

The evaluation of vapour-pressure data

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THE EVALUATION OF VAPOUR-PRESSURE DATA

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THE EVALUATION OF VAPOUR-PRESSURE DATA

1. INTRODUCTION

Many physical and physicochemical properties are dependent on temperature, but the rate of change of vapour pressure with temperature is greater than that of almost all other properties, being approximately exponential when other properties seldom change more rapidly than may be expressed by a quadratic in temperature. Furthermore, the range of values is greater than that pertaining to most other physicochemical properties. There is a maximum, the critical pressure, normally not exceeding 5 MPa (two notable exceptions being water and mercury, for which the critical pressures are 22 MPa, and 151 MPa respectively); and for a substance for which the critical pressure is known, vapour pressures down to 10^{-4} Pa or lower may be of interest (the vapour pressure of mercury at its triple-point temperature (234.53 K) is 3×10^{-4} Pa). However, if we consider all elements and compounds, the lower limit of measurable vapour pressures extends to 10^{-10} Pa. Overall, therefore, there is a possible variation of more than 10^{16} . Measurements in this very long range are made by a variety of techniques, and the data arising are of varying accuracy; they may be considered in four ranges:

very low pressures, below 10^{-3} Pa,
low pressures, 10^{-3} to 1000 Pa,
medium pressures, 1 to 200 kPa, and
high pressures, 200 kPa to critical pressures.

These are arbitrary divisions, and the boundary values are no more than convenient guidelines. Discussion here will be concerned primarily with the medium-pressure and high-pressure ranges, but there will also be some reference to the low-pressure range. Measurements of very low vapour pressures are of very low accuracy in comparison with those of higher pressures, but the general principles outlined will apply in this range also.

Because of its very large variation with temperature, a vapour-pressure value has no meaning unless the temperature is specified, and any critical evaluation and presentation of data must relate pressure to temperature. Graphical means were often used in the past and a best line was drawn through the pattern of experimental points (see, for example, References 22, 24), but today the analysis will be done by use of the computer to fit an equation. However, there is no better method of examining the analysis as it proceeds and presenting the results at its end than by a graph, *e.g.*, of residuals from the equation, which may itself be plotted by the computer; the eye can see at a glance what may not be easy to deduce from columns of numbers and a few statistical parameters. In principle the graphical method could be simulated by the computer and best values obtained without the imposition on the data of the constraint implicit in an equation of fixed form, but there is no need because equations exist that can reproduce the most exact data without bias; moreover since the greater problems in evaluation arise where the data are poor or fragmentary, the constraint offered by an equation is more often desirable than not.

The vapour-pressure curve is a line on the pressure-volume-temperature surface, and if sufficient other volumetric or thermal data were available, it would in principle be possible to calculate vapour pressures from them. In practice vapour pressures are easier to measure and are more usually available than the other related properties, and vapour-pressure data occupy a key position in the construction of thermodynamic diagrams. However, there are occasions when the interrelationships between thermodynamic properties of state are useful for the improvement in reliability of vapour pressures (References 21, 34, 38, 40, 41, 54, 59, 61, 66, 83, 103, 108). In the past, the calculations were laborious, but with the availability now of suitable programs and labour-free calculation by computer, it is to be expected there will be more interest in future in the reconciliation of all related properties. For the present, the usual procedure for evaluation of vapour-pressure measurements is to correlate and compare them by means of a suitable equation. The

equations are empirical, even though in some instances theoretical interpretations have been attached to them after their suitability for the purpose had been demonstrated.

In this Memorandum, after sections on units (Section 2), and the importance of purity of the samples studied (Section 3) (the effects of impurities may be orders greater than those arising from any thermodynamic, statistical or computational finesse); there is, in Section 4 a description of the general shape of vapour-pressure curves, and in Section 5 a discussion of some selected equations; there are many more equations than are listed, and those selected for discussion include those of historical and theoretical interest, those used in extant ESDU Data Items (References 105, 111, 112, 117, 122) and the best currently available. Next are sections on an approach to fitting (Section 6) adopted in the most recent ESDU vapour pressure Data Items (Reference 110), on weighting (Section 7) and on low vapour pressures (Section 8), which last require special consideration because of their generally low accuracy. When data are fragmentary, use of the principle of corresponding states may be useful; there is discussion of this principle in its application to vapour pressures in Section 9, and of the use of comparisons between different substances in Section 10. This Memorandum is written primarily in relation to the vapour pressures of liquids, but Section 11 is devoted to those of solids and the relation between the vapour pressures of liquid and solid in the region of the triple point. The procedure for evaluation is discussed in Section 12 and illustrated by some examples from published work (Section 13). Finally, in Section 14 the naming of some early equations is discussed.

Vapour pressure appears in all equations currently in use as its logarithm. In the past it was arithmetically preferable to work with logarithms to the base 10, but since calculations are now carried out by computer or with calculators providing natural logarithms, logarithms to the base 10 are a hindrance rather than a help and all logarithmic expressions are written here in terms of natural logarithms without regard to the practice when each was first suggested.

Critical evaluation of vapour-pressure data requires understanding of the experimental methods by which they were obtained so that assessment of their relative accuracies can be made. Experimental methods have been reviewed elsewhere (References 87, 95) and these reviews contain references to other sources of information; another publication covers similar ground to the present Memorandum but was directed primarily towards estimation rather than evaluation (Reference 114). A paper by Horvath deals with some aspects covered in this Memorandum (Reference 154).

2. NOTATION AND UNITS

The results of any evaluation will now be expressed in SI, *i.e.* pressures in pascals or its multiples or submultiples and temperatures on the International Temperature Scale. Conversion of other pressure units to SI presents no difficulty, except that in some older papers the atmosphere may not always be the standard atmosphere, $1 \text{ atm} = 101.325 \text{ kPa}$, but a technical atmosphere, $1 \text{ kgf cm}^{-2} = 0.967841 \text{ atm} = 98.0665 \text{ kPa}$. The technique of measurement should be studied to check if possible that the author has calibrated his instruments and applied the proper corrections, especially where the measurement has been made by use of a mercury column since errors have sometimes been made in conversion of the observed heights into units of pressure (Reference 48).

The first internationally agreed temperature scale was the International Temperature Scale of 1927 (ITS-27), and any measurements since that date made with reference to the succeeding International (Practical) Temperature Scales present no difficulty in conversion to the present International Temperature Scale of 1990 (ITS-90). The relationships between ITS-27, IPTS-48, IPTS-68 and ITS-90, and tables for conversion from the earlier scales to the current ITS-90 are set out in ESDU Memorandum 79 (Reference 150). With respect to temperature the greatest problems arise with those who tried hardest and were themselves also concerned with the development of the temperature scale. Such work was of the highest quality attainable at the time, and deserves the trouble required to extract from it the best possible results: an example is

provided by the work at the National Bureau of Standards on the vapour pressure of ammonia, published in 1920 (References 9, 10). There appears to be no contemporary statement that the temperature scale for these measurements was identical with ITS-27, but it is a reasonable assumption, and was so assumed by Baehr, Garnjost and Pollak in a paper on the vapour pressure of ammonia (Reference 100). However, results of the quality of the work by Cragoe *et al.* (References 9, 10) deserve better than an assumption in this respect, and fortunately Haar, quoting Stimson, a colleague of those involved, provided this in 1972 (Reference 86). The measurements made by Giauque and his coworkers (References 13, 18) some years after that by Cragoe *et al.* present a more complex problem since Giauque, who was one of the proponents in the adoption of the modern form of scale with the kelvin defined by a single fixed point (References 17, 30) (now, the triple point of water, 273.16 K), aimed to give thermodynamic temperatures and ignored ITS-27; at the same time, his measurements were probably not as accurate as he thought (see, for example, discussion by Ambrose *et al.* (Reference 116)). There is finally the problem of authors who (around 1955) state that their results are expressed as thermodynamic temperatures, but do not say whether they added 273.15 K (the value usually favoured in Europe) or 273.16 K (the value usually favoured in the U.S.A.) to their Celsius temperatures, and do not make clear whether they subsequently adjusted their measured values by what they believed to be the differences between temperatures on the International Scale and thermodynamic temperatures. The question can only be answered by search in the literature for what was the custom of the particular laboratory.

But these make up a minute minority of the data in the literature, and, as far as the older work is concerned, errors corresponding with 0.5 K or more, often make questions of the temperature scale irrelevant. In general the adoption of ITS-27 ushered in the modern era of accurate measurements made on pure compounds. Prior to that date there are few investigations whose overall errors and corresponding imprecision are not greater than can be resolved by any present adjustments.

There has been confusion about the relationship between International Temperature Scales and thermodynamic temperatures, which in the case of IPTS-68 Ambrose endeavoured to clarify (Reference 98) allegedly with only partial success (Reference 106) but for most practical purposes, including the differentiation of vapour-pressure curves with a view to obtaining enthalpies of vaporization, thermodynamic temperatures T and International kelvin temperatures T_{90} may be taken as interchangeable.

A_0, B_0, C_0, D_0 A_1, B_1, C_1, D_1 A, B, C, D, E, F a, b, c, d $a_0, a_1, \dots a_s$	}	adjustable coefficients specific to each equation and to each substance for which the equation is used.
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$E_s(x)$	Chebyshev polynomial in x of degree s , Equation (5.9)
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d	exponent
-----	----------

e	exponent in Equation (4.4)
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$f^{(0)}(T_r), f^{(1)}(T_r)$	functions of reduced temperature in Equation (9.1)
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g	coefficient in Equation (4.4)
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H	enthalpy
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n	carbon number in Equation (13.1)
n_1, n_2, n_3, n_4, n_5	coefficients for Equations ((5.14), (5.15) and (5.16))
p	vapour pressure
p'	vapour pressure calculated from Equation (5.1)
R	gas constant, $8.314\,472\text{ J K}^{-1}\text{ mol}^{-1}$
T	thermodynamic temperature
V	volume
w_i	weight of data point i in Equation (7.1)
x	$(2T - (T_{\max} + T_{\min})) / (T_{\max} - T_{\min})$ in Equation (5.9)
x	$(1 - T_t/T) / (1 - T_t/T_c)$ in Equation (5.13)
x	function of reduced temperature in Equation (6.3)
y	function of reduced temperature in Equation (6.4)
Z	compression factor
α	Riedel parameter
θ	T/T_t in Equation (11.1)
τ	$1 - T_r$ in Equations (5.14), (5.15) and (5.16)
σ	estimated standard deviation in Equation (7.1)
ω	acentric factor, $-(1 + \ln p_r / \ln 10)$ at $T_r = 0.7$

State descriptors

(g)	denotes gas phase or saturated vapour
(l)	denotes liquid phase or saturated liquid
(s)	denotes solid phase, melting or sublimating solid
Δ	denotes property difference between two states

Subscripts

b	denotes value at the normal boiling point (at 101325 Pa)
c	denotes value at the critical point
calc	denotes value obtained from a fitted equation
exp	denotes an experimental or observed value
fus	denotes melting (solid-liquid transition)

m	denotes molar quantity
max	denotes maximum value or upper limit
min	denotes minimum value or lower limit
r	denotes reduced quantity, <i>e.g.</i> $T_r = T/T_c$
sub	denotes sublimation (solid-vapour transition)
t	denotes value at the triple point
vap	denotes evaporation (liquid-vapour transition)
I, II, <i>etc.</i>	denote reference fluids I, II, <i>etc.</i> in Equation (9.5)
90	denotes temperature on ITS-90 scale.

3. CHEMICAL SPECIES AND PURITY OF SAMPLES

Measured values of vapour pressure are highly dependent on the purity of the sample and if possible the investigator should check the purity both before and after making the measurements. The first task of the evaluator should be to study the method used for purification of the material and consider what are the probable residual impurities and the effect they are likely to have had on the results of an investigation (some methods may be more affected than others by the presence of a given impurity). Though this is the ideal, there is often no choice but to accept that the author has done his best, because the information given is inadequate for a deeper assessment. (This may be no criticism of the author because the information is costly and, certainly in times past, was often impossible to obtain. If we demand perfection always we should have no data.) The discrepancies that are found between sets otherwise apparently satisfactory are most likely to arise from unknown differences in the purities of the samples used.

Chemical change may arise as a result of the vaporization process. For example, when *n*-pentane evaporates at ambient temperature the gaseous molecules are of the same chemical species as those in the liquid, whereas when bismuth telluride (Bi_2Te_3 , melting point 850 K) is heated to 900 K dissociation into the elements takes place and the gaseous species differ from those present in the co-existing liquid. In the second instance there is a chemical equilibrium to be considered, and the total pressure exerted is the sum of the partial pressures of all gaseous species. Inorganic substances vaporizing at high temperatures frequently behave in this way and for the methods usually applicable to these substances at such temperatures it is necessary to know what chemical species compose the gaseous phase. Organic molecules when heated may break down irreversibly so that the vapour pressure is indeterminate but otherwise they vaporize at relatively low temperatures without chemical change, and it is not necessary for the molecular species to be known unless the molar mass of the gaseous substance is required for calculation of the vapour pressure from the measured quantities as in the Knudsen effusion and transpiration methods; in general the molar mass is that corresponding with the chemical formula, but this is not necessarily correct for associating compounds (References 53, 76).

This Memorandum deals only with the correlation and evaluation of the vapour pressures of substances that vaporize without chemical change.

4. SHAPE AND CHARACTERISTICS OF VAPOUR-PRESSURE CURVES

It is well known that when the logarithm of the vapour pressure, $\ln p$, is plotted against $1/T$ an approximately straight line is obtained, and linear interpolation of $\ln p$ against $1/T$ is the simplest way of interpolating accurately in a table of vapour-pressure values. In fact, however, the line has the shape of a shallow S, and such a curve is shown in Figure 1. This shape is implicit, for example, in the graphical presentation by Kay of his results (References 22, 24), but was stated explicitly as a general characteristic of the vapour-pressure curves of n -alkanes by Thodos (Reference 33), and has since been found true for all non-associated substances. The curve of Figure 1 is presented in terms of reduced variables $T_r = T/T_c$ and $p_r = p/p_c$, where the subscript r signifies reduced and c refers to critical conditions, and it was plotted in accordance with the behaviour of an actual substance, but for clarity the departure from the straight line has been exaggerated by ten times the true value. Figure 1 shows three features characteristic of most vapour-pressure curves: the part AB, which is concave with respect to the axes of the graph, the part BO, which is convex with respect to the axes, and the inflection between them at B. Plotting is more practical and sensitive if the straight line CO is made the baseline, as has been done in Figure 2, which is a correct representation of the behaviour of the compounds named. In both figures the straight line, which corresponds with Equation (5.1) below, has been arbitrarily fitted to the vapour-pressure values at $T_r = 0.7$ and 1.0, the point at $T_r = 0.7$ being chosen because it is that at which the acentric factor ω is defined (c.f. Section 9).

Figure 2 includes a curve for water and one other associated compound, ethanol. The curve for water is surprisingly similar to the curves for non-associated compounds but that for ethanol differs significantly - the magnitude of the departure from the straight line is much greater, and for $0.7 < T_r < 1$ the curve lies entirely above the reference line.

If, in the thermodynamically exact Clapeyron equation,

$$dp/dT = \Delta_{\text{vap}} H_m / T \Delta_{\text{vap}} V_m, \quad (4.1)$$

where $\Delta_{\text{vap}} H_m$ is the molar enthalpy of vaporization and $\Delta_{\text{vap}} V_m = V_m(g) - V_m(l)$ is the difference between the molar volumes of the saturated vapour and the liquid, $RT \Delta_{\text{vap}} Z/p$ is substituted for $\Delta_{\text{vap}} V_m$ then

$$dp/dT = p \Delta_{\text{vap}} H_m / RT^2 \Delta_{\text{vap}} Z, \quad (4.2)$$

or

$$\frac{\Delta_{\text{vap}} H_m}{\Delta_{\text{vap}} Z} = RT^2 d \ln p / dT = RT^2 d \ln p_r / dT \quad (4.3)$$

where $\Delta_{\text{vap}} Z = Z(g) - Z(l)$ and $Z = p V_m / RT$.

$\Delta_{\text{vap}} H_m / \Delta_{\text{vap}} Z$ may therefore be calculated in accordance with Equation (4.3) by differentiation of equations relating p and T . Waring (Reference 45) plotted observed values of $\Delta_{\text{vap}} H_m / \Delta_{\text{vap}} Z$ for water, and obtained an approximately parabolic curve with a minimum at $T_r \approx 0.85$. Less precise data, with a variety of other substances, gave similar results and on the assumption that the behaviour thus displayed was universal, he drew up a table of conditions that the differential coefficients of a vapour-pressure equation must fulfil. Reid and Sherwood (Reference 65) extended Waring's graph by adding points for n -pentane, ethylbenzene, carbon disulphide, sulphur dioxide and ethanol. The result was less rather than more convincing because $\Delta_{\text{vap}} H_m$ and $\Delta_{\text{vap}} Z$ are not easy to measure accurately, particularly as T_r approaches unity, and $\Delta_{\text{vap}} H_m / \Delta_{\text{vap}} Z$ by observation is, therefore, liable to large uncertainties. Experience, however, with obtaining $\Delta_{\text{vap}} H_m / \Delta_{\text{vap}} Z$ from vapour-pressure equations that are well controlled by the

experimental data fully bears out the original assumption by Waring of universality in the range $0.5 < T_r < 1.0$. For example, Ambrose and Walton (Reference 145) found the minima for the normal alkanes ranged smoothly up the series from 0.74 to 0.9, while for the associated alcohols the minima were all at reduced temperatures between 0.88 and 0.95 as shown in Figures 3 and 4.

At low pressures, behaviour of the vapour approaches that of the ideal gas, $\Delta_{\text{vap}} Z \approx 1$, $\Delta_{\text{vap}} H_m / \Delta_{\text{vap}} Z \approx \Delta_{\text{vap}} H_m$, and for T_r not exceeding, say 0.55, the plots of Figure 3 and Figure 4 are plots of $\Delta_{\text{vap}} H_m$, the enthalpy of vaporization. In experimental papers the variation of the enthalpy of vaporization with temperature is often expressed by means of a quadratic but for correlation the equation,

$$\Delta_{\text{vap}} H_m = g(1 - T_r)^e, \quad (4.4)$$

has usually been preferred. Equation (4.4) is one of those that have been repeatedly rediscovered; g is a constant for a given substance and values of e between $1/3$ (Thiesen, Reference 8) and 0.4 (Bowden, Reference 46) have been recommended; it is most generally known with $e = 0.38$ as the Watson equation (Reference 20). In the work by Ambrose, Counsell and Hicks (Reference 110) described in Section 6, a value of 0.375 was chosen for e (Kordes (Reference 43), Narsimhan (Reference 60)). (References prior to 1957 are given by Gambill (Reference 49).)

If Equation (4.4) is correct, the curves in Figure 3 ought to bend towards the horizontal as T_r is reduced, but they will not show the maxima in $d(\Delta_{\text{vap}} H_m)/dT$ reported by Scott and Osborn (Reference 118) for a series of alkanes - confirmation of the generality of this behaviour is desirable for the improvement of correlation and extrapolation at low pressures.

Plank and Riedel (Reference 25) studied the variation with temperature of a quantity $\alpha = \ln p_r / \ln T_r$ and from experimental results obtained by many investigators showed that at the critical temperature (References 25, 166)

$$(d(\alpha)/dT)_c = 0. \quad (4.5)$$

They also showed that the values of α , α_c , at $T_r = 1$ lay between 6 and 8 for the majority of substances. Riedel (Reference 44) called this quantity, on which he based his corresponding states scheme referred to in Section 9, the critical parameter.

Equations (4.3) and (4.5) can be combined to give a limiting value for $\Delta_{\text{vap}} H_m / \Delta_{\text{vap}} Z$ as the temperature tends to critical. Rearrangement of Equation (4.3) gives

$$\frac{d \ln p_r}{d \ln T_r} = \frac{1}{RT} \frac{\Delta_{\text{vap}} H_m}{\Delta_{\text{vap}} Z}. \quad (4.6)$$

Differentiation of the expression for α and application of the critical condition, Equation (4.5) gives finally

$$\alpha_c = \left(\frac{d \ln p_r}{d \ln T_r} \right)_c = \frac{1}{RT_c} \left(\frac{\Delta_{\text{vap}} H_m}{\Delta_{\text{vap}} Z} \right)_c \quad (4.7)$$

so that α_c is the limiting value of the 'reduced' quotient $\Delta_{\text{vap}} H_m / \Delta_{\text{vap}} Z$ as $T_r \rightarrow 1$. The limiting value for $\Delta_{\text{vap}} H_m / \Delta_{\text{vap}} Z$ at the critical point is therefore $RT_c \alpha_c$.

5. CORRELATING EQUATIONS

This section comprises a series of equations selected from the many that have been used for the correlation of vapour pressures. There is no end to the devising of equations for this purpose, and a survey of the early history of vapour-pressure equations to that date may be found in Reference 35. The process has continued since the first draft of this Memorandum was written some years ago as investigators have tried to extend the range of applicability and generality of equations (References 138, 139, 144, 147, 160, 164). But none of these more recent ones seems likely at present to displace the Wagner equation described in Section 5.10 for long-range correlation.

In the equations following $A, B, C, \dots; a, b, c, \dots; a_0, a_1, a_2, \dots; \text{ and } n_1, n_2, n_3, \dots;$ are adjustable constants applicable to each equation and peculiar to each individual substance.

5.1 $1/T$ Equation

If the vapour is assumed to behave as an ideal gas and the volume of the liquid is ignored, $\Delta_{\text{vap}}Z = 1$. Furthermore if the enthalpy of vaporization is assumed to be independent of temperature, integration of Equation (4.3) gives

$$\ln p = A + B/T, \quad (5.1)$$

where $B = -\Delta_{\text{vap}}H_m/R$. The equation is accurately applicable over short ranges only; the assumption about $\Delta_{\text{vap}}Z$ on which it is based is only valid at low pressures and, therefore, at low reduced temperatures ($T_r < 0.6$). Also, even at low temperatures, as has just been discussed, $\Delta_{\text{vap}}H_m$ is not independent of temperature although its rate of change is small. It seems probable that the $\ln p$ vs $1/T$ line remains curved however low the temperature, and that this will be demonstrable whenever the measured values available are sufficiently accurate.

In Figures 1 and 2, the straight lines correspond with Equation (5.1). As drawn, they pass through the values of reduced pressure at $T_r = 0.7$ and $T_r = 1$ but they could be adjusted so that they nearly coincide with the actual curves for any short range of temperature; consideration of Figure 1 shows that Equation (5.1) fitted to data near the normal boiling point (say at $T_r = 0.68$, i.e., $1/T_r = 1.47$) may be expected to yield pressures that are too high if it is extrapolated sufficiently far in either direction.

5.2 Antoine Equation

One of the most widely used equations by which account may be taken of curvature in the $\ln p$ vs $1/T$ line is that proposed by Antoine (Reference 23)

$$\ln p = A + B/(T + C), \quad (5.2)$$

where, for the best fit in the region of the normal boiling point, C may range between 0 and -150 K. The fit of Equation (5.2) is relatively insensitive to small changes in the value assigned to C , and Thomson has given some empirical rules by which an approximate value may be estimated (Reference 23). Alternative rules for selection of the value were given by Fishtine (Reference 58). It is therefore possible for an equation of fair accuracy applicable over a limited range to be set up from only two data points. A further simplification for organic compounds is to use the value -43 K (i.e. 230°C when Equation (5.2) is written in terms of Celsius temperatures) for all compounds; this is the basis of the widely used Cox chart, (Reference 12) and of the tables published by Dreisbach (Reference 37).

5.3 Kirchhoff-Rankine Equation

An attempt has been made to justify Equation (5.2) theoretically (Reference 29), but it is not very convincing and a theoretically more acceptable equation is that advanced by Kirchhoff and by Rankine (Reference 23),

$$\ln p = A + B/T + C \ln T, \quad (5.3)$$

because this can be derived from the assumption that the enthalpy of vaporization decreases linearly with increase in temperature. The assumption is not correct and in the medium-pressure range this equation does not represent the results of exact measurements as well as does Equation (5.2). However, in the low-pressure range de Kruif and his coworkers have used equations of this type with the constants related to other thermodynamic properties of the substance, and these have represented the results of their measurements entirely satisfactorily (References 121, 128, 129).

5.4 Cox Equation

If Equation (5.1) is written as

$$\ln(p/101325 \text{ Pa}) = A + B/T, \quad (5.4)$$

the left hand side is zero at the normal boiling temperature T_b , and $-B = AT_b$; then

$$\ln(p/101325 \text{ Pa}) = A(1 - T_b/T). \quad (5.5)$$

If now A is evaluated from observed values of p and T , it is found not to be a constant, but to vary with temperature, passing through a minimum at $T_r \approx 0.9$. Cox expressed this variation by putting

$$\ln A = \ln A_c + E(1 - T_r)(F - T_r), \quad (5.6)$$

where A_c is the value of A at the critical point and $F \approx 0.85$ (Reference 16). Equation (5.6) usually reproduces vapour pressures over short ranges within the precision of the best measurements, and over long ranges (20 kPa to critical pressures) within about 0.5% of the pressure. Alternatively, Equation (5.6) may be written in unreduced form as

$$\ln A = a + bT + cT^2. \quad (5.7)$$

The parabolic curve for $\ln A$ defined by Equation (5.6) or (5.7) was called by Thomson (Reference 51) the "Cox criterion", and he suggested that any long-range vapour-pressure equation should conform with this criterion. Numerically, A behaves similarly to $\Delta_{\text{vap}} H_m / \Delta_{\text{vap}} Z$; the latter, being a defined thermodynamic quantity, is to be preferred to the former, but effectively the "Cox criterion" and the "Waring criterion" discussed in Section 4 are equivalent, so this equation by its form automatically produces the characteristic shape of Figure 3 or Figure 4. Douslin, Harrison and Moore (Reference 69) increased the goodness of fit to their high quality measurements by increasing the number of terms in Equation (5.7) but by this action the equation ceases to conform automatically with the "Cox criterion", and Scott and Osborn (Reference 118) show that the result has "abominably poor extrapolation properties outside of the range of fit". With A given by Equation (5.7) Scott and Osborn claim that the Cox equation is the most reliable of any for extrapolation to low pressures. For exact fitting of precise long-range measurements they recommend expressing $\ln A$ as a power series in T^d where d is a fitted exponent, which is usually between 1.5 and 2.

5.5 Polynomials

The equation used by Cragoe (Reference 14) in the International Critical Tables may be rearranged as

$$\ln p = A + B/T + CT + DT^2. \quad (5.8)$$

This may be used in the form of a series of Chebyshev polynomials (Reference 74) as

$$T \ln p = a_0/2 + \sum_{s=1}^i a_s E_s(x), \quad (5.9)$$

where $E_s(x)$ is the Chebyshev polynomial in x of degree s , i is the order, and $x = (2T - (T_{\max} + T_{\min})) / (T_{\max} - T_{\min})$, $T_{\max}$ and $T_{\min}$ being two temperatures respectively just above and just below the extreme temperatures of the measured values; x varies between the bounds -1 and 1 . For equivalence with Equation (5.8) $i = 3$.

Equations (5.8) and (5.9) are convenient but do not always give such an exact representation of long-range data as, for example, do Equations (5.13) and (5.15). For good representation of data over a long range, a sixth-order equation may be needed, and even higher-order equations have been used (References 64, 84).

Before 1981 Chebyshev polynomials were used in ESDU Data Items, some of which are still extant (References 105, 111, 112, 117, 122). Their use was developed initially to overcome the limitations for numerical analysis of early computers (and for some purposes they may still be useful) but since modern computers have no limitations as far as vapour-pressure calculations are concerned, their future use (or use of any other polynomial) for vapour pressures is unlikely, and between 1980 and 1988 they were replaced in ESDU Data Items by Equation (5.14). Since 1988 the preferred "2.5, 5" form of the Wagner equation, Equation (5.15) has been used (see Section 5.10).

5.6 Planck-Riedel Equation

This equation (Reference 25),

$$\ln p = A + B/T + C \ln T + DT^6, \quad (5.10)$$

has been quite widely used. Riedel used it for the vapour-pressure correlation in his corresponding states scheme and Lee and Kesler used it for their presentation of the scheme by Pitzer *et al.* (References 44, 47 and 97) (see Section 9).

5.7 Frost and Kalkwarf Equation

This equation (Reference 39),

$$\ln p = A + B/T + C \ln T + Dp/T^2, \quad (5.11)$$

has been used particularly by Thodos and his coworkers mainly in a reduced form (References 55, 56, 57); since p occurs on both sides, the equation always requires an iterative procedure for its solution. Its performance in comparison with other equations does not seem sufficient to warrant this inconvenience.

5.8 Scott and Osborn Equation

This equation (Reference 118),

$$\begin{aligned} \ln p_r = & A + B/T_r - 3.013 \ln T_r + 5.512 T_r - \\ & 3.294 T_r^2 + D(-62.646 \ln T_r + 77.392 T_r) - \\ & 19.424 E T_r^2 + 0.176 p_r \exp((1.65 + 0.8E)/T_r - 0.9E), \end{aligned} \quad (5.12)$$

was developed from Equation (5.11) by making the temperature derivative of the enthalpy of vaporization dependent on the reduced temperature and the acentric factor rather than treating it as a constant, and by replacing D/T^2 with a more complex function of reduced temperature and the acentric factor. It may be simplified to an equation with three adjustable constants, A , B and C by substituting a single coefficient C , which has a value close to that of the acentric factor (see Section 9), for both D and E . Scott and Osborn proposed the equation for correlation over a limited range removed from the critical point, and for this purpose the values of T_c and p_c required for calculation of the reduced temperatures and pressures could become mere correlating parameters that might differ from their true values.

5.9 Goodwin Equation

Goodwin used the following equation for representation of the vapour pressures of oxygen and nitrogen (Reference 70). Subsequently it has been used, for example, for para-hydrogen (Reference 71), fluorine (Reference 78), and nitrogen (Reference 81), and as a general correlating equation (Reference 109),

$$\ln(p/p_t) = Ax + Bx^2 + Cx^3 + Dx(1-x)^e, \quad (5.13)$$

where $x = (1 - T_t/T)/(1 - T_t/T_c)$, $e \approx 1.6$ and the subscript t refers to the triple point; x varies between the bounds 0 and 1. This equation cannot be extrapolated above the critical temperature or below the triple point. Since liquids often supercool, the latter does not seem a desirable bound, but an arbitrary $T_{\min}$ may be substituted for the triple-point temperature so that the equation may be extended as far as is useful.

5.10 Wagner Equation

Wagner proposed a method of fitting equations to vapour-pressure data in which the actual terms, as well as their coefficients, are variables; *i.e.* a superfluity of terms is made available and the most significant ones are chosen according to statistical criteria (References 91, 107). Wagner and others (References 90, 91, 100, 102, 107, 123, 130) have applied the method to vapour pressure data for nitrogen, oxygen, argon, water, ammonia, propane, and *n*-butane. The simplest of the equations found in this way, which fitted the data for nitrogen and argon (References 90, 91, 107), are:

$$\ln(p/p_c) = (n_1 \tau + n_2 \tau^{1.5} + n_3 \tau^3 + n_4 \tau^6)/T_r \quad (5.14)$$

and
$$\ln(p/p_c) = (n_1 \tau + n_2 \tau^{1.5} + n_3 \tau^{2.5} + n_4 \tau^5)/T_r \quad (5.15)$$

where $\tau = 1 - T_r$.

In 1976 Wagner, Ewers and Penttermann (Reference 102) reported measurements on oxygen and recommended the following equation for this element,

$$\ln(p/p_c) = (n_1 \tau + n_2 \tau^{1.5} + n_3 \tau^3 + n_4 \tau^7 + n_5 \tau^9)/T_r \quad (5.16)$$