

Chapter Three

Volumetric Properties of Pure Fluids

1. 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 N_2 , O_2 , 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. 3.2. We notice the following behaviour:

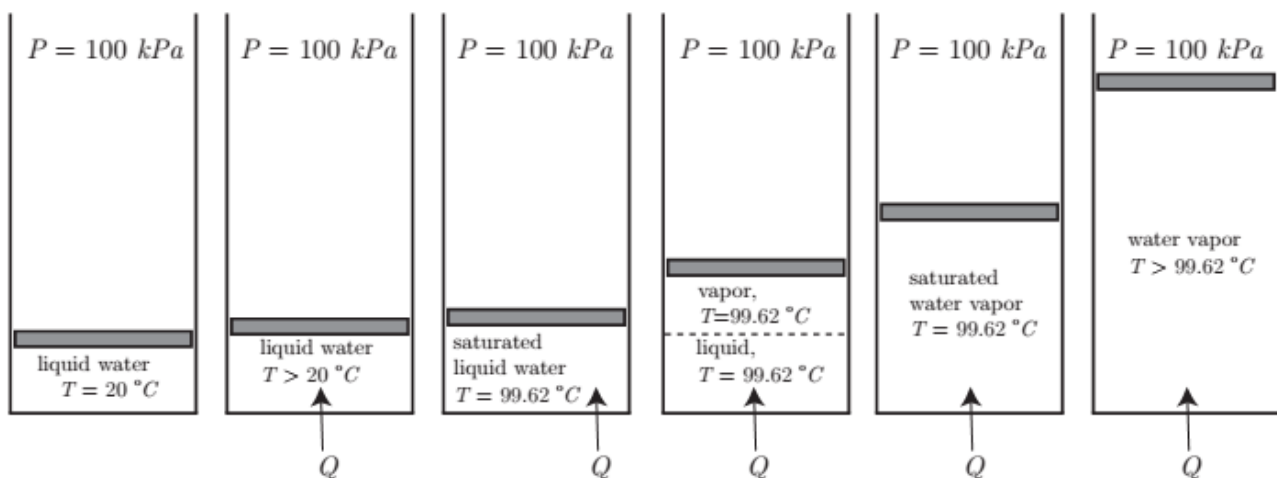


Figure 3.1: Sketch of experiment in which heat is added isobarically to water in a closed-piston-cylinder arrangement.

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 $T = 99.62^\circ\text{C}$, 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 $T = 99.62^\circ\text{C}$ 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. 3.2. Note that the mass m of the water is constant in this.

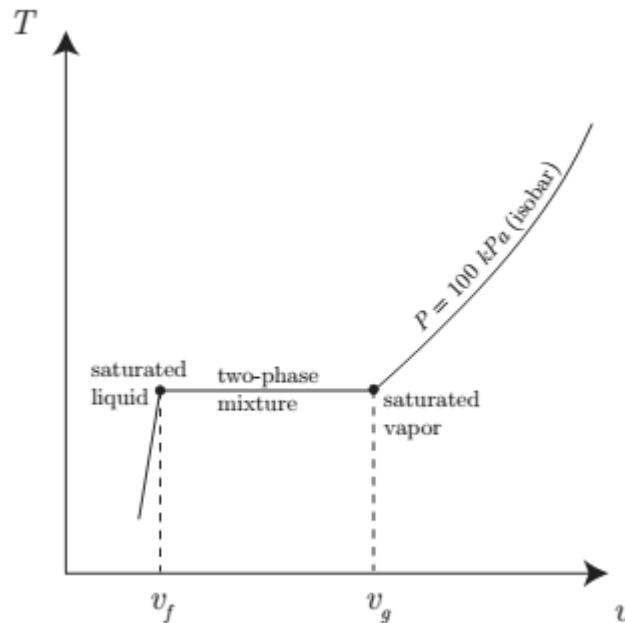


Figure 3.2: Isobar in the $T - v$ plane for our thought experiment in which heat is added isobarically to water in a piston-cylinder arrangement.

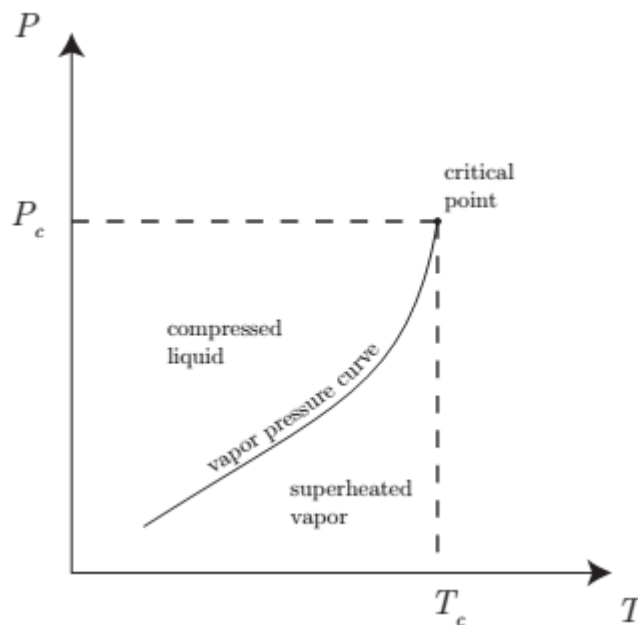


Figure 3.3: Saturation pressure versus saturation temperature sketch.

- 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} .

2. 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.

3. PVT BEHAVIOR OF PURE SUBSTANCES

3.1 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

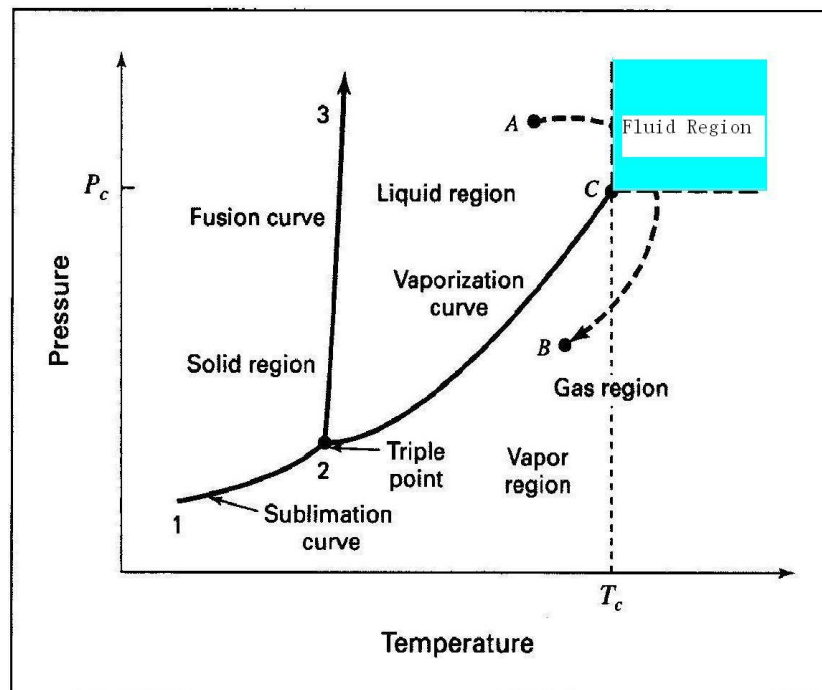


Figure 3.4 PT diagram for pure substance

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.

3.2 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.

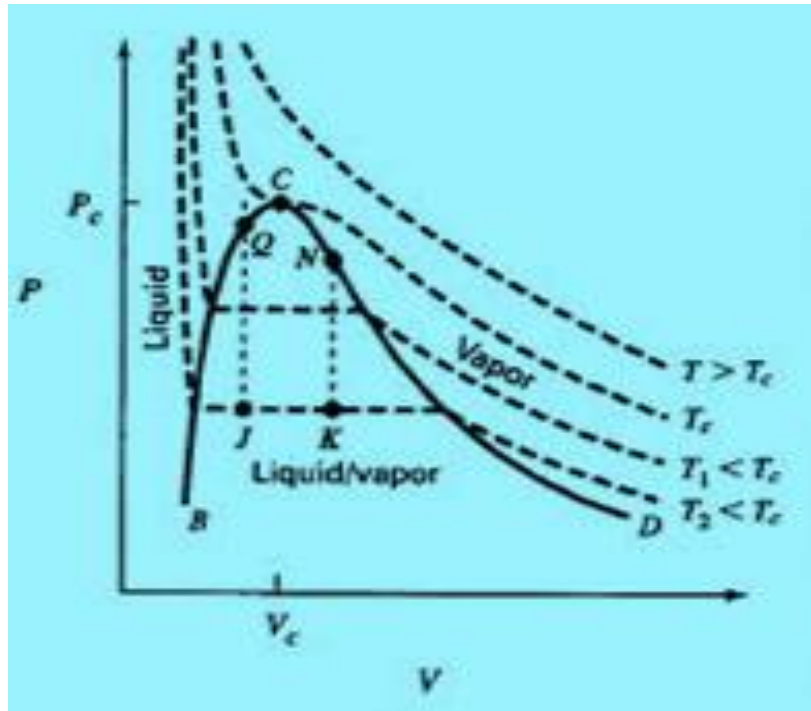


Figure 3.5 PV diagrams for a pure substance. Showing liquid, liquid/vapour, and vapour regions with isotherms

3.3 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. 3.5

if V is considered a function of T and P , then $V = f(T, P)$, and

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP \quad (3.1)$$

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)

$$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (3.2)$$

Isothermal compressibility (compressibility factor):

$$k = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (3.3)$$

Combination of Eqs. (3.1) through (3.3) provides the equation:

$$\frac{dV}{V} = \beta dT - \kappa dP \quad (3.4)$$

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

Thus for small changes in T and P little error is introduced if they are assumed constant. Integration of Eq. (3.4) then yields:

$$\ln \frac{V_2}{V_1} = \beta(T_2 - T_1) - \kappa(P_2 - P_1) \quad (3.5)$$

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

Example 3.1

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 3.1

(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 $dV = 0$:

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

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

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

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

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

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

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

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

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

3.4 VIRIAL EQUATIONS OF STATE

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,

$$PV = a(1 + B'P + C'P^2 + D'P^3 + \dots) \quad (3.6)$$

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

In principle, the right side of Eq. (3.6) 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.

Ideal-Gas Temperatures; Universal Gas Constant:

The limiting value of PV as $P \rightarrow 0$ is the same for all of the gases. In this limit (denoted by the asterisk), Eq. (3.6) becomes:

$$* \text{ means the pressure } (PV)^* = a = f(T) \text{ are near the zero.}$$

The simplest procedure, and the one adopted internationally, is:

Make $(PV)^*$ directly proportional to T , with R as the proportionality constant

$$(PV)^* = a = RT \quad (3.7)$$

Assign the value 273.16 K to the temperature of the triple point of water (denoted by subscript t):

$$(PV)_t^* = R \times 273.16 \text{ K} \quad (3.8)$$

:

Division of Eq. (3.7) by Eq. (3.8) gives:

$$\frac{(PV)^*}{(PV)_t^*} = \frac{T/K}{273.16 \text{ K}}$$

$$\boxed{T/K = 273.16 \frac{(PV)^*}{(PV)_t^*}} \quad (3.9)$$

Eq. (3.9) is known as the ideal-gas temperature scale.

The proportionality constant R in Eq. (3.7) is called the universal gas constant. Its numerical value is determined by means of Eq. (3.8) from experimental PVT data:

$$R = \frac{(PV)_t^*}{273.16 \text{ K}}$$

Since PVT data cannot in fact be taken at zero pressure, data taken at finite pressures are extrapolated to the zero-pressure state. Determined as indicated the accepted value of (PV) is $22.7118 \text{ m}^3 \text{ bar kmol}^{-1}$, leading to the following value of R

$$R = \frac{22.7118 \text{ m}^3 \text{ bar kmol}^{-1}}{273.16 \text{ K}} = 0.0831447 \text{ m}^3 \text{ bar kmol}^{-1} \text{ K}^{-1}$$

Two Forms of the Virial Equation

A useful auxiliary thermodynamic property is defined by the equation:

$$\boxed{Z \equiv \frac{PV}{RT}} \quad (3.10)$$

This dimensionless ratio is called the compressibility factor. With this definition and with $a = RT$ [Eq. (3.7)], Eq. (3.6) becomes:

$$\boxed{Z = 1 + B'P + C'P^2 + D'P^3 + \dots} \quad (3.11)$$

An alternative expression for Z is also in common use

$$\boxed{Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots} \quad (3.12)$$

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. (3.11) and (3.12) are related as follows:

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

3.5 THE IDEAL GAS

Table 3.1 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 $P=0$ $V_g \rightarrow \infty$	Equation of state is $PV=ZnRT$, $Z \neq 1$, depend on (T,P)