Volumetric properties of pure fluids

The equations of the preceding chapter provide the means for calculation of the heat and work quantities associated with various processes, but they are useless without knowledge of property values for internal energy or enthalpy. Such properties differ from one substance to another, and the laws of thermodynamics themselves do not provide any description or model of material behavior. Property values come from experiment, or from the correlated results of experiment, or from models grounded in and validated by experiment. Because there are no internal energy or enthalpy meters, indirect measurement is the rule. For fluids, the most comprehensive procedure requires measurements of molar volume in relation to temperature and pressure. The resulting pressure/volume/temperature (PVT) data are most usefully correlated by equations of state, through which molar volume (or density), temperature, and pressure are functionally related.

For example, 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:
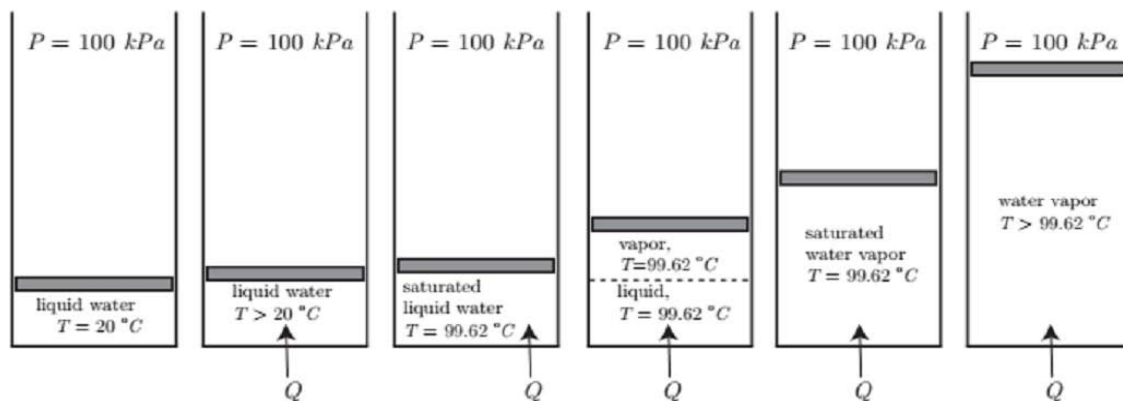

Figure (1): Sketch of experiment in which heat is added isobarically to water in a closed piston-cylinder arrangement.

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 ˚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◦C the saturation temperature at P = 100 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.
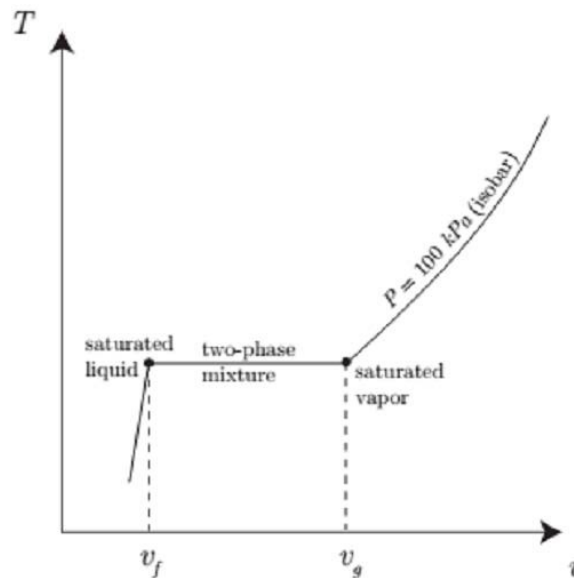

Figure (2): Isobar in the T − v plane for our thought experiment in which heat is added isobarically to water in a piston-cylinder arrangement.
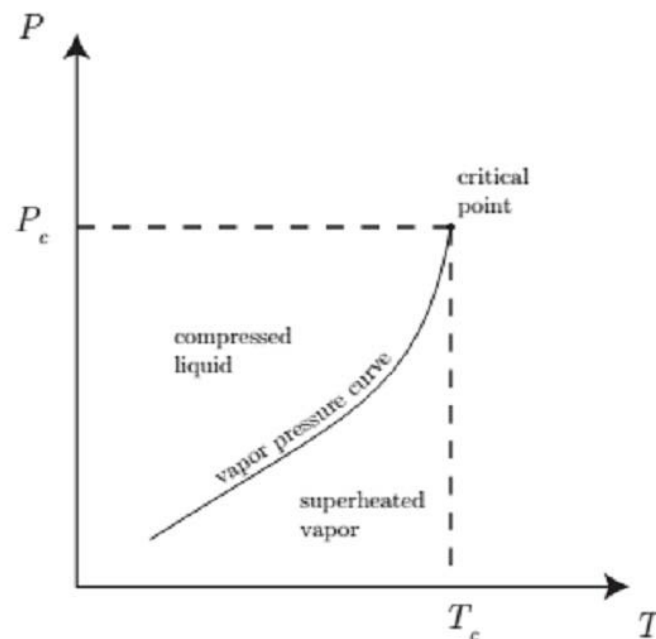

Figure (3): Saturation pressure versus saturation temperature sketch.

- 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 $T < T_{sat}$.
- Superheated vapor: the material is vapor with $T > Tsat$.
- 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 wich three curves are met (sublimation, fusion and vaporization).

Critical point: The point at highest temp. (Tc) and highest Pressure (Pc) 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 Tc and Pc, 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.
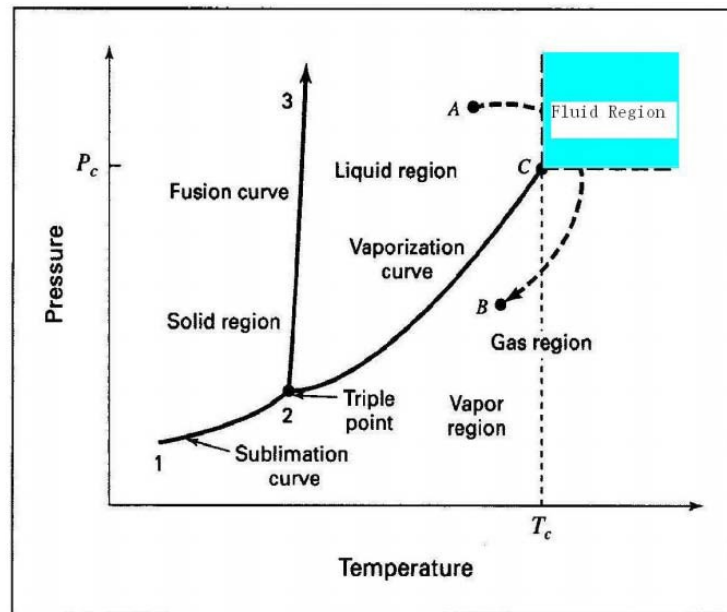
Figure (4) : PT digram for pure substance

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 gas region is sometimes divided into two parts, as indicated by the dotted vertical line of Fig. 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 > Tc including the fluid region, is termed supercritical.

P-V Diagram

Figure 5 shows the liquid, liquid/vapour, and vapour regions of the P V diagram, with four isotherms superimposed. Isotherms on Fig.4 are vertical lines, and at temperatures greater than Tc, do not cross a phase boundary. On Fig. 5 the isotherm labelled T > Tc 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.
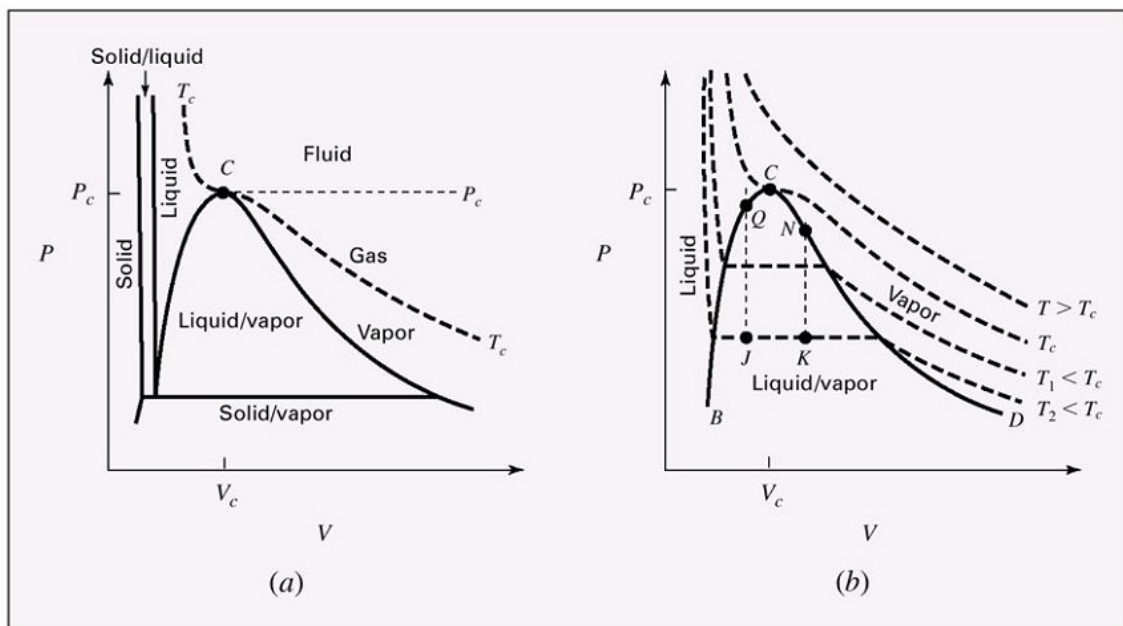

Figure (5): PV diagrams for a pure substance. (a) Showing solid,liquid and gas regions.(b) Showing liquid, liquid/vapour, and vapour regions with isotherms

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:

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

An equation of state may be solved for any one of the three quantities P, V, or T, given values for other two. For example, if V is considered a function of T and P, then V = V(T, P), and

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

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):

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

Isothermal compressibility (compressibility factor):

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

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

$$\frac{dV}{V} = \beta dT - K dP \qquad (3.4)$$

a) β and k are function of T, P they increased as T increased.
b) For real liquid β and K are constant when change in T,P is relative small
c) 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. (3.4) then yields:

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

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

Example :

For liquid acetone at 20°C and 1 bar,

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

For acetone, find:

(a) The value of $(\partial P / \partial T)_V$ at 20°C and 1 bar.

(b) The pressure after heating at constant V from 20°C and 1 bar to 30°C.

(c) The volume change when T and P go 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. (3.5) to the case for which V is constant and $dV = 0$:

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

or

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

(b) If β and κ are assumed constant in the 10°C temperature interval, then for constant volume Eq. (3.6) can be written:

$$P_2 = P_1 + \frac{\beta}{\kappa}(T_2 - T_1) = 1 \ \text{bar} + 24 \ \text{bar} \cdot °C^{-1} \times 10°C = 241 \ \text{bar}$$

(c) Direct substitution into Eq. (3.6) gives:

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

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

Then,

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