

# THE ANTOINE EQUATION FOR VAPOR-PRESSURE DATA

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The vapor pressure-temperature relation may be represented in a variety of ways, none of which is completely satisfactory. Of the simpler relations involving two or three empirical constants none is able to represent the temperature relation faithfully over the entire liquid range. However, many are useful for interpolations and extrapolations, particularly below or above a reduced temperature of 0.75. The commonly used equation

$$\log P = A - B/T$$

has not been found reliable, except for very short temperature ranges or for low-boiling substances. On the other hand, the Antoine equation

$$\log P = A - B/(t + C)$$

has been found to be entirely adequate for data of all but the very highest precision, from the triple point to a reduced temperature of 0.75. This equation introduces a needed correction to the commonly used equation (which may be written in the form  $\log P = A - B/(t + 273.16)$ ), since the best value of  $C$  is not necessarily equal to 273.16 and in fact is usually much lower.

The Henglein equation:

$$\log P = A - B/T^n$$

is similarly useful over the same range but is more difficult to use. The Antoine equation is thus recommended for general use and simple means are described for obtaining the empirical constants, including approximate rules for estimating the value of  $C$ .

Of the equations which are designed to fit over the entire liquid range, those of Cox, Biot, and Gamson and Watson are considered most satisfactory. For practical purposes two Antoine equations, one up to a reduced temperature of 0.75, the other from that point to the critical point and both tangent at their intersection point, are much more convenient to use and are fully as accurate.

A method is presented for calculating the heat of vaporization from vapor-pressure data, using the Antoine equation. This method includes a suitable correlation for estimating the effect of the volume of the liquid compared with the vapor and the deviation of the vapor from the perfect gas laws.

A nomograph is given which is based on the use of  $C = 230$ , a good average value for organic compounds which are liquid at room temperature. This chart may be used for rapid interpolations and also for the estimation of vapor pressures from meager information.

## I. INTRODUCTION

Many different formulas and representations have been presented for the vapor pressure-temperature relationship for pure liquids and their mixtures. This is due not only to the importance of this physical property itself but also to its relation to other thermodynamic properties, such as the latent heat of vaporization. For use in thermodynamic calculations an interpolation formula of some kind is well-nigh essential, particularly since the experimental data are usually fragmentary and located at inconvenient temperature and pressure inter-

vals. The purpose of this paper is to review these representations of vapor-pressure data, with special emphasis on the Antoine equation.

## II. FORMULAS IN USE IN THE PAST

The very earliest vapor-pressure formula was given by Dalton (17), who observed that the pressures increased in geometric progression while the temperatures increased in arithmetic progression, that is:

$$\log P = a + bT \quad (1)$$

This relation was quickly disproved when better measurements became available, but the gentle curvature of vapor-pressure data plotted on semi-log paper demonstrates the approximate validity of the rule.

## III. RELATIONS BASED ON CLAUSIUS-CLAPEYRON EQUATION

Many of the formulas in use have a semi-theoretical background, often being based on the Clausius-Clapeyron equation:

$$\frac{dP}{dt} = \frac{\Delta H}{T\Delta V} = \frac{\Delta H}{T(V_g - V_l)} \quad (2)$$

where  $P$  = vapor pressure of liquid,

$t$  = temperature,

$T$  = absolute temperature,

$\Delta H$  = heat of vaporization,

$\Delta V$  = change in volume on vaporization,

$V_g$  = molecular volume of gaseous phase, and

$V_l$  = molecular volume of liquid phase.

The most familiar vapor-pressure formula is probably the relation:

$$\log P = A - \frac{B}{T} \quad (3)$$

This "1/T form" has a semi-theoretical background, being the integrated form of the Clausius-Clapeyron equation with the assumptions that: (1) the volume of the liquid,  $V_l$ , is negligible compared with the volume of the vapor,  $V_g$ ; (2) the heat of vaporization,  $\Delta H$ , is constant over the temperature range involved; and (3) the vapor is a perfect gas. Obviously these three assumptions are only crude approximations, unless the temperature range involved is small indeed, but the combination of all three leads to a much better approximation because some of the errors cancel. This may be more clearly seen by writing the Clausius-Clapeyron equation in the following form:

$$\frac{d \ln P}{d(1/T)} = -\frac{1}{R} \cdot \frac{\Delta H}{\Delta z} \quad (4)$$

where

$$\Delta z = \Delta z_g - \Delta z_l$$

$$\Delta z_g = PV_g/RT$$

$$\Delta z_l = PV_l/RT$$

The  $\Delta z$  term provides a convenient double correction for both the non-ideality of the vapor and the effect of including the liquid volume in the  $\Delta V$  term. The ratio  $\Delta H/\Delta z$  does not vary very much with temperature, so that for approximate vapor-pressure data it appears to be constant and the  $1/T$  form seems to apply. However, application to more accurate data shows a definite variation of  $\Delta H/\Delta z$  with temperature, so that, in general, the  $1/T$  form does not give a true picture of the vapor pressure-temperature relation. Deviations exceed reasonable experimental error and their systematic trends indicate that extrapolation is unwise even over short ranges.

The assumption that the heat of vaporization is constant was early seen to be one of the chief contributing factors in the inability of the  $1/T$  formula to represent the data within the experimental error. To avoid this difficulty the heat of vaporization was taken to be one of several various functions of the temperature, giving corresponding vapor-pressure equations. For example: if the volume of the liquid is neglected compared with the vapor, the vapor is considered to be a perfect gas, and the heat of vaporization is represented by a polynomial such as:

$$\Delta H = \Delta H_0 + bT + dT^2 + eT^3 + \dots \quad (5)$$

then the vapor-pressure formula becomes

$$\log P = \frac{1}{2.3R} \left\{ a - \frac{\Delta H_0}{T} + 2.3b \log T + dT + \frac{e}{2} T^2 + \dots \right\} \quad (6)$$

where  $2.3 = \ln 10$  and  $2.3R = 4.57566$  for  $\Delta H$  in calories per mole. One of the simpler forms with  $d, e, \dots = 0$  is generally attributed to Kirchoff (30), but Rankine (42) used it nine years earlier.

The assumptions involved in equation 5 may be replaced by the single relation:

$$\Delta H/\Delta z = \Delta H_0 + bT + dT^2 + eT^3 + \dots \quad (7)$$

which may be valid up to the critical point, although the individual assumptions are not.

The constants of equation 7 are directly related to the difference in specific heats of the two saturated phases,  $\Delta C_s$ , but the rigorous relation (19) is complex:

$$\Delta C_s = \Delta C_p - T \frac{dP}{dt} \left\{ \left( \frac{\partial V_g}{\partial T} \right)_P - \left( \frac{\partial V_l}{\partial T} \right)_P \right\} \quad (8)$$

also

$$\Delta C_s = \frac{d\Delta H}{dT} - \frac{\Delta H}{T} \quad (9)$$

where  $\Delta C_p$  = difference in isobaric specific heats of liquid and vapor, and  
 $\Delta C_s$  = difference in specific heats of the saturated liquid and vapor phases.

The rigorous application of these equations is seldom possible because of incomplete  $P$ - $V$ - $T$  data. Below the normal boiling point the following approximation is frequently sufficiently accurate to provide suitable vapor-pressure relations:

$$\Delta C_p = \frac{\partial}{\partial T} \left( \frac{\Delta H}{\Delta z} \right) \quad (10)$$

If the isobaric specific heats of liquid and vapor are available, then the constants of the vapor-pressure equation (equation 6) are easily determined.

In his classical work, Nernst (37) derived a similar formula on the following assumptions:

$$\Delta z = \frac{P\Delta V}{RT} = 1 - \frac{P}{P_c} \quad (11)$$

$$\Delta H = (\Delta H_0 + \beta T - \epsilon T^2) \left( 1 - \frac{P}{P_c} \right) \quad (12)$$

where  $P_c$  = critical pressure. Substitution into the Clausius-Clapeyron equation and integration gives:

$$\log P = \frac{\Delta H_0}{2.3RT} + \frac{\beta}{2} \log T - \frac{\epsilon T}{2.3R} + C \quad (13)$$

In equation 13,  $\Delta H_0$ ,  $\beta$ ,  $\epsilon$ , and  $C$  are empirical constants. Nernst found that  $\beta$  is often close to 3.5 and that  $C$  appeared to be independent of the state of the compound. He therefore called  $C$  a "chemical constant". There was considerable interest in these constants which stimulated interest in vapor-pressure work. In particular, the constants were used to calculate reaction equilibria until they were supplanted by more accurate thermodynamic methods.

This equation has been very widely used, since the addition of the extra two terms to the  $1/T$  form removes many of its disadvantages, although the assumptions are not valid and the relation is purely empirical. Equation 11 satisfies the boundary conditions at zero pressure and the critical point but gives values of  $\Delta z$  which are consistently low. The calculated values are only about 50 per cent of the experimental values (34) above  $P_R = 0.7$ . Fortunately this error is not reflected in the final Nernst vapor-pressure equation, since the quantity  $(1 - P/P_c)$  cancels out.

At low pressures, where equation 10 can be applied, the Nernst equation gives

$$\Delta C_p = \beta - 2\epsilon T, \text{ or} \quad (14)$$

$$= 3.5 - 2\epsilon T \quad (15)$$

Since it is known that  $\Delta C_p$  is usually negative and, for inorganic salts, about - 3.5 per atom in the molecule<sup>1</sup>,  $\epsilon$  will usually be larger than 0.001. Another

<sup>1</sup> This is the value usually used by K. K. Kelley for estimating  $\Delta C_p$  in his vapor-pressure compilations (29).

approximate check on the Nernst equation is obtained from the value of the "chemical constant",  $C$ , which, for all "normal" liquids, should be about 6.0 for  $P$  in millimeters, although low-boiling substances are much lower (hydrogen = 4.5; nitrogen = 5.4) and associated liquids are somewhat higher (water = 6.5).

#### IV. EMPIRICAL EQUATIONS

Another school of thought broke away from the Clausius-Clapeyron equation tradition and proposed frankly empirical vapor-pressure equations, some of which are shown below. An excellent review of many of those proposed prior to 1910 is presented in Chwolson's *Traité de physique* (13). No simple vapor-pressure equation has yet been devised which fits the data from the triple point to the critical point and which is also in agreement with thermodynamic data on the saturated phases.

Bose (8) proposed the equation

$$\log P = a - \frac{b}{T} + \frac{d}{T^2} + \frac{e}{T^3} \quad (16)$$

which he claimed to be better at high temperatures than the Nernst equation.

A different attack on the problem was that of Biot (7), whose exponential equation

$$\log P = a + b\alpha^t + c\beta^t \quad (17)$$

was used by Regnault for much of his early work and more recently by Sidney Young (57) to fit vapor-pressure data for a variety of compounds up to the critical point. By expansion this equation may be shown to be equivalent to a convergent infinite series of the type:

$$\log P = A + BT + DT^2 + \dots \quad (18)$$

Many other similar exponential forms are encountered.

van der Waals proposed the relation

$$\log \frac{P_c}{P} = a \left\{ \frac{T_c}{T} - 1 \right\} \quad (19)$$

where  $a$  was supposed to be a universal constant, but this was soon shown to be inaccurate, since  $a$  depends on both temperature and substance (38).

Carbonelli suggested the modification

$$\log \frac{P_c}{P} = \left\{ \frac{T_c}{T} - 1 \right\} \log \left( b \frac{T_c}{T} \right) \quad (20)$$

where  $\log b$  lies between 2 and 4. This equation does not give a reasonable representation of the data, since  $b$  is a parabolic-type function of temperature, instead of a constant, as claimed.

The variation of these "constants" from substance to substance in equations involving "reduced" properties ( $P/P_c = P_R =$  reduced pressure, for example)

is in line with the well-demonstrated fact that there is no general equation of state possible for compounds along the saturation line.

Several workers have used the form

$$\log P(\text{atm.}) = A \left( 1 - \frac{T_B}{T} \right) \quad (21)$$

where  $A$  is some function of the temperature and substance. One of the most successful studies using this method was made by Cox (16), who showed that  $\log A$  was a parabolic function of temperature over the entire liquid range for all the compounds tested, including hydrocarbons, hydrogen, oxygen, nitrogen, carbon dioxide, water, ammonia, and several alcohols and ethers. The fundamental relationship can be written

$$\log A = \log A_c + E(1 - T_R)(F - T_R) \quad (22)$$

where  $A_c$  = value of  $A$  at critical point,

$T_R$  = reduced temperature,

$E$  = empirical constant, a linear function of boiling point for the paraffins, and

$F$  = empirical constant, equal to 0.85 for hydrocarbons with more than two carbon atoms.

This method of calculation provides an excellent check on the accuracy of vapor-pressure data, since a plot of  $A$  (or  $\log A$ ) against temperature should be smooth. In practice the plot is found to be very sensitive near the boiling point, the critical point, and near  $T_R = F$ , but this sensitivity is of little importance in determining either  $E$  or  $F$ . This equation is important, both because it provides a good fit over the entire liquid range with but few empirical constants and also because the fundamental parabolic relation which appears to be established provides an excellent check on other suggested equations which profess to fit over the the entire liquid range.

The recent work of Gamson and Watson (21) presents a similar ambitious attempt to provide a vapor-pressure equation which is valid over the entire liquid range. They modify the  $1/T$  form by adding an exponential term, as follows:

$$\log P = A - \frac{B}{T} - e^{-20(T_R - b)^2} \quad (23)$$

Methods are presented for estimating the values of  $b$  and the critical constants for fifteen homologous series of organic compounds. Since the exponential term becomes negligible at the higher temperatures, the equation approaches the  $1/T$  form near the critical point. However, the work of Cox (16) described above and similar studies by the author have shown that in general the vapor pressure-temperature relation does not follow a  $1/T$  form equation even at the high range. If the  $1/T$  form were applicable then:

$$\frac{T_c \cdot T(y_c - y)}{T_c - T} = \text{a constant, } B \text{ in equation 3} \quad (24)$$

However, plots of this quantity against temperature, for various compounds, show pronounced minima near  $T_R = 0.75$  instead of leveling off near the critical point as predicted by the Gamson and Watson relation, which may be written:

$$\begin{aligned} \frac{T_c \cdot T(y_c - y)}{T_c - T} &= B + \frac{T \cdot T_c}{T_c - T} e^{-20(\tau_R - b)^2} \\ &= B + \frac{T_c \cdot T_R}{1 - T_R} e^{-20(\tau_R - b)^2} \end{aligned} \quad (25)$$

The only minimum for this function occurs at the critical point, so that, like most other empirical vapor-pressure equations, the Gamson and Watson relation cannot fit exactly over the entire liquid range, although the approximation is very good indeed. When applied to accurate experimental data the equation provides a remarkably good fit up to about  $T_R = 0.80$  and only a small systematic error, of the order of 1 to 2 per cent, from that temperature to the critical point.

It is unfortunate that this useful equation is difficult to handle. The exponential term is not readily calculated and yet it constitutes a large part of the value of  $\log P$  at the lower temperatures (e.g., 20 per cent of  $\log P$  for *n*-heptane at 0°C.). Also, the temperature cannot be obtained from the pressure without a trial solution. The high accuracy of both this equation and the Antoine equation (see below) suggests that an excellent procedure for calculating vapor pressures over the entire liquid range would be to fit a Gamson and Watson equation to the data and calculate from it five or six points, as follows: one or two below the boiling point, at the boiling point, and at  $T_R = 0.8, 0.9,$  and  $1.0$ . Two Antoine equations could then be fitted, one up to  $T_R = 0.8$ , the other from  $T_R = 0.8$  to the critical point. This procedure combines the long-range accuracy of the Gamson and Watson equation with the precision and ease of calculation of the Antoine equation.

The use of polynomials in  $t$  (or  $P$ ) to give  $P$  (or  $t$ ), such as have been employed by the Bureau of Standards for their accurate measurements on water, heptane, and isoöctane, is convenient in that no logarithm tables are required. For example, their equations for isoöctane (51)

$$P = 760 + 21.500(t - b) + 0.2348(t - b)^2 + 0.00126(t - b)^3 \quad (26)$$

where  $b = 99.234$ , the normal boiling point, and

$$\begin{aligned} t &= 99.234 + 0.046511(P - 760) \\ &\quad - 0.042374(P - 760)^2 + 0.07182(P - 760)^3 \end{aligned} \quad (27)$$

give a very close fit to their data over the range from 660 to 860 mm. Equation 27 gives  $t$  with a maximum deviation of only 0.003°C. However, when the work was repeated over a wider range (49) the Antoine equation (see below)

$$\log P = 6.820137 - \frac{1262.707}{t + 221.307} \quad (28)$$

was found to give a much better representation from 100 to 1500 mm.

When a very accurate formula is desired, as that for a primary ebulliometric standard, very elaborate means may be employed. For example, Osborne and Meyers (40) found it necessary to employ the following equation for the vapor pressure of water over the entire liquid range:

$$\log P = A - \frac{B}{T} + \frac{Cx}{T} (10^{Dx^2} - 1) - E(10^{Fy^{5/4}}) \quad (29)$$

where  $T = t + 273.16$ ,

$x = T^2 - K$ , and

$y = t_c - t$ , where  $t_c = 374.11^\circ\text{C}$ ., critical temperature, and the parameters have the following values:

$$\begin{aligned} A &= 5.4266514 & E &= 0.0044 \\ B &= 2005.1 & F &= -0.0057148 \\ C &= 1.3869 \times 10^{-4} & K &= 293,700 \\ D &= 1.1965 \times 10^{-11} \end{aligned}$$

The authors stated that "the resulting formula here presented makes no claim to rationality or apparent simplicity, as these qualities have as yet eluded the inspiration of the authors and their colleagues."

In almost all the equations mentioned the temperature enters the formula as  $T$ , the absolute temperature. Various investigators broke from tradition by modifying the terms in  $T$ . Ashworth (4) plotted  $\log P$  vs.  $1/(\sqrt{T^2 + 108,000} - 307.6)$  for normal paraffins ( $\text{C}_6\text{H}_{12}$  to  $\text{C}_{32}\text{H}_{66}$ ) and obtained straight lines with a common intersection point at  $1249^\circ\text{C}$ . and  $3.63 \times 10^6$  mm. Henglein (24) used an exponent on the  $T$  in the  $1/T$  form giving:

$$\log P = A - B/T^n \quad (30)$$

The proper choice of  $n$  gives a fairly good fit over a large temperature range. Henglein considered that  $A$  was a universal constant, equal to 7.5030 for  $P$  in millimeters. On the other hand, in developing a vapor-pressure slide rule, Miles (35) considered that, although  $n$  varied from 1.05 to 1.56, an average value of 1.3 was suitable for all compounds. Actually the equation, with a proper choice of all three constants, gives a very good fit to the experimental data at the lower temperatures, but diverges appreciably above reduced temperatures of 0.75 to 0.80. Thus, for the S. Young (57) data on  $n$ -heptane the equation

$$\log P = 6.33546 - 11877.85/T^{1.376} \quad (31)$$

fits to about  $\pm 0.2$  per cent in pressure, or to about  $\pm 0.1^\circ$ , up to  $160^\circ\text{C}$ . ( $T_R = 0.80$ ). Above this temperature the equation has an increasingly larger systematic error until at the critical point ( $266.85^\circ\text{C}$ .; 20,430 mm.) the calculated values are 7.8% high and 9 per cent low, respectively. The Antoine equation (see below) through the same data gives a comparable fit over the same range



and a somewhat lower systematic error, which reaches a maximum of 4.2° in temperature and 5 per cent in pressure at the critical point.

The Henglein equation is believed to be reliable for data either below or above  $T_R = 0.75$  to 0.80, but not for data both above and below this temperature, unless the range is very short. The equation is cumbersome to handle but gives direct solutions for both temperature and pressure. Unfortunately the constant  $A$  is not universal, as Henglein claimed, so that all three constants must be determined.

#### V. THE ANTOINE EQUATION

Various disadvantages are associated with the use of many of the formulas described above. The  $1/T$  form suffers from the fact that its fundamental assumptions do not hold. The problem of the proper value of the ice point influences the value of the formula for precise work. Some of the values used are 273, 273.09, 273.1, 273.2, 273.13, 273.16, and 273.167. Unfortunately, many authors do not even say what their ice point is. When  $\log P$  is plotted against  $1/T$ , the data are almost always bowed, indicating that extrapolation is particularly hazardous.

The more complicated formulas represent the data much better, but there are some difficulties connected with their use. The empirical constants are usually tedious to determine. In many cases, it is difficult to find  $t$  as a function of  $P$ , as with the equations of Nernst, Bose, Biot, Cox, Gamson and Watson, and the complicated water equations of the Bureau of Standards, where a trial-and-error or graphical solution must be resorted to. The number of constants used are often more than are justified by the precision of the data.

The Bureau of Standards polynomials for  $t$  and  $P$  are excellent for representing the data over limited ranges but are somewhat tedious to calculate.

The much simpler Antoine equation, originally applied to water (1), simply substitutes  $(t + C)$  for  $T$  in the simple  $1/T$  form giving:

$$\log P = A - \frac{B}{t + C} \quad (32)$$

In a later publication (2) Antoine applied the equation to over twenty compounds and mixtures. A similar extensive study on one hundred fourteen liquids and twenty-seven solids was made by Schmidt (45), who was apparently ignorant of Antoine's work. When applied by Calingaert and Davis (10) to several classes of compounds (metallic elements, hydrocarbons, alcohols, acids, etc.), using  $C = 230$ , good straight lines were obtained on the plot of  $\log P$  vs.  $1/(t + C)$  with an intersection point for each group studied. The hydrocarbon point is at 1240°C. and  $1.3 \times 10^6$  mm., not very different from that found by Ashworth, whose method of plotting is approximately equivalent to the use of  $C = 150$ . Since for most classes of compounds the value of  $C$  decreases with increasing boiling point, the charts with intersecting straight lines<sup>2</sup> are only ap-

<sup>2</sup> These charts are usually known as Cox charts. Cox (15) plotted  $\log P$  against the logarithm of the vapor pressure of water at the same temperature.

proximately correct. However, this chart error is frequently less than the other uncertainties of the data and the choice of  $C = 230$  is fortunate in that it is a good middle value. Many later workers have used the Antoine equation for long-range data of moderate precision and for shorter-range data of high precision, with considerable success. For example, the Bureau of Standards equation for isoöctane (equation 28) reproduces the observed pressures with an average deviation of 0.05 mm. from 100 to 1500 mm. pressure.

The Antoine equation possesses various advantages when compared with the other types of vapor-pressure equations in the literature. It fits every case tried better than the  $1/T$  form, excepting low-boiling compounds and monatomic elements, where the value of  $C$  is close to 273. Extrapolation is safer than with the  $1/T$  type, because the use of a constant other than the ice point, 273, reduces the systematic deviations which cause bowing of the straight line expected when  $\log P$  is plotted against  $1/(t + C)$ . The value of  $t$  is readily obtained from  $P$ . The constants are easily determined. In many cases which have been studied  $C$  lies between 220 and 240, and  $C = 230$  may be used for many compounds. This reduces the Antoine equation to a readily handled two-constant equation, linear in  $\log P$  and  $1/(t + 230)$ .

In many examples of data of moderate precision (0.1–2 per cent in  $P$ ), the Antoine equation reproduces the values closer than the equations suggested by the workers, which are usually more complicated. Several comparisons are shown in a later section.

A striking example in the field of high-precision measurements is the Antoine equation for water suggested by Swietoslowski and Smith (52),

$$\log P(\text{atm.}) = 5.053988 - \frac{1647.6}{t + 226} \quad (33)$$

which reproduces the values from 80° to 100°C. with as high precision as the more complex formula of Osborne and Meyers (equation 29).

A useful scheme for estimating vapor pressures is the application of the Calingaert and Davis work described above. Since groups of similar compounds have often a common intersection point when  $\log P$  is plotted against  $1/(t + 230)$ , the intersection point and a boiling point can be used to estimate the entire vapor pressure–temperature curve. This method was applied in this laboratory to the vapor pressures of the  $R_4\text{Pb}$  compounds (9) where there are good long-range data on both  $(\text{C}_2\text{H}_5)_4\text{Pb}$  and  $(\text{CH}_3)_4\text{Pb}$ , but only scanty data on the other three lead alkyls,  $(\text{CH}_3)_3\text{C}_2\text{H}_5\text{Pb}$ ,  $(\text{CH}_3)_2(\text{C}_2\text{H}_5)_2\text{Pb}$ , and  $\text{CH}_3(\text{C}_2\text{H}_5)_3\text{Pb}$ .

The Antoine equation can also be used to calculate the heat of vaporization quite precisely, as will be shown below.

Although the Antoine equation is certainly a most satisfactory three-constant vapor-pressure equation for interpolation purposes, it can not be extrapolated above a reduced temperature ( $T_R$ ) of about 0.85 without serious error. However, two Antoine equations, one up to  $T_R = 0.8$  or 0.85 and the other from  $T_R = 0.8$  to  $T_R = 1.0$ , preferably through the critical point and contacting the low-range equation at  $T_R = 0.8$ , are usually perfectly adequate to cover the entire liquid range.

As has been described above, Cox showed that for all the compounds tested, his quantity,  $A_{\text{Cox}} = T \log P$  (atm.)/( $T - T_B$ ), gradually decreases with increasing temperature with a minimum at  $T_R = (F + 1)/2$  (about 0.925 for most hydrocarbons), then increases until at the critical point the value of  $A$  equals the values at  $T_R = F$  (about 0.85). It is easily shown that if the vapor pressures follow an Antoine equation, then for  $P$  in atmospheres:

$$A_{\text{Cox}} = A_{\text{Antoine}} (T/(t + C)) \quad (34)$$

Since this equation can never have a minimum, it follows that the Antoine equation cannot possibly fit from low temperatures right up to the critical.

TABLE 1

Comparison of Antoine and Cox equations, using S. Young's data (58) for *n*-pentane

P	LOG P	BOILING POINT				
		Young	Antoine equation		Cox equation	
		t	t	Difference	t	Difference
mm.		°C.	°C.	°C.	°C.	°C.
11	1.0414	-49.4	-49.2	+0.2	-49.2	+0.2
15	1.1761	-44.9	-44.8	+0.1	-44.8	+0.1
30	1.4771	-34.2	-34.2	0.0	-34.2	0.0
50	1.6990	-25.6	-25.6	0.0	-25.6	0.0
100	2.0	-12.7	-12.8	-0.1	-12.7	0.0
199.5	2.3	+1.7	+1.8	+0.1	+1.8	+0.1
398.1	2.6	18.3	18.3	0.0	18.3	0.0
760	2.880	36.1	36.1	0.0	36.1	0.0
1000	3.0	44.4	44.4	0.0	44.4	0.0
1995	3.3	67.9	67.8	-0.1	67.8	-0.1
3981	3.6	95.6	95.6	-0.1	95.4	-0.2
6310	3.8	116.8	116.9	+0.1	116.7	-0.1
10000	4.0	140.7	(141.3)	(+0.6)	140.6	-0.1
15850	4.2	167.2	(169.4)	(+2.2)	167.4	+0.2
19950	4.3	181.8	(185.1)	(+3.3)	181.9	+0.1
25100	4.3997	197.2	(202.0)	(+4.8)	197.2	0.0

However, the Antoine equation is as good an approximation as Cox's empirical parabolic relation up to about  $T_R = 0.85$ . This is illustrated in table 1, which is based on S. Young's (58) best selected values for the boiling points of *n*-pentane at various pressures. (These data are further discussed in a later section.) The Antoine equation used:

$$\log P \text{ (mm.)} = 6.8723 - 1078.4/(t + 234.1) \quad (35)$$

fits the data to well within the reported accuracy up to  $T_R = 0.83$  (about 117°C.), but gives increasingly larger errors from this temperature to the critical. On the other hand, the fit of the following Cox-type equation:

$$\log \frac{P}{760} = A \left( 1 - \frac{T_B}{T} \right) \quad (26)$$

where  $\log A = 0.64673 + 0.1817(1 - T_R)(0.865 - T_R)$ , and  $(37)$

$$T_B = 309.1748^\circ\text{K.}, \quad T_c = 470.3^\circ\text{K.}, \quad T_R = T/T_c$$

is not only almost as good as the fit of the Antoine equation up to  $T_R = 0.83$ , but this goodness of fit persists right up to the critical point.

From a practical point of view it is much more convenient to use two Antoine equations over the entire liquid range rather than the Cox equation. For example, the upper-range equation:

$$\log P = 7.5287 - 1562/(t + 244) \quad (38)$$

provides an excellent fit to  $\pm 0.1^\circ\text{C.}$  for the pentane data from  $100^\circ\text{C.}$  ( $T_R = 0.79$ ) to the critical point. One great advantage of the Antoine equation over equations of a more complex nature, such as the Cox equation, is the ease with which the temperature may be computed from the pressure, without the necessity of a trial-and-error solution.

The Antoine equation does not fit highly precise vapor-pressure data exactly over a large temperature range. The discrepancies are small but appear to be somewhat periodic in nature. Since similar systematic errors have been noted for other three-constant vapor-pressure equations, the author believes that no three-constant equation can adequately and accurately represent the true and complex vapor pressure-temperature relation. It is possible that a major improvement to the goodness of fit of the Antoine equation for these highly precise data, at least for  $T_R$  less than 0.75, could be obtained by a careful study of the deviations from the Antoine equation and the subsequent derivation of a five-constant equation. This problem is outside the scope of the present paper.

## VI. DETERMINATION OF CONSTANTS IN THE ANTOINE EQUATION

The determination of the best values of the constants in empirical equations is a tedious and time-consuming task. Although the methods described below for the Antoine equation are believed to be the most satisfactory available, they still require a considerable amount of time, even for a small set of data. Similar methods may be derived for other simple empirical equations. The three commonest methods of curve fitting—selected-point, graphical, and least-squares—are discussed in order.

### A. Selected-point method

In the selected-point method, three widely spaced and apparently good points are picked from the data and used to set up three simultaneous equations, which are solved for  $A$ ,  $B$ , and  $C$ . If required, the points may well be selected by making a trial plot of  $\log P$  against  $1/(t + 230)$ . Convenient formulas for performing this procedure are shown below. Let

$$y = \log P$$

and use subscripts to denote the three separate points; then we can solve for  $C$ ,  $B$ , and  $A$  in that order, as follows:

$$\frac{y_3 - y_2}{y_2 - y_1} \cdot \frac{t_2 - t_1}{t_3 - t_2} = 1 - \frac{t_3 - t_1}{t_3 + C} \quad (39)$$

$$B = \frac{y_3 - y_1}{t_3 - t_1} (t_1 + C)(t_3 + C) \quad (40)$$

$$A = y_2 + B/(t_2 + C) \quad (41)$$

The great disadvantage of the selected-point method is that it neglects a major and valuable portion of the data, and an examination of the deviations of the calculated values from the observed may well show that the wrong three points were chosen.

#### *B(1). Rapid graphical method*

The rapid method of obtaining the constants in the Antoine equation, which is described below, has been under development by the author for several years. It has proved to be very useful for rapid interpolations and extrapolations, and the results obtained are usually almost as good as those obtained by more elaborate least-squares methods.

*Estimation of  $C$ :* For many purposes  $C$  can be assumed to be about 230°C. or 382°F., but since an incorrect value of  $C$  will cause a systematic error in the application of the equation, it is often desirable to have some way of estimating it. Least-squares studies have shown that the fit is not too dependent on the value of  $C$  used, so for most practical purposes  $C$  need only be obtained to 5° or even 10°C.

Frequently some points of the data are known to a higher degree of precision than others, so that at the start we can assume that one of these points is free from error. This point will be denoted by  $t_0, P_0$ . Since it is assumed that this point fits the Antoine equation perfectly, then:

$$y_0 = \log P_0 = A - B/(t_0 + C) \quad (42)$$

It is easily shown that:

$$\frac{y - y_0}{t - t_0} = \frac{A}{t_0 + C} - \frac{y}{t_0 + C} \quad (43)$$

and

$$\frac{t - t_0}{y - y_0} = \frac{C}{A - y_0} + \frac{t}{A - y_0} \quad (44)$$

Either of these equations may be used to evaluate  $C$ . A plot of  $(y - y_0)/(t - t_0)$  vs.  $y$  is linear if the Antoine equation holds. The value of  $C$  is obtained from the slope, since

$$\frac{dy}{d\left(\frac{y - y_0}{t - t_0}\right)} = -(t_0 + C) \quad (45)$$

Similarly, using equation 44, the ratio of the intercept of the best straight line through  $(t - t_0)/(y - y_0)$  vs.  $t$  to the slope gives the value of  $C$ .

It is usually desirable to plot "uncertainty bands" instead of points in applying equations 43 and 44. The uncertainty band is obtained by using the extreme uncertainties in  $t$  and  $P$  to obtain limits for each ratio, such as  $(y - y_0)/(t - t_0)$ . For example, suppose we have the following data:  $P$  is reported to be accurate to the nearest 0.1 mm., and  $t$  to the nearest 0.1°C.  $P_0, t_0$  is taken to be exact.

$$\begin{array}{ll} P_0 = 760 \text{ mm.} & t_0 = 80.0^\circ\text{C.} \\ P = 50 \text{ mm.,} & t = 11.8^\circ\text{C.,} \\ \text{etc.} & \text{etc.} \end{array}$$

Let us consider the maximum value of  $(y - y_0)/(t - t_0)$  for this first point.

$$\frac{y - y_0}{t - t_0} = \frac{\log 49.9 - \log 760}{11.9 - 80.0} = 0.01737$$

Similarly, the minimum value is 0.01729. The straight line or band connecting these points is plotted with the abscissa of  $\log 50 = 1.699$ . Similar bands are plotted for the other  $P, t$  points. The uncertainty in the ratios and the corresponding width of the bands increases as  $t$  approaches  $t_0$ .

The best straight line through these bands is drawn by eye, and gives the value of  $C$ , which should be rounded off to the nearest unit. It is interesting to note that by drawing the two extreme lines on the plot which will pass through most of the bands we can obtain the extreme values of  $C$  which will "fit" the data within the expected uncertainty.

The value of  $C$  so obtained may be checked by repeating the calculation with a new base point. This is usually not necessary, since the uncertainty in  $C$  is normally large enough to mask minor errors in  $t_0$  and  $P_0$ .

*Estimation of A and B:* Once a good value of  $C$  has been obtained, several methods are available for estimating the values of  $A$  and  $B$ .

The first method does not require much time and is particularly useful when considerable faith can be put in the base point. For each point,  $B$  is computed using the relation:

$$B = \left( \frac{y - y_0}{t - t_0} \right) (t + C)(t_0 + C) \quad (46)$$

Since  $(y - y_0)/(t - t_0)$ , or its reciprocal, has already been calculated and  $(t_0 + C)$  is a constant, this calculation presents no difficulties. If  $B$  systematically increases with temperature, the value of  $C$  chosen is too small and a larger value should be taken. The  $B$  value obtained should be averaged, omitting obviously bad points, and then rounded, usually to the nearest unit. The value of  $A$  is conveniently obtained from the base point, using the same equation as for point 2 in the selected-point method.

The second method is considered to be a rapid and superior variation of the familiar scheme of plotting deviations from a reference line drawn through the

data when  $\log P$  is plotted against  $1/(t + C)$ . A preliminary estimate of  $B$  is obtained in any convenient way, as by the application of equation 46 to a point of the data. Let this value be denoted by  $B_1$ . The value of  $A_1$  is calculated for each point, using the following equation:

$$A_1 = y + \frac{B_1}{t + C} \quad (47)$$

If  $A$ ,  $B$ , and  $C$  denote the final values of the constants we are seeking, then

$$A_1 = B_1 \frac{A}{B} + \frac{B - B_1}{B} y \quad (48)$$

or

$$A_1 = \alpha + \beta y$$

If  $\alpha$  and  $\beta$  are the best values of the intercept and slope of the straight line obtained when  $A_1$  is plotted against  $y$  (or, conveniently  $A_1$  vs.  $P$  on semi-log paper) then  $B$  can be obtained from the equation

$$B = B_1/(1 - \beta) \quad (49)$$

This value of  $B$  may be conveniently rounded off, and the rounded value is used in equation to give  $A$ .

$$A = \alpha B/B_1 \quad (50)$$

### *B(2). Example of graphical method*

As an example of the method which has just been presented, the Antoine equation will be calculated for methylocyclopentane, using seven points from the data of Max Schmitt (46). The serial numbers in table 2 refer to the original data. Point No. 15 was chosen as the base point, since it was believed that the precision of measuring the temperature and pressure is somewhat greater at the higher temperatures.

A graph of  $(t_0 - t)/(y_0 - y)$  against  $t$  shows that a reasonable fit to the values can be obtained by drawing a line through the two points, No. 1 and No. 13. The equation of the line is

$$\frac{t_0 - t}{y_0 - y} = 58.020 + 0.25189 t$$

$C$  is obtained from the slope and intercept and equals  $58.020/0.25189 = 230.3$ . This can be safely rounded to 230.

The provisional value  $B_1$  is then calculated according to equation 46, using the data for either of the two end points (Nos. 1 and 13).

$$B_1 = (230 - 16.00)(230 + 76.65)/53.99 = 1215.5 \text{ and}$$

$$B_1 = (230 + 65.90)(230 + 76.65)/74.62 = 1216.0$$

$A_1$  is now calculated for each point according to equation 47, using  $C = 230$  and  $B_1 = 1216$ , and the values obtained are plotted against  $P$  on semi-log paper

(figure 1). The bands shown correspond to the same uncertainty limits as before ( $\pm 0.2$  mm. in  $P$ ,  $\pm 0.02^\circ$  in  $t$ ). It is obvious that the value of  $B$  has been judiciously chosen, since there is no marked trend of the  $A_1$  values with  $P$ . The

TABLE 2  
*Calculation by rapid graphical method*

No.	$t$	$P$	$y$	$t_0 - t$	$y_0 - y$	$\frac{t_0 - t}{y_0 - y}$
	$^\circ\text{C.}$	$\text{mm.}$				
1	-16.00	16.8	1.22531	92.65	1.71595	$53.99 \pm 0.18^*$
2	0.00	41.8	1.62118	76.65	1.32008	$58.06 \pm 0.11$
4	19.80	109.3	2.03862	56.85	0.90262	$62.98 \pm 0.08$
8	38.45	238.3	2.37712	38.20	0.56414	$67.71 \pm 0.08$
11	50.23	369.9	2.56808	26.42	0.37318	$70.80 \pm 0.10$
13	65.90	626.9	2.79720	10.75	0.14406	$74.62 \pm 0.22$
15	76.65	873.5	2.94126	0.00	0.00000	Indeterminate

\* Uncertainty bands corresponding to the arbitrary, reasonable values  $\pm 0.02^\circ$  in  $t$  and  $\pm 0.2$  mm. in  $P$ .

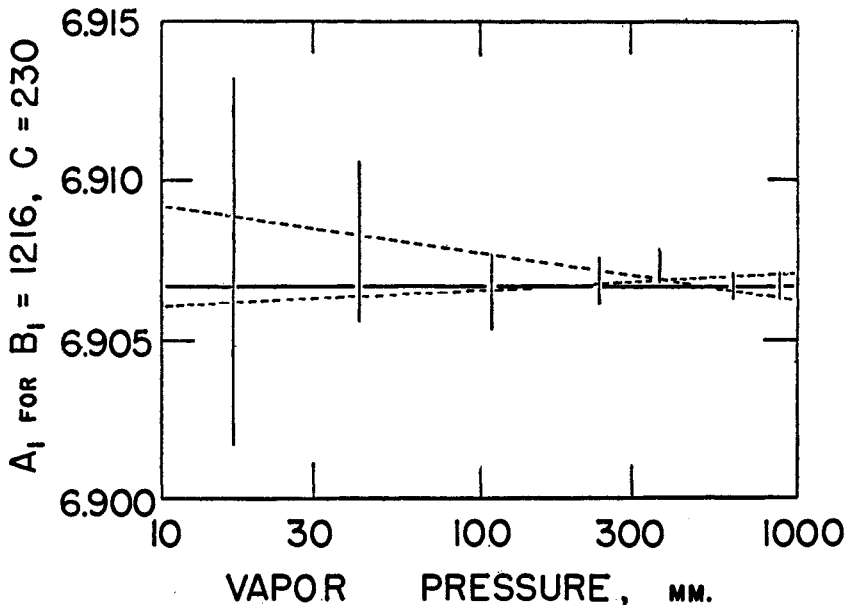


FIG. 1. Graphical determination of  $A$  and  $B$

two broken lines shown in figure 1 represent the extreme values of  $\alpha$  and  $\beta$ , and hence of  $A$  and  $B$ , which fit the data. Their equations are:

$$A_1 = 6.91067 - 0.00147y \text{ and} \quad (51a)$$

$$A_1 = 6.90560 + 0.00050y \quad (51b)$$



whence from equation 51a  $B = 1214.2$ ,  $A = 6.90044$ ; and from equation 51b  $B = 1216.6$ ,  $A = 6.90901$ . The solid line represents a good compromise between these, with the value of  $B$  again rounded off to 1216. It corresponds to  $\beta = 0$  and  $\alpha = A = 6.90669$ , so that the final equation is:

$$\log P = 6.90669 - 1216/(t + 230) \quad (52)$$

The fit is well within the reported precision with one somewhat poor point at 50.23°C. This example is only suitable for illustrative purposes, since but seven of the fifteen experimental points have been used. Actually, the fit is just as good for the other eight.

An alternative and equally suitable plan is to obtain  $A$  first, rather than  $B$ . After obtaining  $C$  by the procedure outlined above, a preliminary value of  $A$  (denoted by  $A_2$ ) is obtained by applying equation 47 to any convenient point of

TABLE 3  
*Comparison of results by rapid graphical method*

NO.	$t$			$P$		
	Observed	Calculated	Deviation	Observed	Calculated	Deviation
	°C.	°C.	°C.	mm.	mm.	mm.
1	-16.00	-15.97	+0.03	16.8	16.8	0
2	0.00	0.06	+0.06	41.8	41.7	-0.1
4	19.80	19.79	-0.01	109.3	109.3	0
8	38.45	38.46	+0.01	238.3	238.2	-0.1
11	50.23	50.27	+0.04	369.9	369.3	-0.6
13	65.90	65.90	0	626.9	626.9	0
15	76.65	76.65	0	873.5	873.5	0

the data preferably not close to the base point.  $B_2$  is then calculated for each point of the data, using

$$B_2 = (t + C)(A_2 - y) \quad (53)$$

and the values are plotted against  $t$  or  $t + C$ . It is easily shown that  $A$  and  $B$ , the final values of the constants we are seeking, are related to the preliminary values by the equation:

$$B_2 = B - (A_2 - A)(t + C) \quad (54)$$

and are, accordingly, readily obtained from the slope and intercept of the best line through the plotted values of  $B_2$  and  $t + C$ .

It should be noted that these methods make no assumption as to the nature of the errors, whether in  $t$  or  $P$  or both. If  $t$  were given free from error, then only uncertainties in  $P$  should be considered for the bands. Similarly, if  $P$  were given free from error.

*Empirical estimation of C:* It would be very desirable if a general correlation of the value of  $C$  with some common physical property of the compound could be obtained. Such a correlation has eluded the author, but the following *approxi-*

*mate* rules have proved of utility, since they predict  $C$  to within  $20^{\circ}$  C. in most instances.

*Rule 1:* For hydrocarbons with  $n$  carbon atoms,

$$C = 271 - 7.6n \quad (55)$$

*Rule 2:* For elements with monatomic vapors and also for substances boiling below  $-150^{\circ}$ C.,

$$C = 264 - 0.034t_B \quad (56)$$

where  $t_B$  is the normal boiling point in  $^{\circ}$ C.

*Rule 3:* For all other compounds,

$$C = 240 - 0.19t_B \quad (57)$$

It is better, however, to determine the value of  $C$  from the data, even if they are not very reliable, since an incorrect value of  $C$  will cause an undesirable systematic error in the application of the equation.

#### *C. Determination of constants by method of least squares*

For very precise vapor-pressure data a better fit may be desired than the one obtained by the graphical method. This can be accomplished by the method of least squares. Unfortunately, although the method provides the most exact way of treating vapor-pressure data, the labor of computation is considerable even with an automatic calculator, and the method often cannot be applied rigorously because of the incomplete information accompanying the data. It is therefore usually not worth the time and trouble to apply least squares, since for most purposes just as satisfactory a solution for the constants can be obtained by the graphical method previously described.

The theory and computational details of least-squares procedures are very clearly and completely set forth in *Statistical Adjustment of Data*<sup>3</sup> by W. Edwards Deming, a revision of his earlier treatise, *Some Notes on Least Squares*. It is therefore not proposed to give a worked-out example of the application to the Antoine equation in detail,<sup>4</sup> although it is of pertinent interest to point out some of the advantages of such least-squares solutions in general.

Least squares may be considered to be based on three assumptions: (1) that the given type of equation is a true representation of the observations, (2) that the observations differ from the "true" values only by random or fortuitous errors, and (3) that these errors are normally distributed. If the degree of error differs from point to point, because of the experimental conditions, a system of weighting has to be imposed on the data. This system has to be based on the methods by which the data were obtained.

Least squares provides a very satisfactory method of curve fitting which gives reliable values of the empirical constants regardless of the form in which the

<sup>3</sup> Published by John Wiley and Sons, Inc., New York (1943).

<sup>4</sup> Such a worked-out example, including a "cookbook" procedure for applying least squares to vapor-pressure equations, may be obtained from the author.

equation is handled. The results are unique since, once the principles are established, the method always gives the same final results.

Least squares also provides a method of adjusting the data to obtain the most probable values of the observational points, subject to the conditions which are imposed on the data. This process of adjustment may be considered as the determination of the most probable values of the residuals (experimental errors) by which the observed values differ from the true relation which we are seeking.

The method also provides a means of measuring the precision of the data, as measured by the goodness of fit, and also the precision of the values of the empirical constants obtained. Another convenient result is the precision (in terms of standard deviation and confidence limits) of the calculated values of either variable. We cannot assign a probability interpretation to values of the empirical constants or to measures of the variability of the data, if the method of least squares is not used.

It is to be noted that although the method of least squares, like any other mathematical treatment for fitting the equation to a single set of data, cannot detect systematic errors, a measure of the precision of a given set of data permits a comparison with the results of other sets of data on the same compound. This comparison does provide a means of determining systematic errors which is similar to the analysis of variance widely used in statistical work.

#### *D. Systematic errors*

Before leaving the subject of curve fitting it is well to point out that none of the curve-fitting procedures described can detect most kinds of systematic errors. An exception is the detection of the presence of inert gas in measurements of vapor pressures over a wide pressure range (11). If precise results cannot be fitted to an Antoine equation because of systematically increasing deviations at the lower pressures, the presence of inert gas should be suspected. A convenient mathematical treatment of the data is as follows: Take a suitable base point near the top of the temperature range involved (but not more than  $T_R = 0.75$  to  $0.80$ , the upper limit of the range of applicability of the Antoine equation) and calculate a preliminary Antoine equation, by the graphical method, for the high-temperature data. Extrapolate to the lower temperatures and estimate the partial pressure of the inert gas from the deviations at the lowest pressures. This partial pressure should be subtracted from the vapor pressures, making allowance for the expansion of the inert gas with temperature. Two further trials using the successively corrected vapor pressures should remove the systematic trend. Table 4 shows the results of the first and last corrections for a group of nine vapor-pressure measurements on hexamethylethane (11). The final adjusted values show a very high precision indeed.

### VII. COMBINATION OF SETS OF VAPOR-PRESSURE DATA

#### *A. Procedure*

If the data of two or more reputable observers on the same compound disagree, then one or both sets are in error and should be discarded. Unfortunately these

sets may be the only available information and a compromise equation is desirable until more reliable data are obtained. The procedure below for obtaining a compromise equation is a reasonable one, based on the fact that the presence of small amounts of impurities has but little effect on the heat of vaporization and hence affects the  $B$  constant of the Antoine equation but slightly. The same  $C$  constant is assumed to apply to all the sets, so that the burden of the systematic error falls on the  $A$  constant. In view of the fact that the sets of data are discrepant, the least-squares procedure is not applicable and a modification of the graphical method described above will be employed.

TABLE 4  
*Correction of systematic error due to inert gas*

$t$ °C.	OBSERVED	CALCULATED <sup>a</sup>	DEVIATION	FIRST COR- RECTION <sup>b</sup>	CORRECTED <sup>c</sup>	CORRECTED <sup>d</sup>	CALCU- LATED <sup>e</sup>	DEVIATION <sup>f</sup>
4.89	7.0	6.0	-1.0	1.0	6.0	5.6	5.6	0.0
10.38	9.5	8.6	-0.9	1.0	8.5	8.1	8.2	+0.1
20.90	17.4	16.7	-0.7	1.0	16.4	15.9	16.0	+0.1
34.90	37.7	37.2	-0.5	1.1	36.6	36.2	36.1	-0.1
44.88	62.9	62.6	-0.3	1.1	61.8	61.2	61.3	0.0
59.97	128.7 <sub>5</sub>	128.7 <sub>7</sub>	0.0	1.2	127.55	127.0 <sub>5</sub>	127.0	0.0
79.96	300.6	300.7	+0.1	1.2	299.4	298.8	298.8	0.0
95.00	531.9	531.8 <sub>5</sub>	0.0	1.3	530.6	530.1	530.1	0.0
98.98	613.2	613.2	0.0	1.3	611.9	611.3	611.4	+0.1

<sup>a</sup> Calculated from the Antoine equation through the four highest points:

$$\log P = 7.8960 - 1701/(t + 234)$$

<sup>b</sup> First correction, by assuming 1 mm. at 10° or 0.00357 mm.

<sup>c</sup> First corrected values, by subtracting 0.00357 mm. from observed values.

<sup>d</sup> Last corrected values, by subtracting 0.00507 mm. from observed values.

<sup>e</sup> Calculated from the final Antoine equation through the corrected values:

$$\log P = 7.78882 - 1625.7/(t + 226)$$

<sup>f</sup> Deviation from final Antoine equation of the final corrected values.

The procedure is first to find an average Antoine  $C$  value using the graphical method on each set of data. A rough equation using this  $C$  and any convenient  $A$  and  $B$  is then used with each set for computing deviations in  $\log P$  (as uncertainty bands), which are plotted against  $1/(t + C)$ , preferably on separate sheets to avoid confusion. The best values of  $B$  and their probable outside limits as judged by eye are then inspected and a suitable average value is chosen. The averaging of  $B$  and  $C$  is a purely arbitrary process, since the data possess unknown systematic errors which invalidate the usual statistical procedures. It is suggested that approximate weights be assigned on the basis of the goodness of fit of the line and perhaps the repute of the observer. The value of  $A$  can be obtained from a reliable boiling point, or from a suitable average point of the data.

*B. Application to data for carbon disulfide*

These principles are illustrated by application to the vapor-pressure data on carbon disulfide.

The precise data of Zmaczynski (59) over the range 30° to 85°C. were treated by least squares in a separate study and the following equation was found to fit the values to within about 0.003°C.:

$$\log P = 7.02814 - 1219.68/(t + 247.826)$$

H. von Siemens (47) made six determinations between -78° and 46°. These give a *C* value around 244, in excellent agreement with the 248 obtained for the

TABLE 5  
*Vapor pressure of carbon disulfide*

<i>t</i>	<i>P</i>			SOURCE
	Observed	Calculated	Deviation	
°C.	mm.	mm.	mm.	
29.942	433.6	432.9	+0.7	Four points from Zmaczynski data (59)
46.262	760.0	760.0	0.0	
62.925	1268.1	1269.9	-1.8	
85.646	2347.4	2353.2	-5.8	
-78.19	0.68	0.65	+0.03	H. von Siemens (47)
-42.59	11.81	11.89	-0.08	
-21.52	42.69	42.93	-0.24	
0.00	127.00	127.15	-0.15	
19.67	294.27	293.16	+1.11	
46.25	760.00	759.70	+0.30	
-25.35	34.3	34.7	-0.4	Henning and Stock (25)
0.0	127.25	127.15	+0.1	
11.34	211.3	210.7	+0.6	
0.32	128.5	128.8	-0.3	M. Roland (44)
15.0	243.0	243.1	-0.1	
15.5	247.8	248.1	-0.3	N. L. Joukovsky (26)
18.0	274.6	274.4	+0.2	
19.3	290.1	288.9	+0.1	
20.5	303.1	302.9	+0.2	
22.8	331.1	331.2	-0.1	
24.3	350.3	350.7	-0.4	

Zmaczynski data. An average *C* value of 246 has been taken accordingly. These two sets of data are the only ones extensive enough to give reliable values of *C* and *B*. Using *C* = 246, we obtain values of *B* of 1205.5 from the Zmaczynski data and about 1211 from the von Siemens data. An average value of 1208

is taken and, together with the good boiling point of Zmaczynski (46.262), gives the final compromise equation:

$$\log P = 7.01409 - 1208/(t + 246) \quad (59)$$

The values from this equation are compared in table 5, not only with the data above but also with other data which were not extensive enough to provide good values of  $B$  and  $C$ . The compromise equation is seen to be a good representation of the data from  $-78^\circ$  to  $85^\circ$ .

### C. Extrapolation to the critical point

By and large, the combination of sets of data requires not only a good deal of judgment but also a special technique for almost every problem handled, although the basic principles remain the same. As an example of such a special method which is very useful on occasion, details are given of the extrapolation of data taken at a lower temperature to the critical point, which is known. Strictly speaking, the Antoine equation provides a reliable fit only up to a reduced temperature of about 0.80, but the error is not serious at the upper range, especially when the equation passes through the critical point. For this type of calculation the deviations caused by this somewhat unwarranted use of the Antoine equation are of a secondary nature compared with the other uncertainties involved.

Suppose that we need an equation from  $85^\circ\text{C.}$  to the critical for carbon disulfide. For the moment we shall ignore the fact that there are data available in this range and simply use the information that the critical point is at  $273^\circ\text{C.}$ , 75 atm.

A reasonable approach to the problem is to make the equation pass through the critical point and through a second point calculated from the known low-range equation at the highest temperature of the available data, and to have the slopes ( $dP/dt$ ) equal at this second point. This gives three conditions enabling the three unknown Antoine constants to be determined.

Let  $A, B, C$  be the constants of the Antoine equation sought, and let  $A', B', C'$  be the constants of the known equation fitted to the low-range data. Also let  $t_1, P_1$  be the highest temperature and calculated pressure of the low-range data and let  $t_c, P_c$  be the critical temperature and pressure. As above, let  $y = \log P$ .

The conditions can be stated as

$$A' - \frac{B'}{t_1 + C'} = y_1 = A - \frac{B}{t_1 + C} \quad (60)$$

$$\log P_c = y_c = A - \frac{B}{t_c + C} \quad (61)$$

$$\frac{B'}{(t_1 + C')^2} = \frac{B}{(t_1 + C)^2} \quad (62)$$

First,  $C$  is obtained from the equation:

$$\frac{B'}{(t_1 + C')^2} \cdot \frac{t_c - t_1}{y_c - y_1} = 1 + \frac{t_c - t_1}{t_1 + C'} \quad (63)$$

then  $B$  from the relation:

$$B = \frac{y_c - y_1}{t_c - t_1} \cdot (t_1 + C)(t_c + C) \quad (64)$$

and  $A$  from equation 60, checked by the value from equation 61.

In the carbon disulfide example,  $A' = 7.01409$ ,  $B' = 1208$ , and  $C' = 246$ ;  $t_1 = 85^\circ$  and  $\log P_1$  (mm.) = 3.36454;  $t_c = 273^\circ$  and  $\log P_c$  (mm.) = 4.75587.

The following equation is obtained after suitable rounding of the constants:

$$\log P \text{ (atm.)} = 4.7253 - 1633/(t + 300) \quad (65)$$

TABLE 6  
*Example of extrapolation to the critical point*

$t$	$P$		
	I.C.T.	Equation 65	Deviation
$^\circ\text{C.}$	<i>atm.</i>	<i>atm.</i>	<i>atm.</i>
100	4.42	4.39	-0.03
150	12.4	12.49	+0.09
200	28.3	28.8	+0.5
230	43.4	44.1	+0.7
260	64.1	64.5	+0.5
273 (critical)	75	75.0 <sub>s</sub>	0.0

A comparison with six points from the high-temperature data correlated in the *International Critical Tables* is shown in table 6. When it is recalled that equation 65 was derived from only the critical point and an extrapolation above  $85^\circ$  of a compromise equation and that the *International Critical Tables* lists twelve references as the basis for their correlation, the agreement is surprisingly good.

#### VIII. ANTOINE EQUATIONS DEVELOPED FOR CERTAIN VAPOR-PRESSURE DATA FROM THE LITERATURE

##### *A. General considerations*

In the course of this investigation over sixty Antoine equations have been derived. These range from approximate equations based on scanty data to careful least-squares studies on data of high precision. Many of them were obtained by earlier methods which are inferior to the direct ones outlined above. However, all provide a reasonable fit to the experimental values and, except for some highly precise data, most of them fit within a plausible estimate of the experimental error.

At this point, it should be noted that most experimenters have a higher

opinion of the accuracy and reproducibility of their measurements than critical examination justifies. Even for a well-known compound like benzene, the discrepancies between competent observers are startling. The vapor pressure at 80°C. has been reported as 750 (Kahlbaum (27)), 751.86 (Regnault (43)), 753.62 (Young (56)), 755.0 (Young (57)), 756.4 (Schmitt (46)), 756.44 (Dejardin (18)), 757.12 (Zmaczynski (59)), 575.5 (Smith and Menzies (48)), 757.72 (E. R. Smith (50)), 757.80 (Smith and Matheson (51)), 759.7 (Nagornov (36)), 760 (Neubeck (39)), 764.5 (Mangold (33)), and 773.64 (Woringer (55))! Obviously several types of errors must be responsible, although it is usually impossible to assign a definite cause for even a large difference, when the work has been apparently carefully carried out. In the light of such discrepancies we should not take equations developed from the data of even reputable observers too seriously. The best we can do is to treat each set as carefully as possible, so that the equation developed represents a reasonable smoothing of the observer's values without the introduction of systematic bias from the equation employed.

In considering the goodness of fit of an empirical equation the nature of the residuals is as important as their magnitude. Bowing of the data, caused by the values being high in the ends but low in the middle or *vice versa*, is especially undesirable, since such a condition causes large errors in extrapolation. Every effort has been made to avoid bowing in the equations which have been developed.

Comparisons of the Antoine equation with the familiar  $1/T$  form and with some of the other equations given in the literature are now presented for several representative compounds, followed by a tabulation of some of the Antoine equations which have been obtained during this investigation.

#### B. Comparison of Antoine and $1/T$ equations

It is not necessary to make extensive comparisons of the Antoine equation and the  $1/T$  form, since it is evident that if vapor-pressure data are satisfactorily fitted by the Antoine equation, as is shown above, then the use of the  $1/T$  equation will lead to systematic errors, unless the Antoine equation happens to have  $C$  equal to, or close to, 273. The examples were chosen to illustrate cases where  $C$  was close to 273 and quite far from it.

*Isobutene:* The recent data by Beattie, Ingersoll, and Stockmeyer (5) on isobutene enable a comparison to be made of their published " $1/T$  form" vapor-pressure equation and an Antoine equation derived from the experimental values (see table 7). The latter equation was obtained graphically and is a better fit than their equation, not only from the viewpoint of the smaller magnitude of the residuals, but also in that the Antoine residuals do not show the systematic bowing which is so markedly evident in the residuals from their  $1/T$  equation.

*International Critical Tables equations:* The I.C.T. employs the  $1/T$  equation as an interpolation equation for many of its vapor-pressure data of lower precision. The form used, in their notation, is as follows:

$$\log P = \frac{0.05223A}{t + 273.1} + B \quad (66)$$



where  $A$  = average heat of vaporization in joules per gram-mole and  $B$  = constant (similar to the usual  $A$  of the Antoine formula). A few comparisons will be made of this equation and the Antoine equation, where the original data are readily available.

TABLE 7  
*Vapor pressure of isobutene*

$t$	$P$	RESIDUALS IN $P$	
		$1/T^*$	Antoine†
°C.	atm.	atm.	atm.
0	1.301	-0.007	+0.001
30	3.444	-0.009	-0.005
50	5.976	+0.010	+0.008
75	10.86	+0.04	+0.03
100	18.08	-0.04	-0.03
125	28.41	-0.03	+0.03

\* Published equation:  $\log P = 4.37592 - 1163.34/(t + 273.13)$ .

† Antoine equation:  $\log P = 4.32423 - 1128.4/(t + 268)$ .

TABLE 8  
*Methyl ether*

OBSERVED		RESIDUALS, OBSERVED - CALCULATED		
$t$	$P$	I.C.T.	Antoine	
°C.	mm.	mm.	mm.	°C.
-66.9	77.7	+0.5	-0.2	0.0
-63.8	95.2	+1.0	0.0	0.0
-60.0	119.6	+0.3	-1.1	+0.2
-52.4	189.2	+2.6	0.0	0.0
-46.6	261.7	+4.4	+0.7	-0.1
-41.4	326.2	-12.4	(-16.9)	(+1.0)
-37.3	426.6	+9.8	+4.7	-0.2
-30.9	524.0	-44.4	(-50.0)	(+1.9)
-28.5	639.4	+3.5	-2.0	+0.1
-27.2	679.2	+4.1	-1.4	+0.1
-26.3	711.5	+8.1	+2.7	-0.1
-25.3	745.0	+9.0	+3.8	-0.1
-24.1	781.7	+4.9	0.0	0.0

*Methyl ether*: The I.C.T. equation is:

$$\log P \text{ (mm.)} = 7.720 - 1202.6/(t + 273.1)$$

The experimental values (31) used to determine the equation and the goodness of fit of the Antoine equation:

$$\log P \text{ (mm.)} = 7.4119 - 1066/(t + 260)$$

are shown in table 8. It should be noted that the temperature measurements are evidently the controlling factor in the measurements, since 0.1°C. corre-

sponds to from 0.5 mm. (at  $-67^{\circ}\text{C}.$ ) to 3.4 mm. (at  $-24^{\circ}\text{C}.$ ). The temperatures are reported to the nearest tenth of a degree and, except for the two bad points, the Antoine equation gives a satisfactory fit to within  $\pm 0.2^{\circ}\text{C}.$  The poorer fit of the I.C.T. equation is caused not so much by the incorrect choice of the value of  $C$ , since the data are not sufficiently precise enough to determine  $C$  accurately, but rather by poor judgment in fitting the  $1/T$  equation. Probably too much weight was given to the two bad points.

*Lead chloride and bromide:* A comprehensive study of the literature on the vapor pressure of these compounds was made in this Laboratory in 1941 and showed that the following equations fit the data to within the experimental error:

$$\text{PbCl}_2: \log P \text{ (mm.)} = 7.212 - 4340/(t + 48)$$

$$\text{PbBr}_2: \log P \text{ (mm.)} = 7.233 - 4400/(t + 95)$$

TABLE 9  
Vapor pressure of lead chloride and of lead bromide

t °C.	P (PbCl <sub>2</sub> )			P (PbBr <sub>2</sub> )		
	I.C.T.	Antoine	Deviation	I.C.T.	Antoine	Deviation
	mm.	mm.	per cent	mm.	mm.	per cent
500	0.24	0.20	+20	1.23	0.69	+78
600	3.0	3.3	-9	10.1	8.0	+26
700	22	26	-15	54	50	+8
800	113	124	-9	209	207	+1
900	440	430	+2	646	647	-0.2
1000	1380	1180	+17	1670	1640	+2

The Antoine  $C$  constants are widely different from 273, so that a considerable discrepancy is to be expected between these values and the I.C.T. equations:

$$\text{PbCl}_2: \log P \text{ (mm.)} = 8.961 - 7411/(t + 273)$$

$$\text{PbBr}_2: \log P \text{ (mm.)} = 8.064 - 6163/(t + 273)$$

The values from the two equations calculated at suitable intervals are shown in table 9, together with the percentage differences between them. Since the Antoine equation curves pass among sixty-three points by five observers (20, 23, 32, 53, 54) for lead chloride and twenty-seven points by three observers (23, 53, 54) for lead bromide, the fit is considered to be entirely adequate and the equations are considered to be a satisfactory representation of the data. The discrepancies of the I.C.T. equations are certainly outside any reasonable estimate of the experimental error.

*Conclusions concerning 1/T equations:* The indiscriminate use of  $1/T$  equations is not recommended. For compounds boiling below room temperature the results may be quite satisfactory, since preliminary studies have indicated that for these compounds the value of  $C$  is usually greater than 250. It is suggested, for such low-boiling compounds, that the  $1/T$  equation be tried and the devi-

ations in  $\log P$  examined by plotting them against  $1/T$ . If a distinct bowing of the points is evident, the use of  $1/T$  is introducing a systematic error and an Antoine equation should be used instead. If, however, no bowing is noticed and the deviations appear to scatter randomly about a straight line, then the  $1/T$  equation is quite satisfactory.

*C. Comparison with Nernst equation, for hydrogen chloride*

The following can be taken as a good example of data of fairly high precision. The authors (Giauque and Wiebe (22)) compared their data with the Nernst equation of Henning and Stock:

$$\log P \text{ (mm.)} = 4.65739 - 905.53/T + 1.75 \log T - 0.005077T$$

The following Antoine equation can be fitted to the data:

$$\log P \text{ (mm.)} = 7.16323 - 743.3/(T - 14.5)$$

TABLE 10  
*Vapor pressure of hydrogen chloride*

OBSERVED		RESIDUAL IN $t$		RESIDUAL IN $P$	
$T$	$P$	Antoine	Nernst	Antoine	Nernst
$^{\circ}\text{K.}$	$\text{mm.}$				
158.91	103.71	+0.01	-0.02	-0.06	+0.14
164.62	162.9	0.00	-0.03	0.00	+0.3
169.28	229.8	-0.01	-0.03	+0.2	+0.5
173.95	317.1	+0.01	0.00	-0.3	-0.1
178.53	428.1	+0.01	+0.01	-0.2	-0.2
181.84	526.4	0.00	0.00	-0.1	-0.1
185.17	643.4	-0.02	-0.01	+0.6	+0.5
188.41	774.8	0.00	0.00	0	+0.1
191.96	943.9	-0.01	-0.02	+0.5	+1.1
195.93	1165.1	0.00	-0.02	+0.1	+1.8

The goodness of fit of both equations is shown in table 10. The residuals are computed, as usual, by subtracting the calculated value from the observed. In these measurements the temperature has evidently a greater effect on the precision than the pressure. The Nernst equation shows more bowing than the Antoine, so is much less safe for extrapolation. For example, on extrapolation to the critical pressure (81.55 atm., a fortyfold change in pressure), the Antoine equation gives  $54.9^{\circ}\text{C.}$ , only  $3.5^{\circ}$  higher than the correct value of  $51.4^{\circ}\text{C.}$ , whereas the Nernst equation gives  $88.0^{\circ}\text{C.}$ , almost  $40^{\circ}\text{C.}$  too high. (This value has to be obtained by a trial-and-error process, since the Nernst equation cannot be solved directly for  $t$ .)

The dangers in extrapolating equations of this type become more obvious when the value of  $d \log P/dT$  is considered. The equation can be written

$$\log P = y = A - \frac{B}{T} + D \log T + ET \quad (67)$$

whence

$$\frac{dy}{dT} = \frac{B}{T^2} + \frac{D}{2.3T} + E = \frac{1}{T} \left( \frac{B}{T} + \frac{D}{2.3} + ET \right) \quad (68)$$

When several constants of an empirical equation have to be obtained from a set of data there is often a fairly wide range of values which they can be given which will fit the data with almost the same precision. In least-squares work this is termed instability. However, values of the first derivative outside of the range studied may be very sensitive to these changes in the constants, so much so that the calculated vapor pressure may actually decrease with temperature. Thus we note that the signs of the terms in  $B$  and  $E$  have been changed, so that while small differences in these constants may cancel out in equation 67, these differences are cumulative in equation 68. A similar line of reasoning may be applied to the two other pairs of constants.

#### *D. Comparison with Biot equation, for heptane and octane*

Sidney Young (57) fitted his long-range vapor-pressure data by means of the Biot equation, which contains five empirical constants. At least up to a reduced temperature of 0.85, a fit as good or better can be obtained with the Antoine equation. For *n*-heptane, the Antoine equation fits with a standard deviation of 0.27 per cent in  $P$  from 0° to 220°C. (the critical point is at 266.85° C.). This is a better fit than Young's Biot equation. Similarly, for *n*-octane the fit is about as good as the Biot equation from 10° to 230°C., with a standard deviation of 0.65 per cent in  $P$ .

#### *E. Comparison with data smoothed by cross plotting, for the normal paraffin hydrocarbon series*

In 1928 Sidney Young (58) made a critical compilation of the available vapor-pressure data on the normal paraffin hydrocarbons. Convenient pressure intervals between 11 and 19,950 mm. were chosen, and a cross-check was obtained by considering the boiling points at these pressures as a function of  $n$ , the number of carbon atoms. The following empirical equation was fitted to the temperatures at each pressure:

$$\log T = a + b \log n + c(\log n)^2 + d(\log n)^3 \quad (69)$$

The cubic term was only required at the three lowest pressures: 11, 15, and 30 mm.

Young also found that the boiling-point increment equation,

$$\Delta = A/T^{B\sqrt{T}} \quad (70)$$

for the change in boiling point ( $\Delta$ ) for each addition of the  $\text{CH}_2$  group, could be generalized to pressures other than 760 mm. The values of  $A$  and  $B$ , respectively, range from 92.6 and 0.0159 (at 11 mm.) to 251 and 0.0133 (at 19,950 mm.).

A third cross-check on the data was afforded by the Ramsay-Young rule, using hexane as the reference compound. If  $T_A, T_B$  represent the absolute boil-

ing points of the two compounds at the same pressure, then the relationship can be formulated as:

$$T_A/T_B = a + bT_A + c(T_A)^2 \quad (71)$$

where  $a$ ,  $b$ ,  $c$  depend on the pressure and the compound under comparison.

Using reliable observational data and the three methods above for intercomparison, Young obtained what he considered the most probable boiling points for pressures ranging from 11 to 19,950 mm. for each member of the series from methane to heptane, from 11 to 15,850 mm. for octane, from 11 to 760 mm. for nonane to nonadecane, and at 11, 15, and 30 mm. for the higher normal paraffins

TABLE 11  
Vapor pressure of the normal paraffins,  $C_nH_{2n+2}$

n	A	B	C	RANGE	RANGE OF DEVIATIONS
				mm.	°C.
1	6.421	352	261	11- 2000	0.0, +0.1
2	6.884	683	259	11-10000	-0.2, +0.4
3	6.919	862	256	11-10000	-0.3, +0.2
4	6.8857	986	247	11- 7000	-0.1, +0.2
5	6.936	1112	238	11-10000	-0.3, +0.2
6	6.910	1192	227	11- 7000	-0.2, +0.3
7	6.926	1284	219	11- 7000	-0.2, +0.1
8	6.9345	1360	210	11- 7000	-0.1, +0.2
9	6.9313	1429	203	11- 760	-0.2, +0.1
10	6.9355	1497	196	11- 760	-0.1, +0.1
11	6.978	1581	191	11- 760	-0.1, +0.2
12	7.051	1681	188	11- 760	-0.1, +0.2
13	7.0972	1758	183	11- 760	0.0, +0.2
14	7.0076	1744	170	11- 760	-0.2, +0.3
15	6.8552	1678	152	11- 760	-0.2, +0.2
16	6.688	1599	133	11- 760	-0.2, +0.2
17	6.545	1535	116	11- 760	-0.1, +0.1
18	6.474	1516	104	11- 760	-0.2, +0.2
19	6.408	1506	94	11- 760	-0.2, +0.4

from  $n = 20$  to 35. This set of data affords an excellent opportunity for determining the systematic variation of the Antoine constants. Antoine equations were accordingly obtained by the usual graphical methods and their constants are given in table 11, together with the maximum deviations between the equations and Young's most probable boiling points. The individual deviations are of about the same size as or smaller than the differences between Young's selected observed values and his values by the three methods of intercomparison. It is believed that the Antoine equations presented are as good a representation of the true values as Young's tabulation.

In line with other physical properties of homologous series we could expect that the Antoine constants would fall on smooth curves when plotted against the number of carbon atoms. Actually, as has been pointed out in the discussion on

instability above, the constants are sensitive to small variations, so that sets of constants which appear to be quite different actually provide about the same fit to the data. The values of  $C$  in the Antoine equations for the paraffins have been somewhat smoothed and fall on a fairly smooth curve with an abrupt inflection at  $n = 14$ . The vapor pressures of the higher members of the series are not known as precisely as those of the lower members and the intercomparison methods are not as satisfactory, so that it is difficult to determine whether a true inflection point exists at  $n = 14$  or not. Since the values of  $A$  and  $B$  were obtained after  $C$  had been decided on, this inflection point is also reflected in the plots of  $A$  and  $B$ . The writer believes that the values of all three constants will fall on smooth curves when more accurate data are obtained. The small variation of  $A$  with structure is of especial interest.

The trend is clear that  $C$  increases as the boiling point decreases. The approximate correlation of  $C$  with boiling point (equations 55, 56, 57) was obtained from a large plot of these data and about fifty other values of  $C$ , obtained from the literature and by calculation, on substances ranging from elements to inorganic salts and a variety of organic compounds. For data of moderate precision,  $C = 230$  appears to be a suitable average value for most organic compounds boiling between  $0^\circ$  and  $150^\circ\text{C}$ .

Some studies have shown that for the upper range of vapor-pressure data, say from a reduced temperature of 0.75 to the critical point, the value of  $C$  is considerably higher than for the lower range, being even higher than 273. A set of equations for this upper range could have been fitted to the paraffin data, but the data are not known to the same precision as for lower temperatures and the present set of equations was believed to be of more general interest in showing the variation of the value of  $C$  for the more useful range of temperatures and pressures.

It should be noted that temperatures calculated from the equations in table 11, above the ranges indicated will be a few degrees too high.

Recent work (54a) at the National Bureau of Standards on the vapor pressures of over fifty hydrocarbons from 48 mm. (or  $15^\circ$ , if the pressure at  $15^\circ$  is above 48 mm.) up to 780 mm. shows some minor differences from the results of table 11. This is to be expected, since the range is much shorter and the data are on pure compounds rather than correlated values.

#### *F. Miscellaneous Antoine equations*

The Antoine equations which are tabulated in this section were obtained in various ways, as has been pointed out. They have accordingly been divided into two groups (see tables 12A and 12B). In the first group all three Antoine constants have been determined. The equations for the following compounds, which have already appeared in the text, have not been included: isoöctane, (page 7); water (page 10); methylcyclopentane (page 15); carbon disulfide (page 23); isobutene (page 24); methyl ether (page 25); lead chloride (page 26); lead bromide (page 26); hydrogen chloride (page 27); normal paraffins (page 30).

TABLE 12A  
Antoine equations: Group 1

COMPOUND	SOURCE OF DATA	A	B	C	s	RANGE
Pentane.....	Young <sup>1</sup>	7.5287	1562	302	±0.1°	100 to 197.2°C.
Neopentane.....	Whitmore, Fleming <sup>2</sup>	7.6061	1462	300	2.5 mm.; 0.25°	-42 to 9.4°C.
n-Heptane.....	E. R. Smith <sup>3</sup>	6.89662	1264.663	216.494	0.045 mm.	40 to 125°C.
Toluene.....	Max Schmitt <sup>4</sup>	6.92834	1335	219	0.42 mm.	14 to 89°C.
Toluene.....	Schouteden, Deveux <sup>5</sup>	6.50924	1088.2	189	0.54 mm.	22 to 111°C.
Methyl chloride.....	Messerly, Aston <sup>6</sup>	7.0601	928.4	246.3	0.014 mm.	191 to 249°K.
Iron carbonyl.....	Trautz, Badstübner <sup>7</sup>	6.8251	1183.6	195	±0.5 mm.	25 to 91°C.
Sulfur dioxide	Giauque, Stephenson <sup>8</sup>	7.27886	998.673	237.1	0.17 mm.	197 to 263°K.
Aluminum chloride	Kelley <sup>9</sup>	5.760	669.2	71	±1 per cent in P	193 to 220°C.

<sup>1</sup> Sci. Proc. Roy. Dublin Soc. **12**, 374 (1910); excellent fit up to critical point.

<sup>2</sup> J. Am. Chem. Soc. **55**, 3803 (1933); good to ±3.5 mm., ± 0.5°C.

<sup>3</sup> J. Research Natl. Bur. Standards **24**, 229 (1940); equation shown is a better fit than the author's Antoine equation from the same data.

<sup>4</sup> Pub. sci. tech. ministère de l'air (France), No. **54** (1934).

<sup>5</sup> Natuurwet. Tijdschr. **18**, 242 (1936).

<sup>6</sup> J. Am. Chem. Soc. **62**, 886 (1940); a very good fit except for two extreme deviations of -0.22 and +0.43 mm. The others range from -0.03 to +0.02 mm.

<sup>7</sup> Z. Elektrochem. **35**, 799 (1929). Their data went down to 67°. Some unpublished measurements by V. Hnizda of this laboratory checked the lower range and extended the range to 25°.

<sup>8</sup> J. Am. Chem. Soc. **60**, 1389-94 (1938); not as good a fit as their four-constant equation, which gives  $s = 0.038$  mm.

<sup>9</sup> Kelley (U. S. Bur. Mines Bull. **383**, 17 (1935)) obtained a good fit using a Rankine-type equation up to 220° C., but his equation gives decreasing values of vapor pressure on extrapolation above 530°C. The Antoine equation shown fits Kelley's calculated values to within mm. and gives much more reasonable values on extrapolation to higher temperatures.

TABLE 12B  
*Antoine equations: Group 3*  
 C = 230 in every case

COMPOUND	SOURCE OF DATA	A	B	s	RANGE
Benzene.....	M. Schmitt <sup>1</sup>	7.0720	1300	0.25 per cent in <i>P</i>	9 to 81°C.
Benzene.....	Compromise <sup>2</sup>	7.06664	1298		9 to 81°C.
Toluene.....	M. Schmitt <sup>1</sup>	7.1386	1449	0.25 per cent in <i>P</i>	13 to 89°C.
Hexane.....	Compromise <sup>2</sup>	6.96473	1220		0 to 80°C.
Cyclohexane.....	M. Schmitt <sup>1</sup>	6.9727	1272	0.16 per cent in <i>P</i>	28 to 81°C.
Methylcyclopentane.....	M. Schmitt <sup>1</sup>	6.9068	1216	0.16 per cent in <i>P</i>	-16 to 77°C.
Methylcyclohexane.....	J. C. Pope <sup>3</sup>	6.8101	1300	2.5 mm.	98 to 113°C.
Cyclobutane.....	Handbook <sup>4</sup>	6.6284	909		
Acetone.....	Handbook <sup>4</sup>	7.1625	1225		
Decalin	I.C.T.	7.2216	1824		
Cyclohexanol.....	Gardner, Brewer <sup>5</sup>	8.3956	2144	2.8 mm.	34 to 149°C.
Ethyl chloride.....	Compromise <sup>2</sup>	6.8994	975.3	±1 per cent	0 to 100°C.
B <sub>2</sub> H <sub>7</sub> N.....	Schlesinger <i>et al.</i> <sup>6</sup>	7.1579	1300	1.9 per cent in <i>P</i>	-27 to 29°C.
Diisopropylzinc.....	V. Hnizda <sup>3</sup>	7.987	1858	±0.5°, ±0.7 mm.	37 to 65°C.
Tetramethyllead.....	Callingaert <i>et al.</i> <sup>7</sup>	6.9381	1378.7	±10 per cent in <i>P</i>	25 to 760 mm.
Trimethylethyllead.....	Callingaert <i>et al.</i> <sup>7</sup>	7.2760	1602.5	±10 per cent	13 to 100 mm.
Dimethyldiethyllead.....	Callingaert <i>et al.</i> <sup>7</sup>	7.5903	1810.7	±10 per cent	10 to 50 mm.
Methyltriethyllead.....	Callingaert <i>et al.</i> <sup>7</sup>	7.8768	2000.5	±10 per cent	4 to 15 mm.
Tetraethyllead.....	Callingaert <i>et al.</i> <sup>7</sup>	8.1547	2184.6	±10 per cent	0.05 to 300 mm.

<sup>1</sup> Pub. sci. tech. ministère de l'air (France), No. 54 (1943).

<sup>2</sup> The compromise equations were obtained from several sets of data, using the methods described above.

<sup>3</sup> Unpublished data from this laboratory.

<sup>4</sup> Approximate equations obtained from data tabulated in various handbooks.

<sup>5</sup> Ind. Eng. Chem. **29**, 179 (1937).

<sup>6</sup> J. Am. Chem. Soc. **60**, 2298 (1938); a slightly better fit than their Nernst equation.

<sup>7</sup> J. Am. Chem. Soc. **61**, 2757 (1939). These equations all converge to 432°C. and  $\log P = 4.8566$  when  $\log P$  is plotted against  $1/(t + 230)$ . This intersection point can be used for obtaining the vapor pressures of mixtures of these alkyls.



In the second group the value of  $C$  has been taken equal to 230. Many of these equations were obtained from data of lower quality than those in the first group.

A rough measure of the goodness of fit is afforded by an estimate of the standard deviation of the residuals in pressure or temperature. This has been denoted by  $s$ . In some instances the spread of the residuals has been shown preceded by a  $\pm$  sign.

#### G. Vapor-pressure nomograph

An alignment chart can be easily constructed for the Antoine equation with  $C$  equal to 230. Such a chart, constructed using data from many sources, is shown in figure 2. The hydrocarbon line was drawn through the Calingaert and Davis intersection point of 1240°C. and  $1.3 \times 10^6$  mm. (see above). The lead alkyl line was similarly drawn through the intersection point of 432°C. and  $7.19 \times 10^4$  mm. For mixtures, or in the absence of other data, these lines can be used to estimate vapor pressures using a normal boiling point. For example, if a hydrocarbon mixture boils at 130°C., what is its vapor pressure at room temperature (25°C.)? The line from 760 mm. to 130°C. intersects the hydrocarbon line determining the vapor-pressure point. Use of this point and 25°C. gives a vapor pressure of 13 mm.

Often a good guess can be made of the vapor pressure of a compound by drawing a curve through the points corresponding to similar compounds and using this curve in a similar manner to the hydrocarbon line.

The chart can be used for interpolations and extrapolations by using two or more vapor pressures to determine the point on the nomograph.

#### IX. HEAT OF VAPORIZATION

The heat of vaporization is related to the vapor pressure by the Clausius-Clapeyron equation, which may be written in the form:

$$\Delta H = \Delta z \cdot RT^2 \frac{d \ln P}{dT} \quad (72)$$

where  $\Delta z = P\Delta V/RT = PV_g/RT - PV_l/RT$ . The calculation of the heat of vaporization thus resolves itself into two parts, the determination of the slope of the vapor-pressure curve and the determination or estimation of  $\Delta V$  or  $\Delta z$ . When the Antoine equation is applicable, equation 72 becomes:

$$\Delta H = \frac{4.57566BT^2}{(T + C)^2} \Delta z \quad (73)$$

Similar expressions may be derived for other empirical vapor-pressure equations. If  $\Delta V$  is known from  $P$ - $V$ - $T$  studies, the following equivalent form may be more convenient:

$$\Delta H = \frac{BPT\Delta V}{13629(T + C)^2} \quad (74)$$

$P$  is in millimeters,  $t$  in °C.,  $\Delta V$  in cubic centimeters per mole, and  $\Delta H$  in calories per mole.

Unfortunately,  $P$ - $V$ - $T$  data for both liquid and gaseous phases are not always

available, but for many purposes a correlation of  $\Delta z$  with reduced temperature and pressure is entirely adequate. Probably the best available correlation is that of Meissner (34), whose figure 4 shows  $\Delta z$  as a function of  $P_R$  and  $T_R$ . A similar correlation (14) was obtained by plotting  $\Delta z$  against  $P_R/T_R$  for Young's

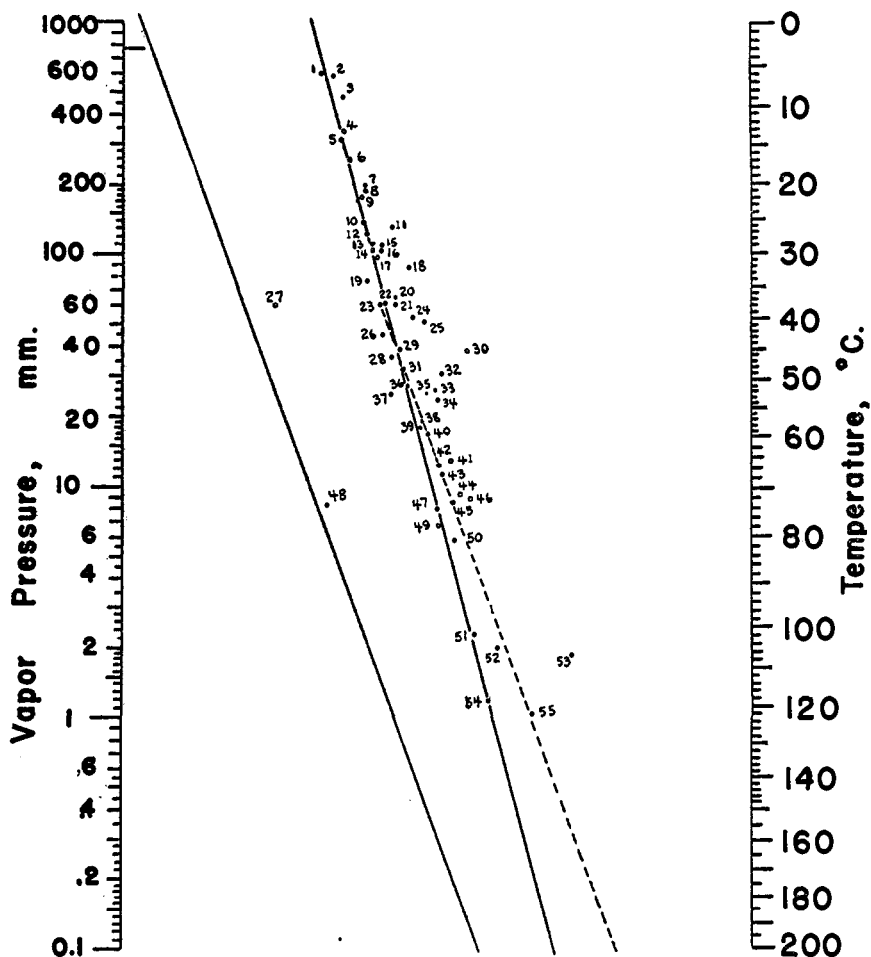


FIG. 2. Vapor-pressure nomograph. The dotted diagonal line applies to the homologous series of lead alkyls and the two solid diagonal lines to most hydrocarbons and their halogenated derivatives, the one at the right for pressure in millimeters as shown and the one at the left for pressure in *atmospheres*.

data on *n*-pentane, isopentane, *n*-hexane, and *n*-heptane (57). The correlating curve is believed to be suitable for predicting  $\Delta H$  to within  $\pm 5$  per cent, at least for non-polar compounds, and has not proved to be far in error for polar compounds. The two equations below are equivalent to the correlation.

For  $P_R/T_R$  from 0 to 0.2,

$$\log \Delta z = 2.106x^2 - 1.0268x \quad (75)$$

For  $P_R/T_R$  from 0.2 to 1.0,

$$\log \Delta z = 0.136x^2 - 0.645x - 0.0185 \quad (76)$$

where  $x = -\log(1 - P_R/T_R)$ .

For the useful range of values of  $P_R/T_R$  less than 0.10, the correlation is reliably represented by the simpler relation:

$$\Delta z = 1 - 0.97P_R/T_R \quad (77)$$

As an example of the use of these methods, the heat of vaporization of *n*-heptane is computed at the normal boiling point.

According to E. R. Smith (49) the normal boiling point is 98.428°C. and the vapor-pressure equation is:

$$\log P = 6.905113 - 1269.821/(t + 217.11)$$

*Vapor-pressure points for figure 2*

1 cyclobutane	8 acetone
13 benzene	3 acetaldehyde
13 cyclohexane	4 ethyl ether
49 naphthalene	
47 kerosene (refined No. 9 oil)	23 tetramethyllead
	31 trimethylethyllead
48 methyl bromide (atm. not mm.)	38 dimethyldiethyllead
2 ethyl chloride	42 methyltriethyllead
10 ethyl iodide	45 tetraethyllead
5 ethyl bromide	
17 ethylene dichloride	29 trimethylaluminum
28 ethylene dibromide	40 methylaluminum dichloride
12 carbon tetrachloride	
9 chloroform	43 triethylbismuth
	50 tri- <i>n</i> -propylbismuth
11 methyl alcohol	51 tri- <i>n</i> -butylbismuth
18 ethyl alcohol	54 tri- <i>n</i> -amylbismuth
25 <i>n</i> -propyl alcohol	
32 <i>n</i> -butyl alcohol	39 diethylmercury
34 <i>n</i> -amyl alcohol	52 di- <i>n</i> -amylmercury
41 cyclohexanol	55 di- <i>n</i> -hexylmercury
44 methyleyclohexanol	
	36 trimethylgallium
7 ethyl formate	33 trimethylindium
15 ethyl acetate	35 diisopropylzinc
20 ethyl propionate	
16 propyl formate	19 iron pentacarbonyl
21 propyl acetate	6 nickel carbonyl
37 ETHYL Aviation Fluid	6 aluminumborohydride (AlB <sub>2</sub> H <sub>12</sub> )
26 ETHYL Motor Fluid	30 berylliumborohydride (BeB <sub>2</sub> H <sub>8</sub> )
24 water	14 mono- <i>N</i> -methyltriborinetriamine
53 aluminum chloride	22 di- <i>N</i> -methyltriborinetriamine
46 solid iodine	5 tri- <i>N</i> -methyltriborinetriamine
27 hydrogen chloride (atm. not mm.)	

The critical point is taken to be 540.17°K. and 27.00 atm. (6) so that:

$$P_R/T_R = (1/27.00)/(371.588/540.17) = 0.0538$$

From equation 77,  $\Delta z = 0.946$  and from the more complicated equation 75,  $\Delta z = 0.947$ . Meissner's chart gives  $\Delta z = 0.95$ .

$\Delta H$  is calculated by equation 73 to be:

$$\frac{(4.57566)(1269.821)(273.16 + 98.248)^2(0.947)}{(217.11 + 98.428)^2} = 7630 \text{ calories per mole}$$

This is an excellent check on the calorimetric value,  $7660 \pm 20$  calories per mole (41), which corresponds to a  $\Delta z$  value of  $0.951 \pm 0.003$ .

TABLE 13  
*Comparison of  $\Delta z$  for a polar liquid: ethyl alcohol above the boiling point*

TEMPERATURE	$\Delta z$	
	I.C.T.*	Correlation†
°C.		
80	0.97 <sub>6</sub>	0.97 <sub>6</sub>
100	0.95 <sub>0</sub>	0.95 <sub>2</sub>
120	0.91 <sub>2</sub>	0.91 <sub>7</sub>
140	0.86 <sub>8</sub>	0.86 <sub>8</sub>
160	0.81 <sub>1</sub>	0.81 <sub>0</sub>
180	0.73 <sub>3</sub>	0.73 <sub>3</sub>
200	0.62 <sub>0</sub>	0.62 <sub>7</sub>
220	0.46 <sub>8</sub>	0.47 <sub>8</sub>
230	0.37 <sub>3</sub>	0.37 <sub>5</sub>
240	0.17 <sub>9</sub>	0.22 <sub>9</sub>
243.1 (critical)	0.0	0.0

\* Using the I.C.T. values for densities of liquid and vapor and for vapor pressure.

† Calculated from the correlation equations, 75 and 76.

For polar liquids the errors in  $z_o$  and  $z_l$  tend to compensate, so that the estimated value of  $\Delta z$  is not as much in error as would be expected. Table 13 shows the excellent agreement for ethyl alcohol between the correlation and values of  $\Delta z$  calculated from density and vapor-pressure values in the *International Critical Tables*. It is believed that the use of the  $\Delta z$  correlation presented above will not cause an error of more than  $\pm 10$  per cent in the estimation of the heat of vaporization at any temperature and that in most instances the error will be less than 5 per cent. The error caused by the use of the Antoine equation, or any other reliable vapor-pressure equation, for computing the slope,  $d \ln P/dT$ , is believed to be a very minor factor in the calculation. However, the use of an unsatisfactory vapor-pressure equation will invalidate the method.

#### X. OTHER APPLICATIONS OF THE ANTOINE EQUATION

The Antoine equation may be used for several kinds of data other than vapor pressures of pure liquids.

Antoine (3) suggested its use for representing the temperature relation of the density of a saturated vapor, and Schmidt (45), apparently independently, proposed a similar scheme for representing the product of the densities of saturated liquid and vapor, or

$$\log (d_l \cdot d_g) = A - \frac{B}{t + C} \quad (78)$$

For *n*-heptane, the following equation gives an excellent fit to Young's data (57) up to 200°C. ( $T_R = 0.88$ ):

$$\log (d_l \cdot d_g) = 1.1391 - \frac{1275.1}{t + 235.9} \quad (79)$$

where  $d_l$ ,  $d_g$  are in grams per cubic centimeter.

The value of  $C$  and the range of applicability are similar to those obtained for vapor pressures.

A useful chart for the fugacities of liquid hydrocarbons was prepared by W. C. Kay (28), using a scheme similar to the Cox chart. It can be shown to be equivalent to the use of Antoine equations of the form:

$$\log f_i = A - B/(t + 180) \quad (80)$$

all passing through the intersection point of the family at 1054°C. and 367 atm. The fugacity of a hydrocarbon can be approximated by using these relations and the additional fact that at sufficiently low pressures, the fugacity becomes equal to the vapor pressure.

Ideal vapor-liquid vaporization constants, usually known as  $K$  values ( $K = y/x$ ), vary with temperature somewhat as vapor-pressure data do. If Antoine equations are used for the temperature relation, the fit is usually as good as the number of significant figures reported.

The Antoine equation may also be used to represent the temperature variation of the kinematic viscosities of certain liquids. Thus, the following equation fitted unpublished data on redistilled commercial xylidine ( $d_4^{20} = 1.5606$ ) to within the experimental error from  $-40^\circ$  to  $130^\circ\text{F}$ .

$$\log KV = -0.912 + 290/(t + 117) \quad (81)$$

where  $KV$  is kinematic viscosity in centistokes and  $t$  is temperature, °F.

The Antoine equation is also useful for ideal relative volatility or vapor-pressure ratio data.

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