)$ shall change by $\lambda_{m/R}$ at the melting point, thus giving the angle at which the curves for solid and liquid intersect. This relation is of considerable assistance in drawing the curves. Some workers have given values of λ_0 which are determined by assuming that $\lambda_0=AR \log_e 10=4.573A$ where A is taken from an empirical Kirchhoff formula for a solid. This assumption would be correct if the whole graph of $\log p$ against $1/T$ were linear down to $T=0$. This is not true even when the graph is nearly linear over the range covered by the observations. Similarly it is sometimes assumed that the value of the constant A for a liquid is less than that for the corresponding solid by $\lambda_{m/R}$ so that $4.573A$ (for the liquid)$=\lambda_0+\lambda_m$. Reference to Eq. (7) shows that this procedure also is not justified and that the error involved is appreciable.

The chemical constant*

Classical thermodynamics makes no prediction concerning the value of the constant i in Eq. (5), which is called the chemical constant, though it would be more appropriate to name it the vapor pressure constant. Statistical mechanics requires that for monatomic vapors this constant should have the value:

$$i=\log\left[\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}g\right], \quad (8)$$

where m is the mass of the atom concerned, k is Boltzmann's constant and g is the ratio of the statistical weights of the vapor and of the condensed phase. For comparison of theory and experiment it is usual to calculate i_0 which is given by

$$i=i_0+1.5 \log M+\log g, \quad (9)$$

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* For further information on this subject the reader is referred to R. H. Fowler's, *Statistical Mechanics* (second edition), Chapter VII.

TABLE I. *Values of the constant C_0 for comparison with the theoretical value $C_0 = -1.589$.*

ELEMENT	REF.	$-C_0$	ELEMENT	REF.	$-C_0$
Helium	91	1.59±0.01	Magnesium	77	1.61±0.2
Neon	49	1.56±0.04	Zinc	77	1.51±0.15
	74	1.59±0.01			
Argon	19	1.61	Cadmium	31	1.63±0.1
	31	1.61±0.04		44	1.51±0.13
Krypton	87	1.59±0.02	Mercury	31	1.62±0.03
Sodium	53	1.57±0.1	Thallium	77	1.40±0.3
	40	1.41±0.03			
Potassium	40	1.47±0.04	Lead	31	1.7 ±0.2
				43	1.21±0.36

where M is the molecular weight and i_0 has the theoretical value 10.17 for all elements. If logarithms are taken to base 10 and pressures are measured in atmospheres the corresponding universal constant C_0 has the value -1.589. For monatomic atoms, the value of g presents no difficulty. Typical values obtained are given in Table I.

It will be seen that the theoretical value (1.589) is nearly always within the range of values given by the experiments. For diatomic molecules, at low temperatures, where rotations and vibrations are not excited i is still given by (7) and the value of g is simply derived when we know the weight of the lowest rotational state. This form may be used for the halogens and for hydrogen. For Cl, Br, and I the values 1.50±0.2; 1.46±0.2 and 1.57±0.2 are obtained.[82] The calculation for hydrogen is complicated by the existence of the ortho- and paraforms. It is also necessary to allow for deviations from the perfect gas laws. When these factors are taken into account the value obtained is 1.567±0.01 which agrees well with the theoretical value.[22] For diatomic molecules at higher temperatures the vapor pressure constant is given by a more complicated expression depending on the extent to which the vibrations and rotations are excited. Under conditions where the rotations can be treated classically the expression reduces to a manageable form. Calculations have been made for H_2, N_2, O_2, Cl_2, Br_2, and I_2 as well as for several other molecules. In all cases the experimental results agree with the values calculated

from what are generally believed to be the correct values for the weights. Unfortunately there is considerable difficulty in regard to the weights to be assigned to the condensed phase and for some elements this gives a freedom of adjustment which reduces the value of the comparison between theory and experiment. Perhaps these results are best regarded as providing experimental confirmation for the weights chosen.

The Nernst heat theorem

We have stated above that classical thermodynamics gives no information concerning the integration constant (i) of the vapor pressure equation. In a similar way it gives no prediction concerning the value of a constant of integration (usually denoted by I) which appears in the expression for the equilibrium constant of a chemical reaction. The Nernst heat theorem is usually regarded as showing that these constants are connected by the relation:

$$\sum \nu_1 i_1 = I, \qquad (10)$$

where the ν's are the stoichiometric numbers and the i's are the chemical constants of the substances taking part in the reaction. Since the value of I is known for many reactions it is possible to check the validity of this relation when the vapor pressure constants of the reagents are known. By this test it now appears certain that the Nernst heat theorem is not of universal validity. In particular it fails for reactions involving hydrogen, the substance about which most is known.

The position of the Nernst heat theorem in relation to statistical mechanics is adequately reviewed by Fowler (*Statistical Mechanics*). We can give here only a general summary of his conclusions. In the light of our present knowledge, not all the formulations of the Nernst heat theorem are precisely equivalent but in the form:

Δ (entropy)→0 as T→0 (for any condensed
  system and any reversible isothermal process)

the theorem is equivalent to a statement that the quantum weights of the lowest states of all condensed systems are the same. This statement, even when restricted to pure crystals, is not

TABLE II. *Vapor pressure formulae for the elements and their range of accuracy. Column 2 gives the state of the element. The columns 3, 4, 5 give the constants A, B, C in the equation:*

$$\log_{10} p_{mm} = -A/T - B \log_{10} T - C.$$

The formula so defined may be used over the ranges given in columns 6 and 8 with the accuracy given in columns 7 and 9, respectively. Column 10 gives the melting point and column 11 the latent heat of fusion in joules per gram atom obtained by direct measurement. (I.C.T., 1926 values). Column 12 gives for comparison the latent heat of fusion calculated from the vapor pressure formulae.

		A	B	C	T_1	%	T_2	%	T_m			REFERENCES
He	*I*	2.611	−2.534	1.9166	4.2−2.19	1			—			47, 66, 86
He	*II*	3.368	−1.992	2.447	2.19−0.85	1						48, 66, 86, 91
Ne	*L*	97.4	0	6.466	30−24.6	1	40−24.6	2	24.6	240	295	36, 49, 74
	S	112.8	0	7.093	24.6−18	1	24.6−15	3				
A	*L*	357.7	0	6.970	90−84	0.5			83.9	1120	1050	19, 31, 60
	S	412.5	0	7.622	84−70	0.5	84−60	5				
Kr	*L*	569	1.45	10.638	167−116	2			116	1500	1570	1, 51, 57, 75, 76, 83, 87
	S	578	0	7.722	116−80	1	116−70	5				
Xe	*L*	662	0	6.919	230−161	1			161	2050	3270	51, 57, 64, 89
	S	833	—	7.980	161−140	5	161−100	20				
Li	*L*	8143	—	8.00	1400−1100	10	1600−700	30	439			45, 58, 61, 88
Na₁	*L*	5728	1.27	11.641	850−370	10	1200−370	20				
Na₂	*L*	7020	—	8.149	800−600	50						58, 63
Na	*L*	5567	0.5	9.235	1200−450	5	1250−370	10	370			7, 15, 17, 30, 39, 40, 42, 46, 53, 54, 55, 58, 63
K	*L*	4552	0.5	8.793	1100−600	5	1200−350	20	335			5, 7, 8, 32, 34, 39, 40, 42, 46, 52, 58, 65
Rb	*L*	4302	1.5	11.722	600−325	20			311			5, 23, 32, 42
Cs	*L*	4042	1.4	11.176	350−299	2	650−299	10	299	2100	2500	5, 8, 23, 28, 42, 67, 80, 81, 84
	S	4120	1.0	10.446	299−275	2	299−240	10				
Cu	*L*	12350	—	7.445					1356			6, 12, 35, 71, 85
Ag	*L*	12270	—	8.39					1233			6, 12, 43, 69, 71
Au	*L*	12450	—	7.028					1336			12, 35, 71
Be	*L*	11710	—	6.494					1620			71
Mg	*L/S*	7167	—	8.088	1400−1000	10	1450−600	20	924			24, 45, 71, 77, 90
Ca	*L/S*	9189	—	8.295	1600−1200	10	1700−800	50	1083			14, 24, 45, 70
Sr	*L*	7400	—	7.33	1400−1200	10			1073			24, 45
Ba	*L/S*	7400	—	6.62	1400−1300	20			1123			24, 45, 78
Zn	*L*	6697	1.2	12.247	1250−692	5			692	7100	7920	10, 13, 29, 33, 71, 77
	S	6750	—	8.916	692−600	10	692−500	20				
Cd	*L*	5982	1.8	14.063	1100−594	5			594	6200	6190	7, 10, 13, 21, 31, 33, 44
	S	6073	0.9	11.720	594−400	10						
Hg	*L*	3308	0.8	10.3735	800−400	2	850−234	5	234	2330	2300	3, 16, 25, 26, 27, 31, 33, 38, 50, 52, 65, 73
	S	3347	—	8.641	234−220	5	234−200	10				
Al	*L*	17250	—	9.705					933			59, 71
Tl	*L*	8927	—	7.993	950−800	10			577			77, 79
Si	*L*	20615	—	10.730					1690			35, 71
Pb	*L*	9870	—	7.85	1700−900	20			600			9, 18, 20, 25, 29, 31, 43, 68, 71
Bi	*L*	10660	—	8.976					544			6, 12, 92
Cr	*L/S*	9432	—	6.100					1888			71
Mn	*L*	13260	—	8.628					1530			6, 71

universally true. Theoretically differences of weight are required by the existence of nuclear spins and possibly by other considerations. Equation (10) may be modified by adding terms to take account of these differences and in the modified form it is approved by statistical mechanics and, as far as is known, is in agreement with experiment. The fact that some elucidation or modification is now needed does not in any way detract from our recognition of the importance of Nernst's fundamental idea.

SECTION 4. TABLES OF VAPOR PRESSURES

Tables II and III contain vapor pressure data for the monatomic elements. The text of this section explains the process by which we have correlated the results of different workers and supplies some additional information which cannot conveniently be put in tabular form. Table II gives the values of the constants in formulae of the type of Eq. (4). With these constants, logarithms are to base 10 and pressures in mm Hg. The ranges over which the formulae are valid and an estimate of their accuracy are given in the table. It should be emphasized that the margin of error will increase rapidly if the formulae are used outside the limits stated. For certain elements and ranges the accuracy of the results does not justify the use of a three-constant formula and for these the best two-constant formula is given. Table III gives the temperature at which the vapor pressure reaches certain chosen values, namely powers of 10 from 10^4 to 10^{-7} mm. The boiling point (at 760 mm) is also included.

Correlation of results of different experimenters

In order to enable us to obtain a general picture of the internal consistency of the results

of each experimenter and of the extent to which different experimenters are in agreement, a graph is constructed for each element in which the variables are $x = 1000/T$ and $y = \log_{10} p + (K/T)$. The value of K is chosen, if necessary by trial and error, so that the graph runs nearly parallel to the x axis. The line has a slight curvature due to the logarithmic term in Eq. (4). Since y is always a slowly varying quantity we are able to have a much more open scale than could be used in a plot of $\log p$ against $1/T$. The way in which this method makes errors and inconsistencies stand out is most readily seen by considering one or two examples.

Figure 10 shows the x, y graph for mercury. In the original all the observations were first plotted. For clarity of reproduction only a typical set are included in the figure. When the points have been plotted the problem is to draw the best curve subject to the following thermodynamic restrictions, discussed in Section 3:

(1) The curve for the solid must intersect that for the liquid at the melting point and the angle between the two curves must be derivable from the latent heat of fusion.

(2) The curvature of the lines for liquid and solid must be derivable from the specific heat data.

From the second requirement we find for mercury that to a sufficient approximation the curve is linear below the melting point and has a small curvature term above the melting point. Since the boiling point of mercury is very accurately known we make the graph pass exactly through the corresponding x, y values. The initial slope of the curve is determined from the very consistent observations of Smith,[3] Menzies,[38] and Rodebush and Dixon,[25] in the range from 1000 mm to 100 mm. The line so drawn is continued (with the correct curvature) to the melting point and thence a straight line, meeting the curve at the correct angle, is drawn. The departure of observations from this line is never much over 5 percent and is generally within the range of

TABLE III. *Temperatures (in degrees absolute) at which various vapor pressures are attained. Figures in italics apply to vapor pressures measured over the solid, those in roman type to vapor pressures measured over the liquid. Figures in parentheses have been obtained by extrapolation outside the range of actual experiments. Where no figures are given extrapolation is likely to lead to large error.*

|	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^0	10^1	10^2	760	10^3	10^4
He	—	—	—	—	—	—	0.981	1.269	1.746	2.645	4.186	4.523	
Ne	—	—	—	—	—	—	(13.9)	15.9	18.5	22.1	27.2	28.1	39.5
A	—	—	—	—	—	—	—	(54)	62.3	73.4	87.5	90.2	(121)
Kr	—	—	—	—	—	—	(66)	74.9	86.0	101.0	120.0	123.6	166.6
Xe	—	—	—	—	—	(84)	92.8	104.4	119.4	139.4	163.9	168.8	227
Li	—	—	—	(680)	740	814	905	1018	1163	1357	1590	(1630)	—
Na₁	—	—	(430)	468	511	564	630	714	826	980	1178	(1210)	—
Na₂	—	—	—	(580)	630	690	770	(860)	—	—	—	—	—
Na	—	—	(430)	468	511	564	630	713	821	969	1154	(1180)	—
K	—	—	(340)	364	396	435	482	540	615	716	854	1033	(1060)
Rb	—	(310)	332	362	397	441	495	567	(660)	—	—	—	—
Cs	274	295	319	348	383	426	480	551	(650)	—	—	—	—
Cu	—	—	—	—	—	—	(1460)	1660	1920	2270	(2700)	—	—
Ag	—	—	—	—	(1080)	1180	1310	1460	1660	1920	2230	(2280)	—
Au	—	—	—	—	—	—	—	(1770)	2070	2480	(3000)	—	—
Be	—	—	—	—	—	—	(1560)	1800	2130	(2610)	—	—	—
Mg	—	—	—	—	(650)	710	789	887	1012	1178	1376	(1410)	—
Ca	—	—	—	(750)	810	890	990	1110	1260	1460	(1700)	—	—
Sr	—	—	—	—	—	—	—	(1010)	1170	1390	(1660)	—	—
Ba	—	—	—	—	—	—	(970)	1120	1320	(1600)	—	—	—
Zn	—	—	(490)	523	567	619	681	762	867	1007	1179	1207	(1510)
Cd	—	—	(420)	456	494	539	594	666	760	886	1039	1066	(1460)
Hg	214	229	246	266	290	319	354	399	457	534	630	645	818
Al	—	—	—	—	—	(1470)	1610	1780	1980	2240	(2530)	—	—
Tl	—	—	—	—	(810)	894	(990)	—	—	—	—	—	—
Si	—	—	—	—	—	—	—	(1920)	2120	(2360)	—	—	—
Pb	—	—	(770)	830	910	1000	1110	1260	1440	1690	(1990)	—	—
Bi	—	—	—	—	(890)	970	1070	1190	1340	1530	1750	(1780)	—
Cr	—	—	—	—	—	—	(1330)	1550	1850	(2300)	—	—	—
Mn	—	—	—	—	—	—	—	(1540)	1740	2000	(2310)	—	—
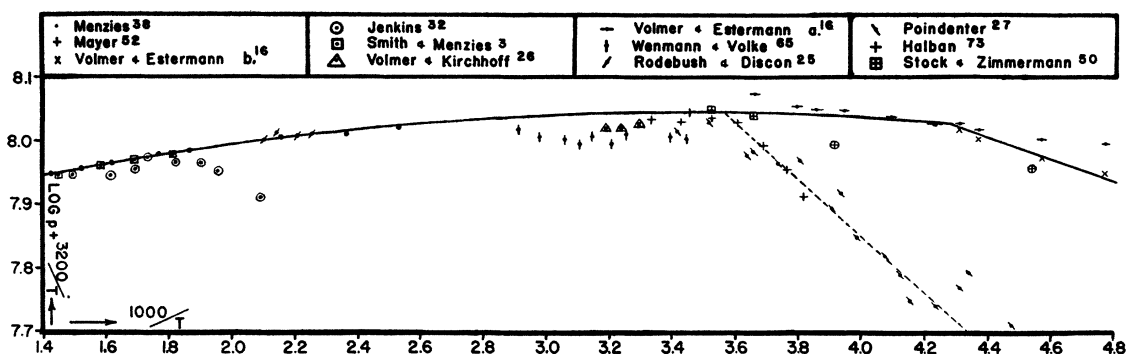
Fig. 10. Vapor pressure data for mercury. Abscissae are $x = 1000/T$ and ordinates are $y = \log_{10} p + (3200/T)$.

experimental error except in region for $x > 3.7$ (i.e., $T < 273°A$). In this region there are two main groups of observations which cannot be reconciled with one another. One must be rejected.

The observations lying near the full line were made with very specially purified mercury and there is independent evidence* that small amounts of impurity in mercury greatly reduce the vapor pressure. The observations lying on the dotted line (which is quite irreconcilable with the results obtained at higher temperatures) are therefore rejected. At this stage it might appear desirable to use least-square methods to determine the best line through the remaining observations, but to do this an entirely arbitrary scheme of weighting of the results of different workers would have to be adopted. Tests show that formulae calculated from the line as drawn fit nearly all the accepted observations within experimental error.

Thus, for mercury, a heavy majority of the results leads to a well-defined line which can be adopted with confidence. A similar situation exists for several elements, but for others the position is not nearly so satisfactory. As an example the diagram for calcium is shown in Fig. 11. Both in the high and low pressure ranges there are discrepancies of up to a factor of 10 and in order to plot all the results on one diagram the scale for y has had to be reduced. The full line is adopted because three of the four sets of results agree to give a line of approximately this slope

* In a paper on the amalgams (Halban, Helv. Phys. Acta 8, 65 (1935)).

and in view of data for other elements the method of Hartmann and Schneider[45] appears to be the most reliable of the four. Also from the design of his apparatus it appears possible that Rudberg's[70] values may be too low owing to the existence of a "cold spot" as described in Section 2. The formulae are calculated from the full line as drawn, but we cannot feel very confident that later work will not show that some very different line (such as one of the dotted lines) is correct. In a case like this we can only choose the best line on the balance of evidence and call attention to the position in a note.

Notes

Helium.—The formula given for helium I (above 2.186°A) is based on the work of Schmidt and Keesom (1937)[86] whose results differ only very slightly from the earlier results of Keesom, Weber, and Nørgaard (1929).[47] It has been adjusted to fit the curve for helium II at the λ point. Slightly more accurate temperature-pressure relations (not expressed by a formula) may be obtained from the paper of Schmidt and Keesom.[86]

Below the λ point (2.186°A) the vapor pressure of helium II was investigated by Keesom, Weber, and Schmidt.[48] They proposed the formula:

$$\log_{10} p_{mm} = 3.035 + 0.922 \log_{10} T - 3.859/T.$$

This was corrected by the results of Schmidt and Keesom.[86] This later work has been criticized by Bleaney and Simon[91] who on theoretical grounds propose a vapor pressure curve giving appreci-

ably different results below 1.6°A. They state that their curve is supported by unpublished results of Bleaney and Hull. The formula given in the table is a purely empirical one which we have fitted to the data given in Table I of the paper by Bleaney and Simon.[91] It fits these data within 1 percent.

Neon.—There is good agreement between the results of different workers and the formulae fit the results well except for deviations near the triple point.

Argon.—The formulae given in Table II are empirical two-constant formulae which we have derived from the results of Born[19] taking into account the value of the latent heat. They differ very little from the formulae proposed by Van Laar.[60] In the original paper of Born the following four-constant formulae are proposed:

$$\log_{10} p_{mm} = -\frac{366.87}{T} + 1.75 \log_{10} T$$

$$-0.0028293T + 3.9506 \text{ for solid argon,}$$

$$\log_{10} p_{mm} = -\frac{339.3}{T} + 1.75 \log_{10} T$$

$$-0.006737T + 3.9506 \text{ for liquid argon.}$$

These formulae are shown to fit the observed results very accurately, and also agree well with theoretical calculations based on the Debye theory of specific heats at low temperatures.

Krypton.—The formulae given fit the most recent results[76, 83] within an accuracy of 1 percent on the vapor pressure at a given temperature. Earlier work of Peters and Weil[51] indicated the existence of a transition point at 90°A. This result is not confirmed by later work. In drawing the vapor pressure curves we have used the current value 116.0°A for the triple point[76, 83, 87] instead of the I.C.T. (1926) value of 104°A.

Xenon.—The results obtained for this element are much less satisfactory than those for the lighter rare gases. The formulae given are purely empirical and do not lead to the correct value of the latent heat of fusion. More accurate results may be given in the paper by Clusius and Weigand[89] which, owing to war conditions, is inaccessible to us.

Lithium.—A line drawn through the points derived from the work of Hartmann and Schneider[45] at high pressures passes through the "center of gravity" of the low pressure points of Bogros[61] and of Maucherat[88] though the scatter of the latter results is considerable. Higher values were obtained by Lewis[58] but it is believed that his lithium was contaminated with sodium. The formula given represents the pressure of a vapor which according to Lewis contains 2 percent of Li_2 molecules at 1000°A and (by extrapolation) about 10 percent at the boiling point. These figures for the proportion of molecules should be regarded as giving only orders of magnitude.

Sodium.—The vapor of sodium contains an appreciable proportion of molecules (about 15 percent at the boiling point) and the accuracy of the results is sufficient to justify giving formulae for the partial pressure of sodium atoms and for the partial pressure of the molecules as well as the vapor pressure formula which represents the sum of these partial pressures. These formulae are obtained in the following way. First all measurements are graphed in the way explained above. There is no theoretical reason for expecting a curve of the type expressed by Eq. (4) to pass through the points, but an attempt was made to fit a curve of this kind determining the values of all three constants empirically. The curve so obtained represents the results well within the range of experimental error. The partial pressure of molecules is obtained from the calculations of Thiele[63] based on the results of Lewis.[58] By subtracting the pressures so derived from the total pressure one obtains the partial pressure of sodium atoms. A three-constant formula is now
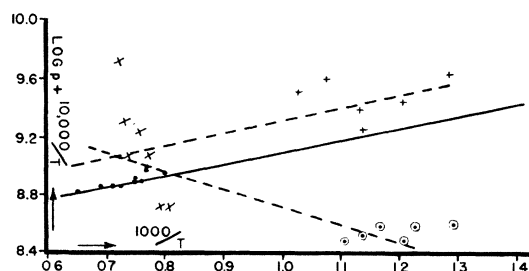

Fig. 11. Vapor pressure data for calcium. Abscissae are $x = 1000/T$ and ordinates are $y = \log_{10} p + (10,000/T)$. ● Hartmann and Schneider, reference 45; × Ruff and Hartmann, reference 24; + Pilling, reference 14; ⊙ Rudberg, reference 70.

fitted to these data in the usual way, the coefficient of the logarithmic term being derived from the specific heat determinations. The separation into two partial pressures thus depends on the result of one rather difficult experiment and the two partial pressure curves are therefore much less accurately known than the curve which represents their sum.

Potassium.—In the pressure range 100 mm to 1 mm the results of Fiock and Rodebush,[34] Kröner,[8] and Lewis[58] are in agreement to within about 10 percent. The line is drawn through the mean of these and through the boiling point determined by several workers.[7, 34] The curve so drawn passes above the points obtained from the results of Neumann and Völker[65] and of Edmondson and Egerton,[39] and beneath those of Mayer,[52] but nearest to those of Edmondson and Egerton. This is desirable since their method is probably more reliable having been tested on a number of other elements. The results of Killian[32] agree with the curve drawn, at a temperature of 350°A, but indicate a more rapid variation with temperature. It does not appear possible to accept Killian's law of variation with temperature since to do so would involve great difficulties in the high pressure region. There are no data for solid potassium. According to Lewis[58] about 2 percent of the vapor is in the form of diatomic molecules at 700°A and by extrapolation about 5 percent at the boiling point.

Rubidium.—The results of Hackspill[5] and of Killian[32] agree within the limits of their experimental error, and the formula is constructed to fit them. The results of Scott[23] indicate a very different value but his results for caesium are also strongly in disagreement with those of other workers. No results are available for solid rubidium and further work is needed in the high pressure ranges.

Caesium.—Three reviews of the data have been published[42, 67, 80] but the conclusions need revision on account of the more recent work of Taylor and Langmuir.[84] This paper gives what we believe to be the most reliable results for this element, but we have adopted formulae differing slightly from those of the authors in order to fit the thermal data more accurately. Taylor and Langmuir assumed that the constant A changed by λ_m/R at the melting point, instead of that the

gradient of the graph altered by this amount (see Section 3 above). When this error is corrected it is seen that their data give a change of gradient which corresponds to a latent heat fifty percent greater than that actually measured. The measured latent heat is only a rough value and we have taken an average between it and the value obtained from the vapor pressure data. Using this averaged value of the latent heat we have calculated formulae which fit the observations as closely as possible. The observations of Taylor and Langmuir differ from the values given by our formulae by 1 percent at 300°A, and 4 percent at 250°A. Further work in the high pressure range is needed.

Copper.—The formula given is very nearly that proposed by Baur and Brunner.[71] This line passes through the mean of the values obtained in three sets of experiments[6, 12, 35] whose internal consistency is considerably inferior to that of Baur and Brunner.

Silver.—The results of Baur and Brunner,[71] Greenwood,[6] and Ruff and Bergdahl[12] are in reasonably good agreement and the formula given is constructed to fit them. The experiments of Harteck[43] and of Fischer[69] indicate vapor pressures about 10 times lower and are almost certainly in error.

Gold.—The formula is based on the work of Baur and Brunner[71] supported as regards order of magnitude by some less accurate earlier determinations.[12, 35]

Beryllium.—The only results for this element have been obtained by Baur and Brunner[71] using Method IIIc. The results are internally consistent to within ±20 percent. Consideration of data obtained for other elements indicates that the mean is probably 10 percent too high. The temperatures used in experiments on these elements are necessarily high and this adds to the difficulties. These considerations indicate that we should allow an uncertainty of perhaps ±30 percent. It is very desirable that the results should be checked by an independent method.

Magnesium.—The results for this element are in fairly good agreement but there are rather few of them and the use of a three-constant formula is not justified.

Calcium.—This element is discussed in the text above. The boiling point given (1700°A)

differs considerably from the I.C.T. (1926) value of 1440°A.

Strontium.—Two sets of determinations have been made indicating very different laws of variation with temperature.[24,45] We have adopted the more recent results of Hartmann and Schneider[45] obtained by the direct boiling point method. The boiling point (1660°A) differs appreciably from the I.C.T. (1926) value (1420°A) which was based on the earlier work of Ruff and Hartmann.[24]

Barium.—The values obtained by Rudberg and Lempert[78] in the low pressure region are about 15 times lower than those derived by extrapolation from the high pressure determinations of Hartmann and Schneider[45] though the two pairs of experimenters are in agreement with respect to the law of variation with temperature. We consider the high pressure determinations to be more reliable and have used them in Tables II and III. The position is obviously very unsatisfactory.

Zinc.—The situation in regard to this element is very similar to that for cadmium (see note below) except that the scatter of the results is a little greater and the check given by the thermal data is not completely satisfactory. Probably the discrepancy is mainly due to impurity of materials making the vapor pressure determinations systematically too low at low temperatures.

Cadmium.—Nearly all the data for the liquid are represented by the formula within 5 percent. The formula for the solid agrees well with the data except that at very low pressures some observations indicate lower values: down to 30 percent of those given by the formula. These observations,[10] made in 1917, are probably explained by impurity in the material. The check on the formula given by thermal data (specific heats and latent heat) is quite satisfactory.

Mercury.—This element is discussed in the text above.

Aluminum.—The formula given is based upon the results of Baur and Brunner[71] in the high pressure region, and upon a single point given by Farkas[59] at a pressure of 10^{-2} mm.

Thallium.—There is only one modern group of experiments.[77]

Silicon.—See note on beryllium.

Lead.—In the high pressure region there are six sets of results of which four[25,29,43,71] are in tolerably good agreement. The line is drawn to pass through the mean of these and also through the points given by Egerton[20] who appears to have made the only recent determination in the low pressure range. The boiling point (1990°A) differs appreciably from the I.C.T. (1926) value (1890°A).

Bismuth.—Results for this element are few and the curve given is in agreement with the work of Weber and Kirsch[92] in the low pressure region, and the mean of the results of Greenwood,[6] and of Ruff and Bergdahl[12] in the neighborhood of the boiling point.

Chromium.—See note on beryllium.

Manganese.—The formula given is due to Baur and Brunner.[71] Earlier work of Greenwood[6] indicates values about 50 percent higher. Probably the values of Baur and Brunner are themselves ten or twenty percent too high. In view of the great experimental difficulties it is necessary to treat all results obtained for this element with some reserve.

SECTION 5. CONCLUSION

From Fig. 1a and from the tables and notes given in the preceding section, it is clear that, in spite of the large number of experiments which have been done, there is still a wide field for further experimental work. For many elements there are no measurements available and for others the measurements are confined to a small range of vapor pressure. Moreover, in addition to the need for exploration of fresh ground there is a necessity for further work of consolidation in relation to ground which has already received some investigation. In view of the technical difficulties and of the ubiquitous possibility of systematic errors, it is not permissible to place unreserved confidence in any single set of determinations however well the work appears to have been done. More care is needed in regard to purity of materials and this is especially important at low pressures.

Considering the elements for which results are given in Table II we see that tolerably complete results are available for Na, K, Cs, Hg, Cd, Zn, He, Ne, A, Kr, though further investigation is

desirable for K (high pressures) and Cd (low pressures). For the elements Xe, Li, Rb, there are considerable gaps and for the remaining elements the position is even less satisfactory. There is also a considerable number of elements not included in the table, the determination of whose vapor pressures should not present any insuperable difficulty. In addition to these there are some elements (e.g. Fe, Ni, Pt, etc.) whose vapor pressures are appreciable only at temperatures of the order of 2000°A or higher and the use of some method (other than that of evaporation from filaments) is desirable.

From the point of view of the theoretical worker the position is satisfactory in that all outstanding differences between theory and experiment may fairly be assigned to experimental error. There is room for further calculations on the chemical constant in which more accurate formulae for the variation of specific heat with temperature are used.

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Conversion Factors:

$$\log_{10} p \text{ mm} + 3.125 = \log_{10} p \text{ (baryes)}.$$
$$\log_{10} p \text{ mm} - 2.875 = \log_{10} p \text{ (bars)}.$$
$$\log_{10} p \text{ mm} - 2.881 = \log_{10} p \text{ (atmospheres)}.$$
$$1 \text{ barye} = 1 \text{ dyne/cm}^2.$$
$$1 \text{ bar} = 10^6 \text{ dynes/cm}^2.$$

Some authors use "bar" to indicate a unit of 1 dyne/cm².

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