

# 1 Introduction

## 1.1 Definitions

Equilibrium intensive thermodynamic properties of pure compounds that exist as a single phase, *e.g.* crystal (solid), liquid or gas, are functions of two independent observables. Temperature and pressure are usually the selected variables, although other pairs may be used.

Properties of pure compounds that exist as two phases in equilibrium are functions of one independent variable. Either temperature or pressure may be chosen as the independent variable. If one of the phases is condensed (solid or liquid) and the other phase is gas (vapor) and temperature is the independent variable, the pressure is the *vapor pressure*. The vapor pressure is a function only of temperature, and it is independent of the volume of the system or of the amounts of phases present. If pressure is the independent variable, the temperature is the *boiling point*. Therefore, the boiling point is a function only of pressure applied to the system and is independent of the total volume or of the amounts of the two phases present.

The terms *vapor pressure* and *boiling point* of a pure component are two equivalent ways of referring to the same physical state. When the condensed phase is a solid the term *sublimation point* is usually used instead of *boiling point*. The boiling (or sublimation) point at one atmosphere is the *normal boiling (sublimation) point*.

Reciprocal temperature in thermodynamics is the integrating factor for reversible energy transfer as heat. Two kinds of temperature exist: *thermodynamic temperature* that is independent of any particular physical system and defined within the Second Law of Thermodynamics and the *practical temperature scale* used with thermometers. The International Committee on Weights and Measures establishes this scale and keeps it as consistent as possible with the thermodynamic temperature. The ITS (International Temperature Scale) is revised every 20 years (most recently in 1990). Temperatures measured on this scale are designated ITS-90. The size of the degree on this scale is determined by the convention that the triple point of water is exactly 273.16 K on the ITS-90 scale. The rest of the scale is defined in terms of *18 fixed points* consisting of melting and boiling points of specified substances. Exact temperatures are assigned to these points. Interpolation between points is made by a series of standard thermometers whose construction is specified in the definition of ITS-90 [90-its]

Pressure is the force per unit area acting perpendicular to a surface. The unit of pressure in the SI system of units is Newtons per square meter. This unit is also called the *Pascal* and abbreviated as Pa. Another unit frequently encountered in practice is the *torr*. This unit corresponds to a millimeter of mercury in a standard barometer. The standard barometer is a glass tube filled with mercury connected to vacuum on one side and to the measured pressure on the other. The mercury is at 0 °C in a location having gravity corresponding to the standard gravitational acceleration,  $g = 9.807 \text{ m}\cdot\text{s}^{-2}$ . One atmosphere (1 atm) is 760 torr exactly, which corresponds to 101325 Pa.

The highest temperature at which a liquid can exist in equilibrium with its vapor is the *critical temperature*. Above this temperature liquid and vapor do not exist as separate phases. Thus, a substance does not have a vapor pressure (or boiling point) above its critical temperature. The pressure exerted by a substance at its critical temperature is its *critical pressure* and the density in this state is the *critical density*. Critical constants are significant not only because they provide the upper limit of vapor pressure,

but also because of their theoretical implications, their use in developing equations of state and the role they play in many physicochemical correlations. A recent compilation of recommended critical constants is being published as a series [95-ambyou, 95-ambtso, 95-tsoamb, 95-gudtej, 96-dau].

## 1.2 Measurement of Vapor Pressure and Boiling (or Sublimation) Point

The experimental determination of a vapor pressure or boiling (sublimation) point for a pure compound using static or quasistatic methods consists of measuring the temperature and pressure of a sample of the compound when a condensed phase exists in equilibrium with the gas phase. Temperature is measured with a *thermometer*. Examples of thermometers are mercury-in-glass thermometers, thermocouples, electrical resistance thermometers, thermistors, quartz crystal oscillators, and optical pyrometers [82-guahon]. Pressure usually is measured with a manometer, mercury barometer, Bourdon gage or dead-weight gage. The choice of instrument depends upon the accuracy desired and the range of temperatures and pressures, among other considerations.

Manometers are used in two general ways. The manometer may be placed in direct contact with the system at equilibrium, usually in contact with the vapor phase. When used this way, the manometer must be kept at a temperature equal to or greater than that of the system. The other technique uses a pressure transducer. A pressure transducer compares the two pressures on either side of the transducer. It responds when the two pressures are equal. One side of the transducer contacts the system and the other side contacts an external fluid (usually a gas) that contacts the manometer. The external pressure is adjusted to equal the system pressure, and then the manometer reads the system pressure. In this technique, the manometer can be maintained at any convenient temperature.

A pressure transducer may consist of no more than a simple U-shaped glass tube containing an inert liquid such as mercury. Pressure equality occurs when the liquid is at the same level in both legs of the tube. However, pressure transducers also may be elaborate instruments based upon detecting the movement of some type of diaphragm.

Besides the thermometer and pressure gauge, the experimental apparatus requires a means to hold the two phases at equilibrium in close contact long enough for the pressure and temperature to be measured. The thermometer and pressure gauge must respond to the temperature and pressure existing at phase equilibrium. Finally, the measurement requires using a sample of sufficient purity.

Errors in measurement arise from calibration and reading of the thermometer and pressure gauge, inappropriate placement of the sensors of these instruments, failure to achieve equilibrium and impurities in the sample. Impurities may be present in the original sample or may arise from decomposition of the sample or other chemical changes that occur during the course of the measurement.

Two experimental techniques are used for vapor pressure measurements. In one, the sample is contained in a constant temperature environment (thermostat). When the pressure reaches its equilibrium value, the observed value at the established temperature is the vapor pressure. With the other technique, the sample is maintained at a fixed pressure using a manostat and the system is allowed to reach its equilibrium temperature. The observed temperature at this pressure is the boiling point.

Experimental techniques may be somewhat arbitrarily classified as *static*, *quasistatic* (also called *dynamic*), and *kinetic* [51-par, 93-fre].

## 1.2.1 Static Techniques

### 1.2.1.1 Direct Sealed Container

Conceptually, this is the simplest type of vapor pressure apparatus. The sample is placed in a closed container and all air and other volatile impurities are removed as completely as possible. The container is placed in a thermostat kept at constant temperature until phase equilibrium occurs. The temperature and pressure are measured. The pressure gauge can be connected to the system directly or through a pressure transducer.

The main drawback with this technique is the difficulty associated with removing volatile impurities, which involves a sequence of freeze-thaw cycles of the sample under high vacuum. This procedure becomes more difficult to implement for systems having low vapor pressures because the effects of volatile impurities become greater. The procedure also is sensitive to sample decomposition because decomposition products are usually volatile. The lower limit of usefulness is around 100 Pa.

The direct sealed container technique is used more often for mixtures than for pure substances. The possibility of preparing mixtures of accurately known composition compensates for the difficulty in removing volatile impurities.

### 1.2.1.2 The Isoteniscope

Smith and Menzies [10-smimen] first describe the isoteniscope. This instrument operates as a special type of static method using a glass U-tube as a pressure transducer. Generally, the apparatus includes a sample bulb made from glass for visibility. The U-tube may contain mercury but is more likely to contain the liquid phase of the sample being measured. The apparatus usually is placed in a thermostat and the external pressure is adjusted to equal that of the vapor in contact with the sample. The advantage of this technique is that, when the external pressure is lowered, the sample vapor can bubble through the U-tube, which assists in removing volatile impurities. This sample purging is repeated until constant pressure readings are attained. This procedure is also valid for samples that undergo slow decomposition. The accuracy of this method is limited by the sensitivity of the pressure transducer, in normal use about 20 Pa.

### 1.2.1.3 The Inclined Piston Gage

This device employs another variation of the static method. The sample is placed in a cylinder closed at the bottom and fitted with a freely moveable piston at the top. The pressure of the gas sample balances the weight of the piston. The effective weight of the piston can be adjusted by tilting the cylinder from a vertical position. The pressure can be calculated from the tilt angle when the sample pressure balances the piston weight. Although it is difficult to remove volatile impurities, this method provides the most accurate measurements made in the range of 100 to 1500 Pa. It is applicable to solids as well as liquids.

## 1.2.2 Quasistatic Techniques

In quasistatic (or dynamic) techniques, a steady rate of boiling or evaporation is established, and it is assumed that the pressure attained in this steady state is the same as the equilibrium pressure. In careful experiments, pressures are measured at several evaporation rates to verify that they do not depend upon the rate within the experimental conditions.

### 1.2.2.1 Ebulliometric Techniques

Construction details vary considerably for these devices. In all cases, liquid boils when subjected to steady heating. The vapor passes through a reflux condenser and the resulting liquid returns to the boiler, thus

achieving a steady cycle. Generally, a constant pressure is maintained at the top of the condenser and the temperature of the boiling liquid and vapor is measured. This temperature is the boiling point.

An advantage of this technique is that volatile impurities, especially air, that do not condense in the condenser are removed at the top of the device. The chief limitations are difficulties in attaining smooth, steady boiling without superheating the liquid and in locating the thermometer such that it records to the equilibrium temperature. Special pumps that spray the thermometer with a mixture of liquid and vapor exist. Difficulties in reaching steady boiling limit this technique to pressures greater than 1000 Pa (greater for some substances).

Crude measurements are easy to perform with this technique. With careful attention to details, however it is possible to make the most accurate measurements over the range of 2000 to 200000 Pa using ebulliometers. With high quality samples, boiling point accuracy of 0.01 °C or better is possible.

A variation on this technique is twin ebulliometers. In this technique, two matched ebulliometers are connected to the same external pressure at the top of the condenser. A standard substance with accurately known vapor pressure is placed in one ebulliometer and the test sample in the other. When steady boiling is attained in both sides, they are at the same pressure. Pressure is not measured directly; rather the two boiling temperatures are measured. Pressure is established by converting the boiling point of the standard to pressure using a previously determined relationship. For organic liquids, water, benzene, or decane are often used as standards.

Diverting some of the liquid from the condenser enables a sample distillation. For a pure sample, the observed boiling point should not change as the distillation proceeds. Any change in boiling temperature is a measure of sample purity.

This method also produces vapor-liquid equilibrium data for mixtures. It is restricted to liquid samples, however.

#### 1.2.2.2 Transpiration Technique

In this method, a steady stream of inert gas passes over or through the sample held at a constant temperature. The concentration of the sample in the emerging stream is measured. This concentration is then converted to partial pressure, usually by assuming an ideal gas mixture. This partial pressure is the vapor pressure. The method is applicable for solid or liquid samples.

The accuracy of this technique is limited by the difficulty in maintaining steady gas flow, in achieving a sample concentration corresponding to equilibrium without entrainment of liquid drops or solid dust particles, and in analyzing the gas stream. Analysis sometimes employs condensing the sample in a cold trap, and sometimes using some type of chemical analysis. Occasionally, data of high accuracy results from this method, but usually they range from 0.5 to 5%. This method is most useful over the range 100 to 5000 Pa. Its sensitivity to impurities depends upon the method of analysis.

### 1.2.3 Kinetic Methods

In kinetic methods, a steady rate of evaporation, not necessarily close to equilibrium, is established and measured. Temperature is constant but pressure is not measured directly. Rather, pressure is calculated from the evaporation rate using kinetic theories. Accuracies are low using such methods. The techniques are used exclusively for pressures below about 100 Pa where other methods are not applicable. Even when kinetic methods do not yield meaningful absolute pressures, they may produce a temperature derivative of pressure that can provide the enthalpy of vaporization using Eq. (1.1).

#### 1.2.3.1 Knudsen Effusion Method

In this method, the sample is placed in a small heated chamber with a small hole in either a side or the top. The chamber is placed in a continuously pumped, high vacuum environment. As the sample evaporates gas effuses through the hole into the external vacuum. The flow rate of gas through the hole is a function of

internal pressure, temperature, and the diameter and length of the hole. Under ideal conditions, kinetic theory provides this flow rate (see [93-fre] for this derivation). Measurement of the sample weight loss during evaporation at constant temperature provides the rate of evaporation. Using a continuous weighing technique that does not require removal of the sample chamber greatly increases the speed of making measurements. One method consists of suspending the sample chamber from a quartz spiral spring and measuring its change in length as the sample evaporates. However, temperature measurement is difficult using this technique.

#### 1.2.3.2 Langmuir Method

In this method, the rate of evaporation from an open surface directly into a vacuum is measured. This rate bears some relation to vapor pressure, but it also depends in complicated way upon many other variables. Among these variables are the effective surface area and the coefficient of vaporization. A discussion appears in [93-fre]. This method is confined almost exclusively to solids, and the magnitude of the pressure is subject to large errors.

#### 1.2.4 Measurement of Critical Constants

Special techniques have been developed to measure critical temperature, pressure and density. The most common manner to observe the critical temperature is to heat a sample in a closed tube and measure the temperature at which the boundary (meniscus) between liquid and vapor disappears. This method produces an accuracy of about 0.5 degree in most cases. More sophisticated methods for detecting the merging of the two phases are available, but achieving a reproducibility of better than 0.1 degree is difficult. Some properties of a substance change rapidly in the vicinity of the critical point and many organic compounds decompose at or below the critical temperature. Rapid methods of observation have been developed for these compounds.

The force of gravity influences the measurement of critical temperature. Some have suggested that accurate measurements of the critical temperature must be made in the absence of gravity, such as in an orbiting satellite. This experiment has not yet been performed.

Given the critical temperature of a substance, the critical pressure can be obtained by measuring the pressure at that temperature. It is more common to measure the vapor pressure over a range near the critical temperature, and then to extrapolate to the critical temperature.

## 1.3 Mathematical Representation of Vapor Pressure

### 1.3.1 Thermodynamic Relationships

A consequence of the second law of thermodynamics is that the chemical potential of any component in equilibrium phases at a particular temperature or pressure is the same in all phases. For a pure compound the chemical potential is the Gibbs energy per mole of the substance. The following equation results for a condensed phase in equilibrium with the gas phase.

$$dP/dT = (\Delta_v H)(\Delta_v V)^{-1} T^{-1} \quad (1.1)$$

In this equation  $\Delta_v H$  is the molar change in enthalpy for the conversion of substance from the equilibrium liquid to the equilibrium vapor phase.  $\Delta_v V$  is the molar change in volume when the substance changes from the liquid to the gas. This equation allows calculation of the enthalpy of vaporization from vapor pressure, and it is the *second law method*. Measurement of enthalpy of vaporization with a calorimeter is the *first law method*. The quantities  $\Delta_v H$  and  $\Delta_v V$  are functions of temperature along the phase boundary. Equation (1.1) can also be written as,

$$d(\ln P)/dT = (\Delta_v H)(\Delta_v Z)^{-1} R^{-1} T^{-2} \quad (1.2)$$

where  $Z$  is the compression factor ( $Z = PV/RT$ ). At temperatures well below the critical temperature, the liquid volume is negligible compared to the gas volume. If, furthermore, the gas is ideal, then  $\Delta_v Z$  is 1.0 and Eq. (1.2) becomes,

$$d(\ln P)/dT = (\Delta_v H)R^{-1}T^{-2} \quad (1.3)$$

known as the Clausius-Clapyron equation. The total derivative of  $\Delta_v H$  along the boundary is a function of heat capacities and volumes,

$$d(\Delta_v H)/dT = \Delta_v C_p + \Delta_v V - T(\partial \Delta_v V / \partial T)_p \quad (1.4)$$

If the functional forms of the heat capacities and volumes of the phases are known, they can be substituted into Eqs. (1.2) and (1.4) and upon integration provide an accurate, functional representation of the vapor pressure:

$$\ln P = \ln P_0 + \int_T^{T_0} \left[ (\Delta_v H)(\Delta_v Z)^{-1} R^{-1} \right] dT^{-1} \quad (1.5)$$

Here,  $P_0$  is the pressure at some reference temperature,  $T_0$ . However, it is rare that the functions are known sufficiently well to derive an accurate vapor pressure equation in this way (see [82-mos/van, 96-ruzmaj] for a more complete thermodynamic analysis of vapor pressure).

More approximate vapor pressure equations result from making various assumptions and simplifications. For example, the terms  $\Delta_v V - T(\partial \Delta_v V / \partial T)_p$  nearly cancel at temperatures well below the critical temperature. At these temperatures the liquid volume is much smaller than the gas volume and can be neglected. Neglecting these terms, assuming the gas phase is ideal, and assuming  $\Delta_v C_p$  is constant, Eq. (1.5) becomes

$$\ln P = \ln P_0 - [\Delta_v C_p(1 + \ln T_0) + ((\Delta_v H_0)T_0^{-1} - (\Delta_v H_0) + T_0)(\Delta_v C_p)(T^{-1}) + (\Delta_v C_p) \ln T]R^{-1} \quad (1.6)$$

If  $\Delta_v C_p$  is zero, Eq. (1.6) becomes,

$$\ln P = a + bT^{-1} \quad (1.7)$$

where  $a$  and  $b$  are constants. Equation (1.7) is used often to represent approximate vapor pressure data, especially for low pressures where experimental data are seldom accurate.

### 1.3.2 Empirical Vapor Pressure Equations

During the past century many empirical mathematical functions have been used to relate vapor pressure to temperature; most are modifications of Eq. (1.7). These functions have several parameters that are characteristic of the compound. Curve fits off experimental data, usually by minimizing the sum of the squares of the deviations between the calculated and observed pressures or temperatures (least squares criterion), provide these parameters. The first and most widely used of these equations is the Antoine equation [1888-ant, 46-tho]. The original form is,

$$\log P = A - B (C + T)^{-1} \quad (1.8)$$

Sometimes the natural logarithm is used instead of the base-10 logarithm or Celsius temperature is used instead of Kelvin. When  $C = 0$  (for  $T$  in kelvins) Eq. (1.8) is identical to Eq. (1.7). The *Thermodynamics Research Center Thermodynamic Tables - Hydrocarbons* [xx-trhc] and *Nonhydrocarbons* [xx-trcnh] - use an extended version of the Antoine equation:

$$\log P = A - B (C + T)^{-1} + 0.43429\chi^n + E\chi^8 + F\chi^{12} \quad (1.9)$$

where  $n$ ,  $E$ , and  $F$  are additional adjustable parameters.  $T_c$  is the critical temperature,  $T_0$  the lower boundary temperature and  $\chi = (T - T_0)/T_c$ .

Examples of functions obtained by adding terms to Eq. (1.7) are the polynomial in temperature used in the *International Critical Tables* [26-ano],

$$\ln P = A + BT^{-1} + CT + DT^2, \quad (1.10)$$

the Chebyshev polynomial [70-ambcou]

$$T \ln P = a_0 / 2 + \sum_{s=1}^i a_s E_s(\chi) \quad (1.11)$$

$$\chi = [2T - (T_{\max} - T_{\min})] / (T_{\max} - T_{\min}) \quad (1.12)$$

in which  $E_s(\chi)$  is a Chebyshev polynomial in  $\chi$  of degree  $s$  (the advantage of this is that the  $E_s$  functions are orthogonal), the Kirchoff-Rankine equation [48-tho],

$$\ln P = A + BT^{-1} + C \ln T, \quad (1.13)$$

(same form as Eq. (1.6)); the Planck-Riedel equation [48-plarie]

$$\ln P = A + BT^{-1} + C \ln T + DP^6, \quad (1.14)$$

and the Frost-Kalkwarf equation [53-frokal]

$$\ln P = A + BT^{-1} + C \ln T + DPT^{-2} \quad (1.15)$$

Another popular type of function is the Cox equation [36-cox]:

$$\ln (PP_0^{-1}) = A (1 - T_b T) \quad (1.16)$$

where  $A$  is a function of temperature often taken to be

$$\ln A = a + bT + cT^2 \quad (1.17)$$

Wagner and others [73-wag, 73-wag-1, 77-wag, and 86-amb-1] have proposed a series of related equations. The simplest is

$$\ln (PP_c^{-1}) = (A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6) / T_r \quad (1.18)$$

where  $\tau = 1 - T/T_c$ ,  $P_c$  is the critical pressure and  $T_c$  is the critical temperature. One of the variations [76-wagewe] is:

$$\ln (PP_c^{-1}) = (A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6 + E\tau^9) / T_r \quad (1.19)$$

Iglesias-Silva *et al.* [87-iglh] have proposed an accurate, three parameter equation that can fit data from the triple point to the critical point:

$$p = \left\{ \left[ a_0 + a_1 (a_3 t + 1)^{b_0/R} \exp((-a_2 + b_0/R)/(a_3 t + 1)) \right]^N + \left[ 2 - a_4 (1 - t) + a_5 (1 - t)^{2-\theta} + a_6 (1 - t)^3 + a_7 (1 - t)^4 \right]^N \right\}^{1/N} \quad (1.20)$$

in which

$$p = 1 + (P - P_t)/(P_c - P_t)$$

$$t = (T - T_t)/(T_c - T_t)$$

$$a_0 = 1 - P_t/(P_c - P_t)$$

$$a_1 = -(a_0 - 1) \exp(a_2 - b_0/R)$$

$$a_2 = b_1/RT_t$$

$$a_3 = (T_c - T_t)/T_t$$

$$\theta = 0.2$$

$$N = 87T_t/T_c$$

$$a_5, a_6, \text{ and } a_7 \text{ are polynomial functions of } a_4$$

An important characteristic of a function is its number of adjustable parameters. When fitting a function to a set of observed data, the number of data values minus the number of fitting parameters is *the degrees of freedom* ( $f$ ). One measure of how well a function fits data is the *standard deviation*,

$$S = (\sum (P_{\text{obs}} - P_{\text{calc}})^2)^{0.5f^{-1}} \quad (1.21)$$

Functions with more parameters are more flexible than those with fewer and can fit experimental data better over a wider temperature range. If the degree of freedom is zero, any function can fit the data exactly, however, this is undesirable. Experimentally based data contain experimental errors. A major objective in fitting data to a function is to obtain a smooth representation of the data that reduces the effect of random errors and provides a means to interpolate and extrapolate the function. Parameters calculated with too few degrees of freedom not only fail to reduce random errors, but they may give unreliable interpolations. It is not wise to make calculations for which the degrees of freedom are less than half the number of data. For vapor pressure, more degrees of freedom are better. Even when the degrees of freedom are acceptable, fitting functions with a large number of parameters to data with large errors may give less reliable results than using a function with fewer parameters.

Vapor pressure equations have been tested and compared [64-mil, 78-amb, 79-scoosb, 80-ambdav, 83-mcg, 85-amb, 90-yalmis, 96-ruzma]. Comparing functions with the same number of adjustable parameters does not always give a clear indication of which is best. Some functions work better for certain ranges of temperature or pressure, or for certain compounds or classes of compounds. None of the equations listed above is clearly preferable in all situations. Variations of the Wagner equation are effective near the critical temperature, but they have no advantage at lower temperatures.

All of the above equations relate the logarithm of pressure to a function of temperature. Thus, the adjustable parameters are non-linear functions of pressure. Using the least squares criterion with pressure as a direct function of temperature requires a non-linear fit. It is more common, however, to take  $\ln(P)$  as a function of temperature and to select a form from among the Eqs. (1.7, 1.9, 1.10, 1.11, 1.12, 1.17, 1.18).

Non-linear least squares calculations are more complex than linear calculations. They start with an initial estimate and find the minimum variance by using a sequence of iterations. It is possible, and common, to converge upon local minima rather than the global minimum. Numerical least squares techniques are described in [88-prefla].

The Antoine Eq. (1.8) may be rearranged as:

$$T \log P = AC - B + AT - C \log P \quad (1.22)$$

Thus, if  $T \log(P)$  is a function of  $\log(P)$  and  $T$ , it is linear in the parameters  $(AC-B)$ ,  $A$ , and  $-C$  and easily yield  $A$ ,  $B$  and  $C$ . This is the usual procedure for calculating Antoine parameters.

If the truncated virial equation of state ( $V = RT/P + B'$ ) provides the gas volume, the enthalpy of vaporization can be calculated from the  $B$  and  $C$  parameters of Eq. (1.8):

$$\Delta_v H = 2.30258 R(T(T + C)^{-1})^2 (1 + B'P T^{-1}) \quad (1.23)$$

## 1.4 Description of the Tables

The Antoine Eq. (1.8) has been used to represent vapor pressures of pure compounds more than any of the others because it has several important advantages:

- It is a simple equation, with 3 adjustable parameters that easily can calculate vapor pressure
- It can be solved for temperature, as well as pressure, in closed form

$$T = B(A - \log P)^{-1} - C \quad (1.24)$$

- Linear least squares may be used to obtain the parameters using Eq. (1.20)
- It fits most experimental vapor pressures in the range of 1.5 to 150 kPa
- Useful correlations exist among the Antoine parameters (or at least relationships among them) and molecular structure.

Data of sufficient accuracy to show significant deviation from the Antoine equation in the 1.5 - 150 kPa exist for only a few compounds. To fit accurate data over a wider range requires a more complex equation. However, as indicated above using an equation with too many parameters may give undesirable results.

The Antoine equation, using parameters fit to reliable data in the range 1.5 - 150 kPa, under predicts higher vapor. This difference increases regularly and smoothly up to the critical temperature. To represent pressures in this range, the Thermodynamics Research Center at Texas A&M University (TRC) uses the extended Antoine Eq. (1.9). The additional term  $0.43429\chi^n$ , where  $n$  is a fit parameter, approximate real data very closely. Because  $\chi < 1$ , and  $E$  and  $F$  have opposite signs the pair of terms  $E\chi^8 + F\chi^{12}$  contribute appreciably only near the critical temperature. Unless accurate vapor pressures are available in this region,  $E$  and  $F$  can be set to zero.

Generally the  $A$ ,  $B$ , and  $C$  constants are the same in Eqs. (1.8) and (1.9) for the same compound. The major exceptions are the alcohols with low carbon numbers. Because the exponent  $n$  is greater than or equal to 2.0, Eqs. (1.8) and (1.9) give equal  $P$  and  $dP/dT$  at the boundary temperature,  $T_0$ , thus, effecting a smooth transition. The usual procedure is to fit the simple Antoine equation to data in the 1.5 - 150 kPa region, which contains most of the accurate data. Then, while keeping the same  $A$ ,  $B$ , and  $C$ , the parameters  $n$ ,  $E$ , and  $F$  are fit to the data for temperatures above  $T_0$ . Good results are obtained for  $T_0$  corresponding to vapor pressures in the range of 120 to 150 kPa.

To retain the Antoine equation for data below 1.5 kPa, a separate set of constants can be fit to the low range. The *TRC Thermodynamic Tables* [xx-trhc, xx-trcnh] use a least squares procedure that forces continuity in  $P$  and  $dP/dT$  for the same phase at the boundary.

The vapor pressure of the two condensed phases existing at a triple point is the same. However, the slopes of the vapor pressure curves below and above this temperature are different. Calculation of the parameters  $A$ ,  $B$ , and  $C$  that characterize a particular compound requires accurate vapor pressure data over a sufficient range of temperature (about 20 deg or more). The constant  $C$  is especially sensitive to errors in the data. When suitable data are used,  $C$  is always negative. Within a group of related compounds  $C$ , decreases in a smooth manner as the normal boiling point increases. Examples of groups are isomers or members of a homologous series. By plotting  $C$  vs.  $T_b$  for members of a group that have reliable data, it is possible to estimate a  $C$  value for members that do not have reliable data. A positive  $C$  obtained from a least squares fit is an indication that the data contain large errors or cover a narrow temperature range or both. The corresponding Antoine equation may give a rough reflection of the data, but it should not be used for extrapolation.

Parameters of the Antoine Eq. (1.8) and the extended Antoine Eq. (1.9) based upon experimental data appear as tables in sections 2 to 4 of this volume.

In the Tables the following information is given:

One line presents the substance identification (bold faced):

- 1. An identification number for the compound.
- 2. The empirical (Hill system) gross formula of the compound (the compounds are listed in formula order sorted by the number of carbon atoms (C), hydrogen atoms (H), and other elements in alphabetical order).
- 3. The compound name and zero or more synonyms.
- 4. The Registry Number assigned by Chemical Abstracts Services, when available. When a CASRN is not available, numbers starting at 50000-00-0 identify compounds in the SOURCE Database maintained by the Thermodynamics Research Center.

The lines following the substance identification provide the data

- 1. Column: Identification of the phase transition (cr - crystal, l - liquid, g - gas).
- 2. Column:  $A$ , ( $n$ ) - The value of  $A$  parameter in Eq. (1.8) with  $P$  expressed in units of kPa. The value in parentheses, if present, is the value of  $n$  in Eq. (1.9).
- 3. Column:  $B/K$  ( $E$ ) - The value of  $B$  in Eq. (1.8). The value in parentheses, if present, contains the value of  $E$  in Eq. (1.9).
- 4. Column:  $C/K$  ( $F$ ) - The value of  $C$  in Eq. (1.8) with  $T$  in kelvins. The value in parentheses, if present, contains the value of  $F$  in Eq. (1.9).
- 5. Column:  $T$ -range [K] - The approximate minimum and maximum temperatures covered by the data.
- 6. Column: Range [K], Rating - The range of temperatures recommended for reliable use of the equation. If this line contains constants for the extended Antoine Eq. (1.9), the lower limit of the range is  $T_0$  and the upper limit is  $T_c$ . The lower limit for a liquid phase is never less than the triple point. The upper limit for crystal phases is never greater than the triple point. The "rating" consists of letters A through D. The ratings indicate a rough order of reliability for the data used to develop the parameters: A - 0.1%; B - 1%; C - 5%; D - 10%.
- 7. Column:  $T_b$  [K]/ $P_b$  [kPa] - The boiling point at the indicated pressure as calculated from the Antoine equation with the listed parameters.
- 8. Column: Ref. - An identification of the source of the Antoine constants listed for the designated compound and phases. Complete references appear in the section 'References'.
- 8. Column: Note - The numbers refer to the text included in the section 'Notes'.

The data represented in the Tables has been obtained from several sources:

- *TRC Thermodynamic Tables - Hydrocarbons*. Identified by [xx-trchc] in the Ref. column. 'xx' is the last two years of the date of issue of the data sheet.
- *TRC Thermodynamic Tables - Nonhydrocarbons*. Identified by [xx-trcnh] in the Ref. column. 'xx' is the last two years of the date of issue of the data sheet. The original sources of data used for these Tables appear in the Specific Reference sheets of the *TRC Thermodynamic Tables*.
- Compilations prepared by the Slovakian Academy of Sciences [79-dykrep, 84-dykrep].
- Other sources - References to original sources of data are given. These refer to sources not used in the [xx-trchc, xx-recnh, 79-dykrep, 84-dykrep].

The number of significant digits given for the parameters values is also a rough indication of the data quality for values from [xx-trchc, xx-trcnh] but not for data from other sources.

## 1.5 References for 1

- xx-trchc TRC Thermodynamic Tables - Hydrocarbons, Thermodynamics Research Center, Texas A&M University System, College Station, TX, (19xx).
- xx-trcnh TRC Thermodynamic Tables - Non-Hydrocarbons, Thermodynamics Research Center, Texas A&M University System, College Station, TX, (19xx)
- 1888-ant Antoine, C.: C. R. Acad Sci. (Paris) **107** (1888) 681.
- 10-smimez Smith, A., Menzies, A.W.C.: Ann. Phys. **33** (1910) 971.
- 10-smimez Smith, A., Menzies, A.W.C.: J. Am. Chem. Soc. **32** (1910) 1412.
- 10-smimez Smith, A., Menzies, A.W.C.: J. Am. Chem. Soc. **32** (1910) 1448.
- 26-ano International Critical Tables of Numerical Data: Physics. Chemistry. Technology. Vol. 1 (and following volumes). Washburn, E.W.(ed.), New York: McGraw-Hill, 1926.
- 46-tho Thompson, G.W.: Chem. Rev. **38** (1946) 1.
- 48-plarie Plank, R., Riedel, L.: Ing. Arch. **16** (1948) 255.
- 51-par Partington, J.R.: An Advanced Treatise on Physical Chemistry, Vol. 2, Properties of Liquids, London: Longmans, Green and Co., 1951.
- 53-fro/kal Frost, A.A., Kalkwarf, D.R.: J. Chem. Phys. **21** (1953) 264.
- 64-mil Miller, D.G.: Ind. Eng. Chem. **56** (1964) 46.
- 70-amb/cou Ambrose, D., Counsel, J.F., Davenport, A.J.: J. Chem. Thermodyn. **2** (1970) 283.
- 73 wag Wagner, W.: Cryogenics **13** (1973) 470.
- 73-wag-1 Wagner, W.: Bull. Inst. Int. Froid Annexe. **4** (1973) 65.
- 76-wagewe Wagner, W., Ewers, J., Pentermann, W.: J. Chem. Thermodyn. **8** (1976) 1049.
- 77-wag Wagner, W.: A New Correlation Method for Thermodynamic Data Applied to the Vapor Pressure Curve of Argon, Nitrogen, and Water, IUPAC Thermodynamic Tables Project Centre, London: Imperial College, 1977.
- 78-amb Ambrose, D.: J. Chem. Thermodyn. **10** (1978) 765.
- 79-dykrep Dykyi, J., Repas, M.: Saturated Vapor Pressure of Organic Compounds, Bratislava, Czech.: Slovakian Academy of Science, 1979.
- 79-scoosb Scott, D.W., Osborn, A.G.: J. Phys. Chem. **83** (1979) 2714.
- 80-ambdav Ambrose, D., Davies, R.H.: J. Chem. Thermodyn. **12** (1980) 871.
- 82-guahon Guang, L., Hongtu, T.: Temperature. Its Measurement and Control in Science and Industry, Vol. 5, 1982 (see also earlier volumes).
- 82-mosvan Mosselman, C., van Vugt, W.H., Vos, H.: J. Chem. Eng. Data **27** (1982) 248.
- 83-mcg McGary, J.: Ind. Eng. Chem. Process Des. Dev. **22** (1983) 313.

- 
- 84-dykrep Dykyi, J., Repas, M., Svoboda, J.: Saturated Vapor Pressure of Organic Compounds, Bratislava, Czech.: Slovakian Academy of Science, 1984.
- 86-amb Ambrose, D.: The Evaluation of Vapour-Pressure Data, London: Dept. of Chemistry, University College, 1986.
- 86-amb-1 Ambrose, D.: J. Chem. Thermodyn. **18** (1986) 45.
- 88-prefla Press, W.H., Flannery, B.P., Teukolsky, S.A., Vetterling, W.T.: Numerical Recipes in C, Cambridge, UK: Cambridge University Press, 1988.
- 90-its International Temperature Scale: Metrologia **27** (1990) 3; 107.
- 90-yalmis Yalkowsky, S.H., Mishra, D.S., Morris, K.H.: Chemosphere **21** (1990) 107.
- 93-fre Frenkel, M.(ed.): Thermochemistry and Equilibria of Organic Compounds, New York: VCH Publishers, 1993.
- 95-ambtso Ambrose, D., Tsonopoulos, C.: J. Chem. Eng. Data **40** (1995) 531.
- 95-ambyou Ambrose, D., Young, C.: J. Chem. Eng. Data **40** (1995) 345.
- 95-gudtej Gude, M., Teja, A.S.: J. Chem. Eng. Data **40** (1995) 1025.
- 95-tsoamb Tsonopoulos, C., Ambrose, D.: J. Chem. Eng. Data **40** (1995) 547.
- 96-dau Daubert, T.E.: J. Chem. Eng. Data **41** (1996) 365.
- 96-ruzmaj Ruzicka, K., Majer, V.: AIChE J. **42** (1996) 1723.