APRIL 15, 1932 PHYSICAL REVIEW VOLUME 40

THE CALCULATION OF NORMAL VAPOR PRESSURES FROM THE DATA OF THE GAS CURRENT METHOD, PARTICULARLY IN THE CASE OF IODINE

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(Received February 20, 1932)

Abstract

The gas current method of determining the vapor pressure of slightly volatile substances is capable of a high degree of experimental precision and has often been applied. The question—whether the vapor pressure, so determined and subsequently corrected only for the Poynting effect, is accurately equal to the normal vapor pressure of the substance—has not hitherto been the subject of theoretical investigation. A method, dependent on recent developments in the thermodynamic treatment of mixtures of real gases is here developed for calculating the normal vapor pressure from the data of the gas current method. The suggested method requires data at varying total pressure for one inert gas at several temperatures and relatively accurate data at one atmosphere total pressure for two inert gases over the range of temperature. The one-atmosphere data for at least one of the inert gases must be of the precision desired on the normal vapor pressures. The method is applied to the case of the vapor pressure of solid iodine from 0 to 100°C, for which substance data exist which are suitable, though not obtained for the most appropriate choice of experimental conditions. The new corrections (for deviations from the laws of ideal gases) are found to be important numerically in the case of the best measurements. The errors inherent in the various methods of applying the gas current method are briefly discussed. A graphic, empirical, method is found liable to a characteristic source of error.

Introduction

A METHOD frequently employed for the determination of vapor pressures is the so-called gas current method, in which a stream of air or other gas is passed over the substance at constant temperature, causing it to volatilize, and the content of substance in the gas stream is determined. Precautions must be taken that the gas stream is just saturated with the substance at the known temperature. In the calculation of the vapor pressure small corrections are theoretically necessary, as is well understood, for any lowering of vapor pressure occasioned by solubility of the gas in the substance, and for the slight increase of vapor pressure due to the pressure of the gas. It does not appear to be universally understood that the calculations, as hitherto always carried out, assume laws of pure gases or of gaseous mixtures which are not exact.

The vapor pressure of a substance is defined as the pressure of the vapor (under a negligible influence of a gravitational or other external field) when it is pure and in equilibrium with the pure substance at a definite tempera-

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ture. If the substance is under a pressure greater than that of the vapor, the equilibration takes place through a semipermeable membrane, and the pressure as well as the temperature must be specified. It is the object of the gas current method to determine the *normal* vapor pressure, i.e., the vapor pressure when the pressure is the same on liquid and vapor and both phases are pure.

The methods previously used for the calculation of vapor pressures from the data are in general of three types. One form in which the gas current method has very often been applied is based on the assumption that the vapor pressure under the experimental conditions of pressure and gas solubility is equal to the product of the total pressure of the gas stream times the mol fraction of the substance in the gas stream. This assumption includes the laws of Boyle and Avogadro.[1,2]

Another way of applying the gas current method is to determine the concentration of the substance in the gas stream, i.e., the mass of substance per unit of volume of the gas mixture. Ordinarily the assumption would then be made that this concentration is equal to the concentration of pure vapor in equilibrium with liquid when this contains the same quantity of dissolved gas as in the experiment and is under the same total pressure as then. If the volume of the gas mixture has been directly measured, which in general is a difficult procedure, this method of calculation does not assume the ideal gas laws in any way,[3] but assumes[2] Gibbs' form of Dalton's law, which under the usual conditions for gas current vapor pressures is likely to result in an error greater than that of the previous method, as will be shown later.

A graphical method of extrapolation of the results to zero pressure of the inert gas is uncertain, due to the fact that the deviations from the ideal gas law are functions not only of the pressure but also of the composition of the gas mixture. In the variation of the total pressure under the experimental conditions the mol fraction also varies, and in such a manner as to introduce probably a curvature at pressures below the usual experimental range. The nature of this difficulty in extrapolation will be further discussed in a later section.

From recent work on the thermodynamics of gas mixtures from the point of view of equations of state[4] we are able to calculate with a considerable degree of accuracy normal vapor pressures from the data of the gas current method, provided that certain additional data are available. This method does not require the assumption of certain inexact laws such as the ideal gas law, Dalton's law, or the fugacity rule of Lewis and Randall.

In the present instance we shall follow the low pressure treatment of

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[1] Lurie and Gillespie, J. Am. Chem. Soc. **49,** 1146 (1927).

[2] Gillespie, Phys. Rev. **36,** 121 (1930).

[3] Except that the ideal gas law may be used, usually with no appreciable error, for calculating the normal vapor pressure from that under the pressure of the gas stream.

[4] See Gillespie and Beattie, Phys. Rev. **36,** 743 (1930), for a summary of previous work and for new evidence.

Gillespie[5] of the equilibrium pressure of a gas in a mixture, making certain slight modifications in the method of combination of constants which appear from recent unpublished work to give a better general agreement with the experimental data. By the use of a sufficient amount of data from the gas current method, approximate values of the three most important constants of the vapor under consideration in the Beattie-Bridgeman equation of state[6,7] can be obtained, and these are then used to calculate normal vapor pressures from the pressure, temperature and mol fraction data of the gas current method.

This method will then be applied to the data of Braune and Strassman[8] on iodine and extended to calculate corrections to other data on the vapor pressure of iodine.

The Calculation of Normal Vapor Pressures

The low pressure equation of Gillespie for a binary mixture is modified by the use of linear square root combination of c similar to that used for A_0 instead of linear combination of c as was previously used. This change seems justified in the light of recent unpublished work by Dr. Eli Lurie and by others in this laboratory. The effect of this change is small except in the case of gases whose c constants are large, where a markedly superior agreement with experiment is obtained. The resulting equation is

$$2.303\log\frac{p_1}{px_1} = \left(B_{01} - \frac{A_{01}}{RT} - \frac{c_1}{T^3}\right)\frac{p-p_1}{RT} + \left[\frac{(A_{01}^{1/2}-A_{02}^{1/2})^2}{RT} + \frac{(c_1^{1/2}-c_2^{1/2})^2}{T^3}\right]\frac{px_2^2}{RT}\cdot \quad (1)$$

The constants B_{01}, A_{01}, and c_1 are the constants in the Beattie-Bridgeman equation for the vapor of the liquid or solid, A_{02} and c_2 are the corresponding constants in the same equation for the inert gas used, p is the total pressure of the gas mixture, p_1 the vapor pressure of the liquid or solid under the total pressure p and saturated with inert gas. R is the gas constant, 0.08206 liter atmospheres per degree per mol, T the absolute temperature $(t°C+273.13)$ and x_1 the mol fraction of the vapor and x_2 that of the inert gas in the gas mixture. Common logarithms are denoted by log.

In general, p_1 will be sufficiently low in ordinary gas current vapor pressure measurements that the perfect gas volume may be used in calculating the normal vapor pressure from that under the experimental conditions, and the liquid or solid may also be considered incompressible in this correction. By a proper choice of inert gases the effect of solubility may usually be made small enough for Raoult's law of vapor pressure lowering to be sufficiently exact. The normal vapor pressure is then given by

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[5] Gillespie, Phys. Rev. **34**, 1605 (1929) Eq. (37). In this paper a subscript 1 was unfortunately applied to the last p of the equation. This subscript should be omitted.

[6] Beattie and Bridgeman, Proc. Amer. Acad. Arts and Sci. **63**, 229 (1928).

[7] Beattie and Bridgeman, J. Am. Chem. Soc. **50**, 3133 (1928); Zeits. f. Physik **62**, 95 (1930).

[8] Braune and Strassman, Zeits. f. physik. Chem. **143A**, 225 (1929).

$$\log p_0 = \log p_1 - \frac{V_1(p - p_0)}{2.303RT} - \log y. \tag{2}$$

V_1 is the molal volume of the solid or liquid in the condensed phase and y is the mol fraction of the liquid or solid in the liquid or solid phase.

Since the constants A_{02} and c_2 are known for practically all gases that are likely to be used as inert gases[6,7] and the volume V_1 and the mol fraction y are either known or readily determined to the accuracy required, the constants A_{01}, B_{01} and c_1 for the vapor are the only further quantities required for a calculation of the normal vapor pressure when p, x_1 and T are determined by experiment. If they are known the calculation proceeds readily in spite of the double occurrence of the unknown in both equations. The solution will of necessity proceed by successive trial and approximation but the convergence is very rapid in practice.

In general the necessary constants A_{01}, B_{01}, and c_1 will not be known and some method of evaluating them is necessary. This can be done by the use of suitable data and Eqs. (1) and (2). If the available data were of extraordinary accuracy and we could count implicitly on the form of the temperature functions in Eq. (1), then gas current vapor pressure data over a range of temperature and of varying pressure at each temperature using a single inert gas would be sufficient to solve for the desired constants. In practice, however, additional data must be used in determining them. Since the coefficient of $(p-p_1)$ is independent of the inert gas used, it is possible to obtain information on the coefficient of px_2^2 from additional data with a different inert gas.

The simplest method of carrying out such a computation requires the following data:

(1) Accurate values of p and the corresponding mol fractions over the desired temperature range with the given vapor in the gas stream for two different inert gases whose equation of state constants are known. These data need only be for one value of the pressure in each gas provided the pressures used in the two gases are the same at any given temperature. Since these data are those to be used for determining the normal vapor pressures, their accuracy should be that desired on the vapor pressures. As the most reproducible results are usually most readily obtained at pressures of about one atmosphere, this is probably the best pressure to choose. The inert gases chosen should preferably be two whose equation of state constants are as different as possible.

(2) Values of p and the corresponding mol fractions for various values of the pressure, with one of the two inert gases used above, at certain temperatures covering the temperature range desired. These data need not be as accurate as the one atmosphere data.

(3) Values of the molal volume of the liquid or solid and the solubility of the inert gases used over the temperature range. Since the corrections by Eq. (2) are in general small the accuracy required is not very great.

At a given pressure and temperature the value of the actual vapor pressure p_1 will be independent of the inert gas used except for a small term in y. Since, in the type of experiments used, p is in general much larger than p_1, $(p-p_1)$ will vary negligibly from gas to gas at a given total pressure. Consequently by applying Eqs. (1) and (2) to each inert gas at constant temperature and total pressure p, the term in $(p-p_1)$ can be eliminated and there results, using the asterisk to designate values for the second inert gas,—

$$\frac{2.303(RT)^2}{p}\left(\log\frac{x_1^*}{x_1} - \log\frac{y^*}{y}\right) = (A_{01}^{1/2} - A_{02}^{1/2})^2 x_2^2 - (A_{01}^{1/2} - A_{02}^{*1/2})^2 x_2^{*2} + R\,\frac{(c_1^{1/2} - c_2^{1/2})^2 x_2^2 - (c_1^{1/2} - c_2^{*1/2})^2 x_2^{*2}}{T^2}\cdot \quad (3)$$

In almost every case for gas current vapor pressures the difference between x_2^{*2} and x_2^2 will be small enough so that an average value may be used, so that the right hand side of the equation reduces to

$$\left[2A_{01}^{1/2}(A_{02}^{*1/2} - A_{02}^{1/2}) + A_{02} - A^*_{02} + R\,\frac{2c_1^{1/2}(c_2^{*1/2} - c_2^{1/2}) + c_2 - c_2^*}{T^2}\right] x_2^2 \equiv M x_2^2. \quad (4)$$

If values of M are plotted against $1/T^2$ a line will result whose intercept determines A_{01} and whose slope determines c_1. The normal experimental errors are such that the slope will seldom be determined very accurately and usually must be readjusted after using the variable pressure data.

Using the approximate values of A_{01} and c_1 found in this way, a value of B_{01} can be found which when Eqs. (1) and (2) are applied to the variable pressure data gives a value of p_0 which is constant within the experimental error. This is simpler to carry out than might appear, since in most cases an assumed approximate value of p_0, one for example based on the one-atmosphere value of px_1, applied to the right hand side of Eq. (2) and the same value used for p_1 on the right hand side of Eq. (1) will be sufficient for all except the final calculations. Unless the values of A_{01} and c_1 are right the values of B_{01} thus calculated will show a trend with temperature. This means that the line drawn on the M, $1/T^2$ plot from Eq. (4) must be readjusted in slope and new values of A_{01} and c_1 used. Usually, if B_{01} decreases as the temperature increases, it indicates that the c_1 value and consequently the slope chosen was too large. This readjustment is carried on till the deviations on the M, $1/T^2$ plot are not excessive, and a satisfactory constancy of B_{01} with temperature is obtained.

The final values of A_{01}, B_{01} and c_1 are then used in Eq. (1) to correct the more accurate one-atmosphere px_1 observations to give p_1. Normal vapor pressures may then be calculated by Eq. (2).

Constants thus obtained can probably be justifiably used in determining also the pressure, volume, temperature relationships for the vapor of the liquid at low pressures by the use of the Beattie-Bridgeman equation of state for low pressures by means of either of the two simple forms

$$V/n_1 = RT/p + [B_{01} - A_{01}/RT - c_1/T^3]$$

$$p = n_1RT/V + [B_{01} - A_{01}/RT - c_1/T^3]n_1^2RT/V^2.$$

The accuracy of these corrections on the perfect gas law will probably be considerably less when so used than when the constants are used to calculate corrections on the same type of data from which they were determined; but in many cases, such as the case of iodine which we are about to discuss, there is little possibility of being able to determine the equation of state with equal accuracy by direct measurement.

The Vapor Pressure of Iodine

Practically the only substance for which suitable data exist at present for the application of this method is iodine. Braune and Strassman[8] have recently published data from which the variation of px_1 from one atmosphere to about forty atmospheres with carbon dioxide could be calculated over a temperature range of about 60°C. They also give observations at one atmosphere with both carbon dioxide and hydrogen as inert gases. Due to a lack of smoothness of their vapor pressures as a function of temperature, the best results for normal vapor pressures will probably be obtained by correcting the results by Baxter, Hickey and Holmes[9] and of Baxter and Grose,[10] who used air as an inert gas. However, the use of a different gas for the determination of vapor pressures from either of those used in determining the constants introduces a certain possibility of error in the calculation of the corrections, as will be discussed more fully in the next section.

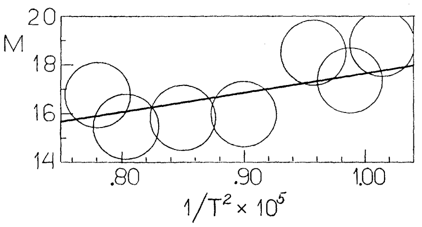

Fig. 1. Plot of the function M.

Unfortunately Braune and Strassman do not give their direct experimental quantities but calculated values, which fact necessitates a reversal of their calculations to get their experimental variables p and x_1. At ten temperatures they give values at one atmosphere for hydrogen and carbon dioxide. Three of these are sufficiently inconsistent to fall off the plot in Fig. 1 where the quantity of M of Eq. (4) is plotted against $1/T^2$. The radii

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[9] Baxter, Hickey and Holmes, J. Am. Chem. Soc. **29**, 127 (1907).

[10] Baxter and Grose, J. Am. Chem. Soc. **37**, 1061 (1915).

of the circles correspond to an accumulated error of 0.2 percent on their combined results for hydrogen and carbon dioxide at the temperature in question. The line corresponds to the final values of A_{01} and c_1 chosen after obtaining a proper value of B_{01} as described above.

The values of the constants found for iodine are given in Table. I. Carbon dioxide and hydrogen were assumed insoluble in solid iodine and the International Critical Tables[11] values for the density of solid iodine were used. The deviations in percent of the observed values of the quantity px_1/p_1 in the high pressure observations with carbon dioxide from the values calculated by Eq. (1) using these constants are shown in Fig. 2. The circles correspond to the claimed experimental accuracy of the measurements. It can be seen that the deviations are not systematic from temperature to temperature except possibly for the low temperature higher pressure points where we might well expect the low pressure equation we are using to be insufficient, since the magnitude of the correction in that region is about the size of p_1 itself.

TABLE I. *Values of the constants for iodine vapor in the Beattie-Bridgeman equation of state for low pressures.*

Constant	A_{01}	B_{01}	c_1	R	Molecular weight
Value	17.0	0.325	4000×10^4	0.08206	253.864

Units: atmospheres, liters, moles, $T=t°C+273.13$.

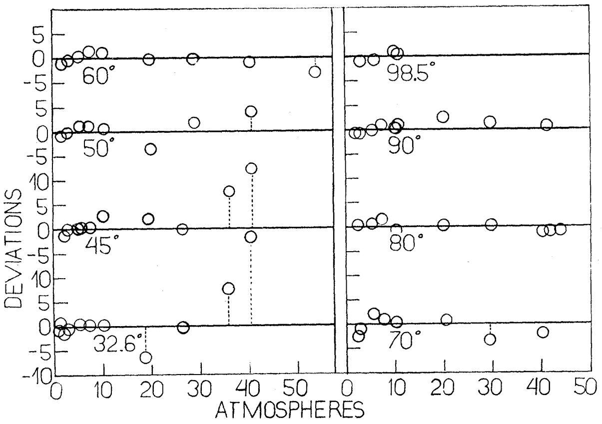

Fig. 2. Deviations: px_1/p_1, observed minus calculated, in percent of the calculated.

Since the one-atmosphere observations are probably more exact than those at higher pressures, the one-atmosphere points were used to calculate the normal vapor pressure of iodine with the aid of the above constants. For the purpose of showing the importance of the corrections, the values of

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[11] International Critical Tables **3,** 21 (1928).

px_1 as well as the normal vapor pressures obtained from them are given in Table II, together with the best values from the high pressure carbon dioxide experiments.

TABLE II. *Values of px_1 at one atmosphere, and normal vapor pressures of iodine in millimeters of mercury.*

	Values of px_1		Normal vapor pressures			
t°C	px_1 CO_2	px_1 H_2	High p CO_2	p_0 CO_2 1 atm.	p_0 H_2 1 atm.	Average of last two
32.6	0.5778	0.5608	0.5687	0.5642	0.5635	0.5639
45.0	1.504	1.467	1.482	1.473	1.474	1.4735
50.0	2.243	2.185	2.207	2.199	2.196	2.197
60.0	4.281	4.191	4.244	4.206	4.211	4.208
70.0	8.254	8.095	8.185	8.124	8.131	8.127
80.0	15.23	14.96	15.14	15.01	15.02	15.015
85.0	21.20	20.82	—	20.91	20.90	20.90

A comparison of the px_1 values with the corrected values of the vapor pressure shows that the corrections are quite significant and bring about a much better agreement between the two sets of data.

The normal vapor pressures calculated from the data of Braune and Strassman are found not to be smooth when their logarithms are plotted against $1/T$. This is however true of the original observations.

The measurements of Baxter and his co-workers, [9,10] who used dry, carbon-dioxide-free air as an inert gas in the gas current method at one atmosphere, appear very accurate. The vapor pressures are a smooth function of the temperature.

As already noted, [5] the algebra of combination of constants is such that a mixture such as air may without any inconsistency be treated as a pure substance in applying Eq. (1). The values of the constants used for air were those determined for air [6,7] when dry and free from carbon dioxide, rather than by using the method of combination of constants for its constituent gases.

Using these values for the constants of air and the values in Table I for iodine the normal vapor pressure was found for various temperatures from the data given by Baxter and Grose. The data are represented by the equation given by them:

$$\log p' = 9.7522 - \frac{2863.54}{273 + t^\circ - 19} \qquad (5)$$

where p' is equal to px_1 under the supposition that the volumes of dry air may be correctly calculated from the measured volumes of moist air by the use of the customary procedure involving the ideal gas laws.[12]

With the aid of Eqs. (1) and (2) and the assumption that air is insoluble in solid iodine, values of the normal vapor pressure of iodine were calculated

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[12] This supposition we shall here accept. The method which we are here applying may in principle be applied to improve the usual procedure, but at present the necessary constants for water are lacking.

from the data in Eq. (8) for even values of the temperature. These are given in Table III together with the corresponding values of px_1.

TABLE III. *Values of px_1 and of the normal vapor pressure of iodine in millimeters of mercury according to the measurements of Baxter and collaborators by the gas current method.*

$t°C$	0	10	20	30	40	50
px_1	0.03009	0.0804	0.2001	0.4670	1.0287	2.1511
p_0	0.02981	0.0798	0.1988	0.4643	1.0235	2.1419

$t°C$	60	70	80	90	100
px_1	4.292	8.206	15.092	26.79	46.04
p_0	4.276	8.179	15.047	26.71	45.89

The effect of the correction is decidedly important, compared with the precision obtainable in the best measurements by the gas current method. The normal vapor pressures of Braune and Strassman are in approximate agreement with those given in Table III; the average deviation being about 1.6 percent when only their one-atmosphere observations with hydrogen and carbon dioxide are considered.

Giauque[13] has recently smoothed the data of Baxter and his co-workers with the aid of spectroscopic and specific heat data. Application of his method to the above corrected results of Baxter gives an equation which fits the data well within the probable experimental accuracy. This equation is

$$\log p_{0\text{atm.}} = -\frac{3512.8}{273.1 + t°} - 2.013 \log (273.1 + t°) + 13.3740. \qquad (6)$$

Due to the theoretical advantages of this form, the vapor pressures calculated from it are probably more accurate than those given in Table III using Baxter's empirical smoothing function. The coefficient of the reciprocal absolute temperature is the only constant which differs numerically from that used by Giauque, as the other constants were derived by him from specific heat and spectroscopic data. The agreement of Eq. (6) with the data is slightly better than the empirical Eq. (5).

A COMPARISON OF METHODS OF CALCULATION

It can readily be seen from the results for iodine that even in the case of observations taken at as low a pressure as one atmosphere, the commonly used assumption that vapor pressures can be calculated from the gas current method data directly from the pressure mol fraction product may be seriously in error. Since it is known[1,2] that the assumption of this form of Dalton's law includes most of the perfect gas law we should expect deviations with real gases, but even where this is recognized it is often assumed that at such low pressures these deviations are within the experimental error.

The second usual method of calculation, that using Gibb's form of Dalton's law, makes no restriction on the equation of state of pure gases though it involves the rule of additivity of pressures[14] for mixtures. Both the addi-

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[13] Giauque, J. Am. Chem. Soc. **53**, 507 (1931).

[14] Gibbs "Collected Works of J. Willard Gibbs", **1**, 155, Longmans Green and Co., 1906 and 1928.

tivity of pressure rule and the Gibbs form of Dalton's law have experimentally been shown to be inexact for real gas mixtures. In many of the cases studied this form of Dalton's law is superior to the previously mentioned form but this is not necessarily the case, as can be readily seen from studying the identity

$$\frac{px_1/p_1}{(n_{1m}/V_m)/(n_1/V)} = \frac{pV_m/(n_{1m}+n_{2m})}{p_1V_1/n_1} \tag{7}$$

where p, V_m, n_{1m}, n_{2m}, are the pressure, volume, moles of substances 1 and 2 in a gas mixture, and p_1, V_1, and n_1 are corresponding values for pure gas 1 in equilibrium with it through a semipermeable membrane. The deviation of $(n_{1m}/V_m)/(n_1/V)$ from unity gives the deviation from the Gibbs-Dalton law, as the deviation of px_1/p_1 gives it for the simple rule. By using a low pressure form of the Beattie-Bridgeman equation of state corresponding to Eq. (1) we have for the pressure volume product of a pure gas

$$pV/n_1 = RT + [B_{01} - A_{01}/RT - c_1/T^3]p \tag{8}$$

and for a gas mixture, where the summations are over the various components of the mixture,

$$pV_m/\sum n_1 = RT + [\sum x_1B_{01} - (\sum x_1A_{01}{}^{1/2})^2/RT - (\sum x_1c_1{}^{1/2})^2/T^3]p. \tag{9}$$

By combining the last three equations we can calculate the deviations from the Gibbs-Dalton law from that known for the simple rule. This has been done for two temperatures in air, hydrogen and carbon dioxide as inert gases with iodine, and the deviations from both methods of computation are given in Table IV. It can be seen that the deviations from the Gibbs-Dalton law are of the same order of magnitude and in general slightly greater than for the simple rule. This is what we would expect from Eq. (7) in the case of small mol fractions where p is much greater than p_1 as is the usual case in gas current vapor pressure determinations. It can be seen that this method is equally unsatisfactory for our purpose as the first.

TABLE IV. *Deviations in percent in the calculation of the vapor pressure of iodine in various gases by simple methods.*

Inert gas	Air		H_2		CO_2	
t°C	25	75	25	75	25	75
$100\left(\frac{n_{1m}}{V_m}-\frac{n_1}{V_1}\right)\Big/\frac{n_1}{V_1}$	0.45	0.07	−0.77	−0.73	2.95	1.57
$100\frac{px_1-p_1}{p_1}$	0.42	0.13	−0.71	−0.61	2.43	1.31

A graphical method of extrapolating the px_1 values for various values of p to the limit where p equals p_0 is much more likely to be accurate than the two previous methods. There is here however an uncertainty due to the dependance of the corrections on the two variables p and x, which vary simultaneously, and a rapid change of x with p takes place at values of p (near p_0) below the values of p usually obtaining in gas current vapor pressures. This may be shown as follows.

The customary method for obtaining constants or virial coefficients in an equation of state for gas mixtures is to use a function of the form

$$b_m = b_1x_1^2 + 2b_{12}x_1x_2 + b_2x_2^2 \tag{10}$$

where b_1 and b_2 are the constants of the gases 1 and 2 and x_1 and x_2 the corresponding mol fractions with b_{12} an interaction constant. Any such method applied to the β term, the only one of importance at low pressures, or to its component constants, in a virial expansion in p of the equation of state of a mixture

$$pV_m/\sum n_1 = RT + \beta_m p + \cdots \tag{11}$$

gives for the equilibrium pressure calculation a relation of the form

$$2.303RT \log (p_1/px_1) = \beta_1(p - p_1) + F_{12}px_2^2 \tag{12}$$

where β_1 is the β of equation (11) for the pure gas 1 and F_{12} is a function of the constants of gas 1, gas 2 and their interaction constants. Such a function gives a curve of the general form shown in Fig. 3 for the value of log px_1/p_1 against $(p-p_1)$. It can be seen that when the mol fraction x_1 becomes very small at higher pressures the results are nearly linear but the straight line does not pass through the origin. Since the experimental results in gas current vapor pressure determinations are usually in this higher pressure range, direct extrapolation is likely to introduce appreciable errors. This error will usually be negligible when the vapor pressure is less than two or three millimeters.

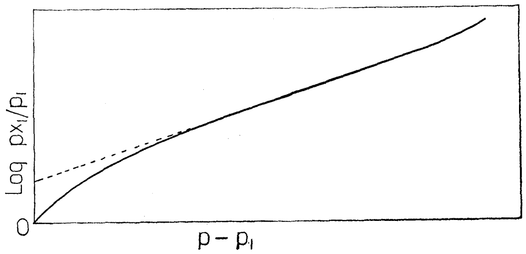

Fig. 3. A typical plot, showing failure of purely empirical treatment.

Extrapolation of values of the quantity $(n_{1m}/V_m)/(n_1/V_1)$ against the density of the inert gas offers theoretical advantage in that the extrapolation should be very nearly linear. However, this method offers in practice uncertainties equal to or greater than that using pressures, as the usual experimentally measured quantities are the total pressure and the mol fractions. In order to obtain mols per unit volume assumptions must be made about the equation of state of gas mixtures, and further assumptions about the equation of state of the pure vapor are necessary to convert the resulting extrapolated density into a vapor pressure. Due to the considerable possibility of substantial systematic errors from this source it seems advisable to use only methods involving pressures and mol fractions.

The method we are using in this paper uses the functions for β_1 and F_{12} in Eq. (12) taken from the Beattie-Bridgeman equation of state for pure gases and gas mixtures, which has received considerable experimental justification. It seems possible that certain small changes in the equation may have to be introduced in certain instances. These, however, are not of such a nature as to invalidate our method but only to limit the amount of extrapolation that is possible of the results from the conditions of temperature and of inert gases used in determining the constants to quite different conditions.

In the case where the available variable pressure data are with the same inert gas as the best one-atmosphere data from which the normal vapor pressures are to be determined, the method we are using can be regarded as simply a means of determining the amount of curvature at low pressures illustrated in Fig. 3 for a single isotherm and of smoothing the corrections as a function of the temperature. Under these circumstances we should expect very precise results in the determination of the normal vapor pressures over the experimental temperature range.

Where the corrections are applied to data with a different inert gas from either of those used in determining the constants of the equation, the possibilities of error are multiplied. We have applied it above in this way in the case of the iodine-air work of Baxter and his collaborators. In a case such as this, particularly as the corrections are intermediate between those for the two inert gases used in determining the constants, it seems entirely probable that the corrections are of the right order of magnitude though probably of considerably less accuracy than those calculated for carbon dioxide. The uncertainties of the method as a whole appear in any event to be less than those of the other methods used for the calculation of normal vapor pressures from data of the gas current method.