

Volumetric properties of pure fluids

The pure substance

We define a

- Pure substance: a material with homogeneous and invariable composition. To elaborate,
- Pure substances can have multiple phases: an ice-water mixture is still a pure substance.
- An air-steam mixture is not a pure substance.
- Air, being composed of a mixture of N₂, O₂, and other gases, is formally not a pure substance. However, experience shows that we can often treat air as a pure substance with little error.

We slowly add heat to the cylinder, and observe a variety of interesting phenomena. A sketch of what we observe is given in Fig. below. We notice the following behavior:

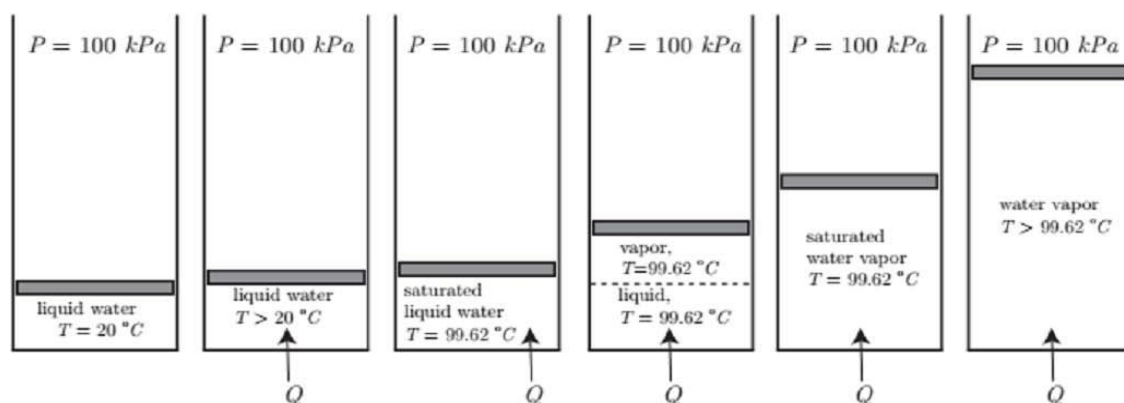


Figure (1): Sketch of experiment in which heat is added isobarically to water in a closed piston-cylinder arrangement.

The pressure remains at a constant value of 100 kPa. This is an isobaric process.

- The total volume increases slightly as heat is added to the liquid.
- The temperature of the liquid increases significantly as heat is added to the liquid.

• At a special value of temperature, observed to be $T = 99.62\text{ }^\circ\text{C}$, we have all liquid, but cannot add any more heat and retain all liquid. We will call this state the saturated liquid state. We call $T = 99.62\text{ }^\circ\text{C}$ the saturation temperature at $P = 100\text{ kPa}$. As we continue to add heat, we have just boiled water! We sketch this process in the temperature-specific volume plane, that is, the $T - v$ plane, in Fig. Note that the mass m of the water is constant in this.

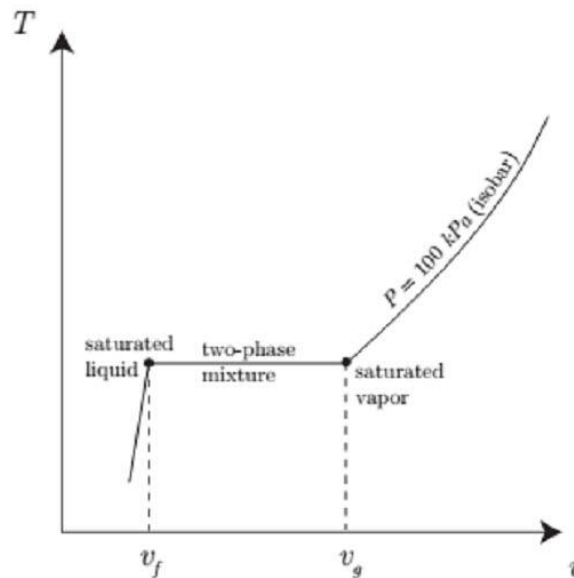


Figure (2): Isobar in the $T - v$ plane for our thought experiment in which heat is added isobarically to water in a piston-cylinder arrangement.

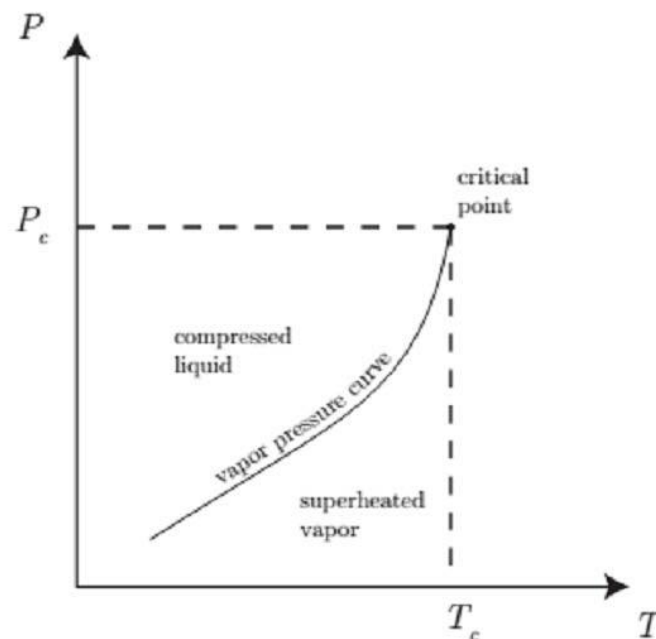


Figure (3): Saturation pressure versus saturation temperature sketch.

- Saturated liquid: the material is at T_{sat} and is all liquid.
- Saturated vapour: the material is at T_{sat} and is all vapour.
- Compressed (subcooled) liquid: the material is liquid with $T < T_{\text{sat}}$.
- Superheated vapor: the material is vapor with $T > T_{\text{sat}}$.
- Two-phase mixture: the material is composed of co-existing liquid and vapor with both at T^{sat} .

Some Definitions

Triple point: triple point of a substance is the temperature and pressure at which the three phases (gas, liquid, and solid) of that substance coexist in thermodynamic equilibrium. Also it is the point at which three curves are met (sublimation, fusion and vaporization).

Critical point: The point at highest temp. (T_c) and Pressure (P_c) at which a pure chemical species can exist in vapour/liquid equilibrium. The point critical is the point at which the liquid and vapour phases are not distinguishable; because of the liquid and vapour having same properties.

Fluid region: it is a region of higher temperature and pressure than T_c and P_c , and it is termed supercritical.

PVT Behavior of Pure Substances

The P-T or Phase Change Diagram

This is called phase diagram since all three phases are separated from each other by three lines. Most pure substances exhibit the same behaviour.

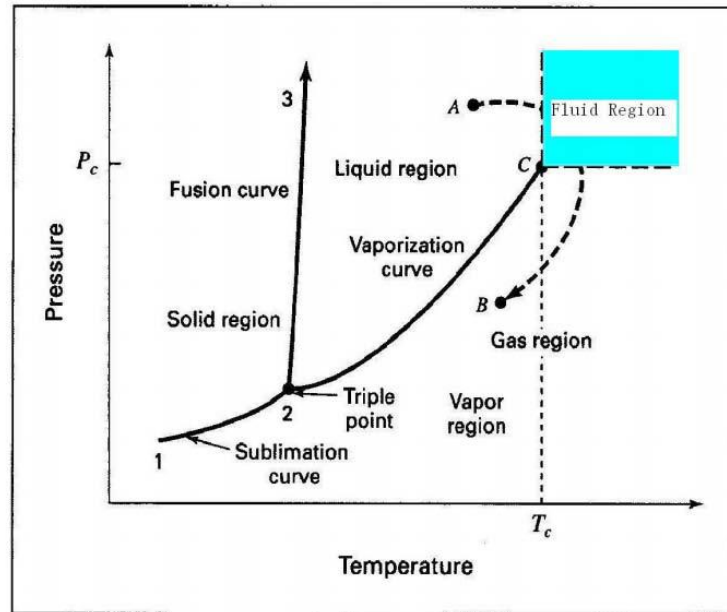


Figure (4) : PT digram for pure substance

There are two ways that a substance can pass from solid phase to vapour phase
 i) it melts first into a liquid and subsequently evaporates, ii) it evaporates directly without melting (sublimation).

- The sublimation line (1-2) separates the solid and the vapor.
- The vaporization line (2-C) separates the liquid and vapour regions .
- The melting or fusion line (2-3) separates the solid and liquid and gives the solid /liquid equilibrium relationship.
- These three lines meet at the triple point, where the three phases coexist in Equilibrium.
- From A to B lead from the liquid region to the gas region without crossing a phase boundary. The transition from liquid to gas is gradual. On the other hand, paths which cross phase boundary 2-C include a vaporization step, where an abrupt change from liquid to gas occurs. if $P < P_{TP}$, the solid phase can change directly to a vapour phase. at $P < P_{TP}$ the pure substance cannot exist in the liquid phase. Normally ($P > P_{TP}$) the substance melts into a liquid and then evaporates.

The triple point is invariant ($F = 0$). If the system exists along any of the two-phase lines of Fig. 3.4, it is univariant ($F = 1$), whereas in the single-phase regions it is divariant ($F = 2$).

The gas region is sometimes divided into two parts, as indicated by the dotted vertical line of Fig. 3.4. A gas to the left of this line, which can be condensed either by compression at constant temperature or by cooling at constant

pressure, is called a vapor. The region everywhere to the right of this line, where $T > T_c$ including the fluid region, is termed supercritical.

P-V Diagram

Figure 3.5 shows the liquid, liquid/vapour, and vapour regions of the P V diagram, with four isotherms superimposed. Isotherms on Fig. 3.4 are vertical lines, and at temperatures greater than T_c , do not cross a phase boundary. On Fig. 3.5 the isotherm labelled $T > T_c$ is therefore smooth. The lines labelled T_1 and T_2 are for subcritical temperatures, and consist of three segments. The horizontal segment of each isotherm represents all possible mixtures of liquid and vapours in equilibrium, ranging from 100% liquid at the left end to 100% vapours at the right end. The locus of these end points is the dome-shaped curve labelled BCD, the left half of which (from B to C) represents single-phase (saturated) liquids at their vaporization (boiling) temperatures, and the right half (from C to D), single-phase (saturated) vapours at their condensation temperatures.

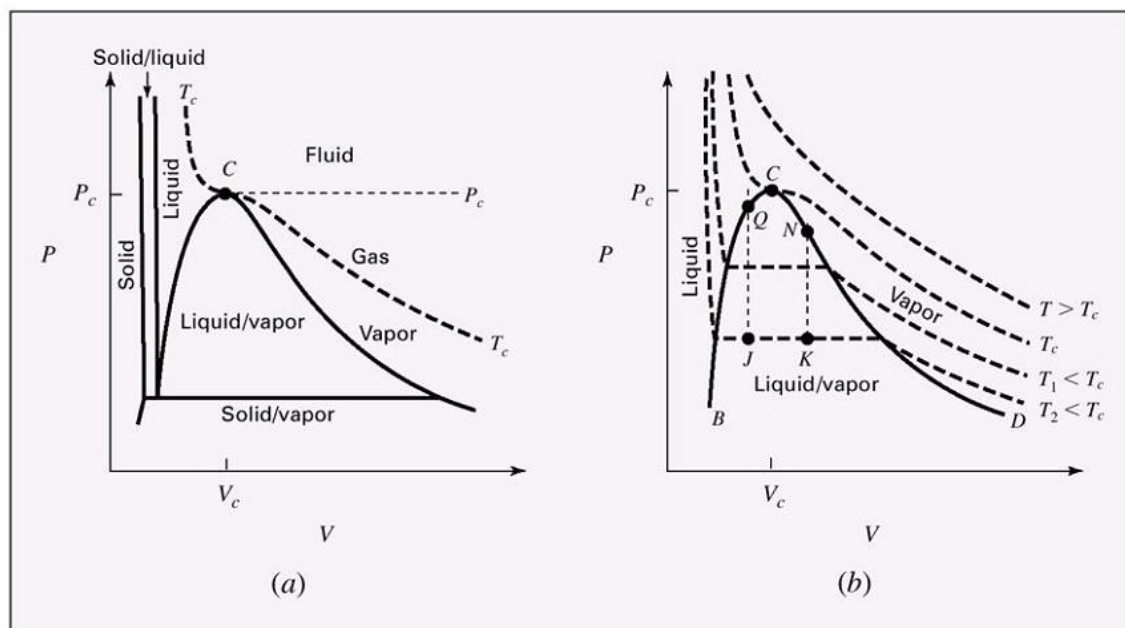


Figure (5): PV diagrams for a pure substance. (a) Showing solid, liquid and gas regions. (b) Showing liquid, liquid/vapour, and vapour regions with isotherms

Single-Phase Region

For the regions of the diagram where a single phase exists, Fig. 5 implies a relation connecting P, V, and T which may be expressed by the functional equation:

$$f(P, V, T) = 0$$

The simplest equation of state is for an ideal gas, $P V = RT$ a relation which has approximate validity for the low- pressure gas region of Fig. 5 if V is considered a function of T and P, then $V = f(T, P)$, and

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad (1)$$

The partial derivatives in this equation have definite physical meanings, and are related to two properties, commonly tabulated for liquids, and defined as follows:

Volume expansivity (expansion factor):

$$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad (2)$$

Isothermal compressibility (compressibility factor):

$$K = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \quad (3)$$

Combination of Eqs. (1) through (3) provides the equation:

$$\frac{dV}{V} = \beta dT - K dP \quad (4)$$

- β and k are function of T, P they increased as T increased.
- For real liquid β and K are constant when change in T,P is relative small
- When a fluid is incompressible β and K are zero

Thus for small changes in T and P little error is introduced if they are assumed constant.

Integration of Eq. (4) then yields:

$$\ln \frac{V_2}{V_1} = \beta(T_2 - T_1) - K(P_2 - P_1) \quad (5)$$

This is a less restrictive approximation than the assumption of an incompressible fluid.

Example

For liquid acetone at 20°C and 1 bar,

$$\beta = 1.487 \times 10^{-3} \text{ } ^\circ\text{C}^{-1} \quad \kappa = 62 \times 10^{-6} \text{ bar}^{-1} \quad V = 1.287 \text{ cm}^3 \text{ g}^{-1}$$

For acetone, find:

- The value of $(\partial P/\partial T)_V$ at 20°C and 1 bar.
- The pressure generated by heating at constant V from 20°C and 1 bar to 30°C.
- The change in volume for a change from 20°C and 1 bar to 0°C and 10 bar.

Solution

(a) The derivative $(\partial P/\partial T)_V$ is determined by application of Eq. (3.4) to the case for which V is constant and $dV = 0$:

$$\beta dT - \kappa dP = 0 \quad (\text{const } V)$$

$$\text{or} \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa} = \frac{1.487 \times 10^{-3}}{62 \times 10^{-6}} = 24 \text{ bar } ^\circ\text{C}^{-1}$$

(b) If β and κ are assumed constant in the 10°C temperature interval, then the equation derived in (a) may be written ($V = \text{const}$):

$$\Delta P = \frac{\beta}{\kappa} \Delta T = (24)(10) = 240 \text{ bar}$$

$$\text{and} \quad P_2 = P_1 + \Delta P = 1 + 240 = 241 \text{ bar}$$

(c) Direct substitution into Eq. (3.5) gives:

$$\ln \frac{V_2}{V_1} = (1.487 \times 10^{-3})(-20) - (62 \times 10^{-6})(9) = -0.0303$$

$$\frac{V_2}{V_1} = 0.9702 \quad \text{and} \quad V_2 = (0.9702)(1.287) = 1.249 \text{ cm}^3 \text{ g}^{-1}$$

$$\text{Then,} \quad \Delta V = V_2 - V_1 = 1.249 - 1.287 = -0.038 \text{ cm}^3 \text{ g}^{-1}$$

Virial Equations of State

Figure (5) indicates the complexity of the PVT behavior of a pure substance and suggests the difficulty of its description by an equation. However, for the gas region alone relatively simple equations often suffice. Along a vapor-phase isotherm such as T_1 in Fig. (5 b), V decreases as P increases. The PV product for a gas or vapor should therefore be much more nearly constant than either of its members, and hence more easily represented. For example, PV along an isotherm may be expressed as a function of P by a power series:

$$PV = a + bP + cP^2 + \dots$$

If $b = aB'$, $c = aC'$, etc., then,

$$PV = a(1 + B'P + C'P^2 + D'P^3 + \dots)$$

where a , B' , C' , etc., are constants for a given temperature and a given chemical species.

In principle, the right side of Eq. above is an infinite series. However, in practice a finite number of terms is used. In fact, PVT data show that at low pressures truncation after two terms usually provides satisfactory results.

Two Forms of the Virial Equation:

A useful auxiliary thermodynamic property is defined by the equation:

$$Z \equiv \frac{PV}{RT} \quad (7)$$

This dimensionless ratio is called the compressibility factor. With this definition and with Eq. of $a = RT$, and Eq. (6) becomes:

$$Z = 1 + B'P + C'P^2 + D'P^3 + \dots \quad (8)$$

An alternative expression for Z is also in common use:

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \quad (9)$$

Both of these equations are known as *virial expansions*, and the parameters B' , C' , D' , etc., and B , C , D , etc., are called *virial coefficients*. Parameters B' and B are *second* virial coefficients; C' and C are *third* virial coefficients; etc. For a given gas the virial coefficients are functions of temperature only.

The two sets of coefficients in Eqs. (8) and (9) are related as follows:

$$B' = \frac{B}{RT} \quad C' = \frac{C - B^2}{(RT)^2} \quad D' = \frac{D - 3BC + 2B^3}{(RT)^3} \quad \text{etc.}$$

The derivation of these relations requires first the elimination of P on the right of Eq. (8). An expression for P comes from Eq. (9) with Z replaced by $P V/RT$. The resulting equation is a power series in $1/V$ which is compared term by term with Eq. (9) to provide the equations relating the two sets of virial coefficients.

Many other equations of state have been proposed for gases, but the virial equations are the only ones having a firm basis in theory. The methods of statistical mechanics allow derivation of the virial equations and provide physical significance to the virial coefficients. Thus, for the expansion in $1/V$, the term B/V arises on account of interactions between pairs of molecules; the C/V^2 term, on account of three-body interactions; etc. Since twobody interactions are many times more common than three-body interactions, and three-body interactions are many times more numerous than four-body interactions, etc., the contributions to Z of the successively higher-ordered terms decrease rapidly.

The Ideal Gas

Table below shows the differences between the ideal gas and the real gas.

Ideal gas	Real gas
1. No attraction between the molecules	There is an attraction force between molecules
2. Volume of molecules is negligible	Volume of molecules is not negligible
3. Equation of state is $PV=nRT$, $Z=1$ when $P=0$ $V_{g=\infty}$	Equation of state is $PV=ZnRT$, $Z \neq 1$, depend on (T,P)

Application of The Virial Equations

The two forms of the virial expansion are infinite series. For engineering purposes their use is practical only where convergence is very rapid, that is, where two or three terms suffice for reasonably close approximations to the

values of the series. This is realized for gases and vapours at low to moderate pressures.

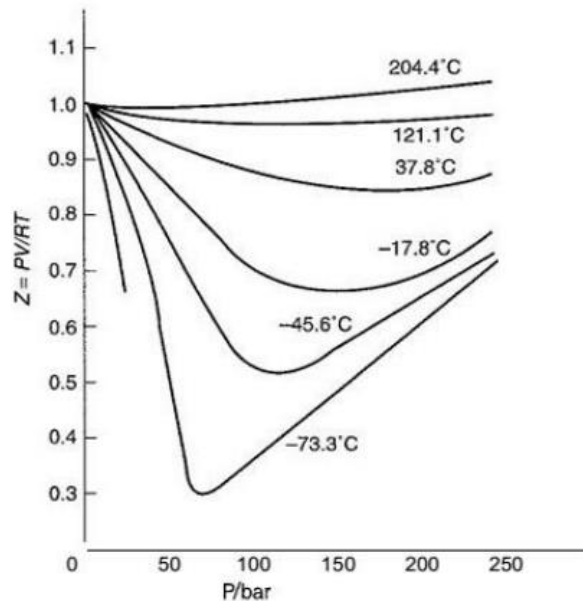


Fig.: Compressibility factor for methane

Values of the compressibility factor Z (as calculated from $P-V-T$ data for methane by the defining equation $Z = PV/RT$) are plotted vs. pressure for various constant temperatures. All isotherms originate at the value $Z = 1$ for $P = 0$. In addition the isotherms are nearly straight lines at low pressures. Thus the tangent to an isotherm at $P = 0$ is a good approximation of the isotherm from $P \rightarrow 0$ to some finite pressure. Differentiation of Eq. (8) for a given temperature gives:

$$\left(\frac{\partial Z}{\partial P}\right)_T = B' + 2C'P + 3D'P^2 + \dots$$

from which,

$$\left(\frac{\partial Z}{\partial P}\right)_{T;P=0} = B'$$

Thus the equation of the tangent line is:

$$Z = 1 + B'P$$

a result also given by truncating Eq. (8) to two terms. A more common form of this equation results from the substitution, $B' = B/RT$:

$$Z = \frac{PV}{RT} = 1 + \frac{BP}{RT}$$

Equation (9) may also be truncated to two terms for application at low pressures:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V}$$

However, this Eq. is more convenient in application and is more accurate. Thus when the virial equation is truncated to two terms, Eq. is preferred. This equation is satisfactory of pressure about up to 5 bar. The second virial coefficient B is substance dependent and a function of temperature.

For pressures above the range of applicability of Eq. above but below the critical pressure, the virial equation truncated to three terms often provides excellent results. In this case the appropriate form is:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2}$$

This equation can be solved directly for pressure, but is cubic in volume. Solution for V is easily done by an iterative scheme with a calculator.

Example 3.8

Reported values for the virial coefficients of isopropanol vapor at 200°C are:

$$B = -388 \text{ cm}^3 \text{ mol}^{-1} \quad C = -26,000 \text{ cm}^6 \text{ mol}^{-2}$$

Calculate V and Z for isopropanol vapor at 200°C and 10 bar by:

(a) The ideal-gas equation; (b) Equation (3.38); (c) Equation (3.40).

Solution 3.8

The absolute temperature is $T = 473.15 \text{ K}$, and the appropriate value of the gas constant is $R = 83.14 \text{ cm}^3 \text{ bar mol}^{-1} \text{ K}^{-1}$.

(a) For an ideal gas, $Z = 1$, and

$$V = \frac{RT}{P} = \frac{(83.14)(473.15)}{10} = 3,934 \text{ cm}^3 \text{ mol}^{-1}$$

(b) Solving Eq. (3.38) for V gives:

$$V = \frac{RT}{P} + B = 3,934 - 388 = 3,546 \text{ cm}^3 \text{ mol}^{-1}$$

Whence,
$$Z = \frac{PV}{RT} = \frac{V}{RT/P} = \frac{3,546}{3,934} = 0.9014$$

(c) To facilitate iteration, write Eq. (3.40) as:

$$V_{i+1} = \frac{RT}{P} \left(1 + \frac{B}{V_i} + \frac{C}{V_i^2} \right)$$

where subscript i denotes the iteration number. For the first iteration, $i = 0$, and

$$V_1 = \frac{RT}{P} \left(1 + \frac{B}{V_0} + \frac{C}{V_0^2} \right)$$

where $V_0 = 3,934$, the ideal-gas value. Numerically,

$$V_1 = 3,934 \left[1 - \frac{388}{3,934} - \frac{26,000}{(3,934)^2} \right] = 3,539$$

The second iteration depends on this result:

$$V_2 = \frac{RT}{P} \left(1 + \frac{B}{V_1} + \frac{C}{V_1^2} \right) = 3,934 \left[1 + \frac{388}{3,539} - \frac{26,000}{(3,539)^2} \right] = 3,495$$

Iteration continues until the difference $V_{i+1} - V_i$ is insignificant, and leads after five iterations to the final value,⁷

$$V = 3,488 \text{ cm}^3 \text{ mol}^{-1}$$

from which $Z = 0.8866$. In comparison with this result, the ideal-gas value is 13% too high and Eq. (3.38) gives a value 1.7% too high.