1. PVT behavior of pure substances

Measurements of the vapor pressure of a pure substance, both as a solid and as a liquid, lead to pressure-vs.-temperature curves such as shown by lines 1-2 and 2-C in Fig. 3.1. The third line (2-3)gives the solid/liquid equilibrium relationship. The three lines display conditions of P and T at which two phases may coexist, and are boundaries for the single-phase regions. Line 1-2, the sublimation cuwe, separates the solid and gas regions; line 2-3, the fusion cu we, separates the solid and liquid regions; line 2-C, the vaporization cu we, separates the liquid and gas regions. All three lines meet at the triple point, where the three phases coexist in equilibrium. According to the phase rule, Eq. (2.7),the triple point is invariant (F = 0). If the system exists along any of the two-phase lines of Fig. 3.1, it is univariant (F = I), whereas in the single-phase regions it is divariant (F = 2).

The vaporization curve 2-C terminates at point C , the critical point. The coordinates of this point are the critical pressure PC and the critical temperature Tc, the highest pressure and highest temperature at which a pure chemical species can exist in vapor/liquid equilibrium.

Homogeneous fluids are usually classified as liquids or gases. However, the distinction cannotalwaysbesharplydrawn,becausethetwophasesbecomeindistinguishableatthecritical point. Paths such as the one shown in Fig. 3.1 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.

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The area existing at temperatures and pressures greater than T, and P, is marked off by dashed lines in Fig. 3.1, which do not represent phase boundaries, but rather are limits fixed by the meanings accorded the words liquid and gas. A phase is generally considered a liquid if vaporization results from pressure reduction at constant temperature. A phase is considered a gas if condensation results from temperature reduction at constant pressure. Since neither process occurs in the area beyond the dashed lines, it is called the fluid region.

The gas region is sometimes divided into two parts, as indicated by the dotted vertical line of Fig. 3.1. 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,, including the fluid region, is termed supercritical.

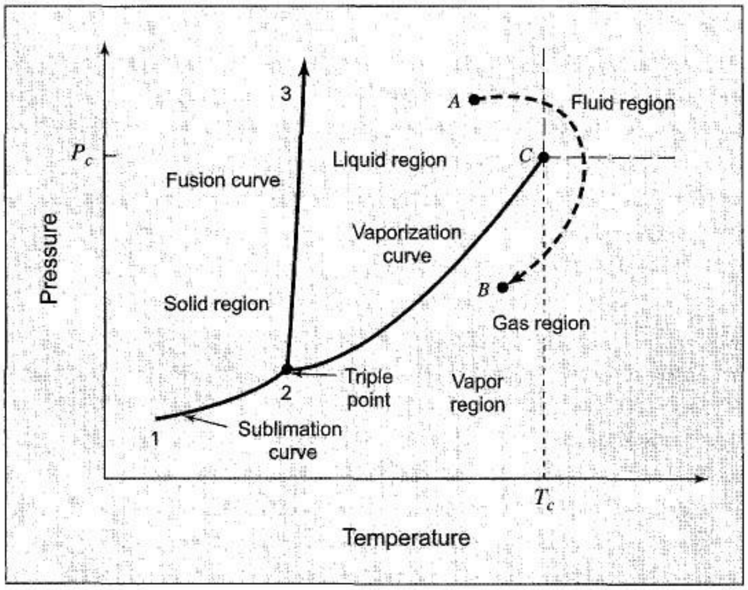

Fig. 3.1: PT diagram for a pure substance

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PV Diagram

Figure 3.1 does not provide any information about volume; it merely displays the phase boundaries on a *PT* diagram. On a P V diagram [Fig. 3.2(a)] these boundaries become areas, i.e., regions where two phases, solid/liquid, solidlvapor, and liquidvapor, coexist in equilibrium. For a given *T* and *P*, the relative amounts of the phases determine the molar (or specific) volume. The triple point of Fig. 3.1 here becomes a horizontal line, where the three phases coexist at a single temperature and pressure.

Figure *3.2(b)* shows the liquid, liquidvapor, and vapor regions of the *P* V diagram, with four isotherms superimposed. Isotherms on Fig. 3.1 are vertical lines, and at temperatures greater than *T,* do not cross a phase boundary. On Fig. 3.2(b) the isotherm labeled *T* > *T,* is therefore smooth.

The lines labeled *Tl* and *T2* are for subcritical temperatures, and consist of three segments. The horizontal segment of each isotherm represents all possible mixtures of liquid and vapor in equilibrium, ranging from 100% liquid at the left end to 100% vapor at the right end. The locus of these end points is the dome-shaped curve labeled BC D, 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) vapors at their condensation temperatures. The horizontal portion of an isotherm lies at a particular saturation or vapor pressure, given by the point on Fig. 3.1 where the isotherm crosses the vaporization curve.

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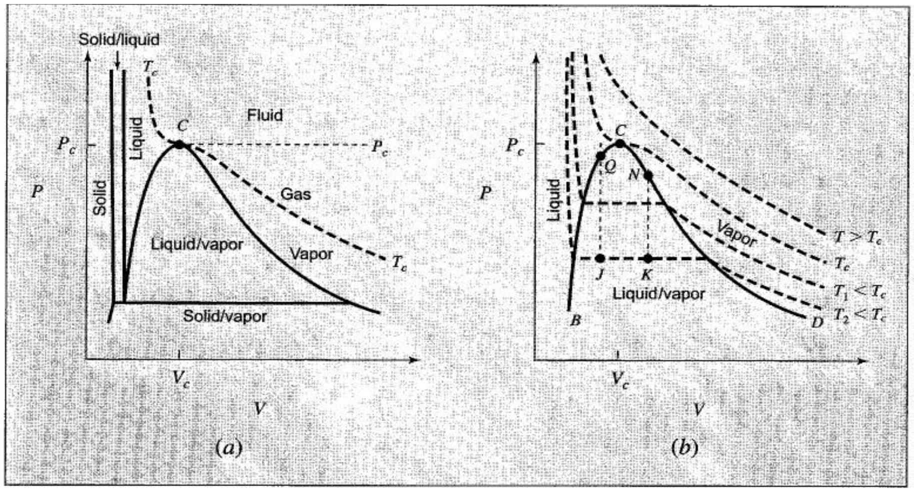

Fig. 3.2: PV diagrams for a pure substance. (a) Showing solid, liquid, and gas regions. (b) Showing liquid, liquidlvapor, and vapor regions with isotherms

The two-phase liquidlvapor region lies under dome BC D, whereas the subcooled-liquid and superheated-vapor regions lie to the left and right, respectively. Subcooled liquid exists at temperatures below, and superheated vapor, at temperatures above the boiling point for the given pressure. Isotherms in the subcooled-liquid region are very steep, because liquid volumes change little with large changes in pressure.

The horizontal segments of the isotherms in the two-phase region become progressively shorter at higher temperatures, being ultimately reduced to a point at C. Thus, the critical isotherm, labeled *T*,, exhibits a horizontal inflection at the critical point C at the top of the dome. Here the liquid and vapor phases cannot be distinguished from each other, because their properties are the same.

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Critical Behavior

Insight into the nature of the critical point is gained from a description of the changes that occur when a pure substance is heated in a sealed upright tube of constant volume. The dotted vertical lines of Fig. 3.2(b) indicate such processes. They may also be traced on the P T diagram of Fig. 3.3, where the solid line is the vaporization curve (Fig. 3.1), and the dashed lines are constant-volume paths in the single-phase regions. If the tube is filled with either liquid or gas, the heating process produces changes which lie along the dashed lines, e.g., by the change from E to F (subcooled-liquid) and by the change from G to H (superheated-vapor). The corresponding vertical lines on Fig. 3.2(b) lie to the left and to the right of BCD.

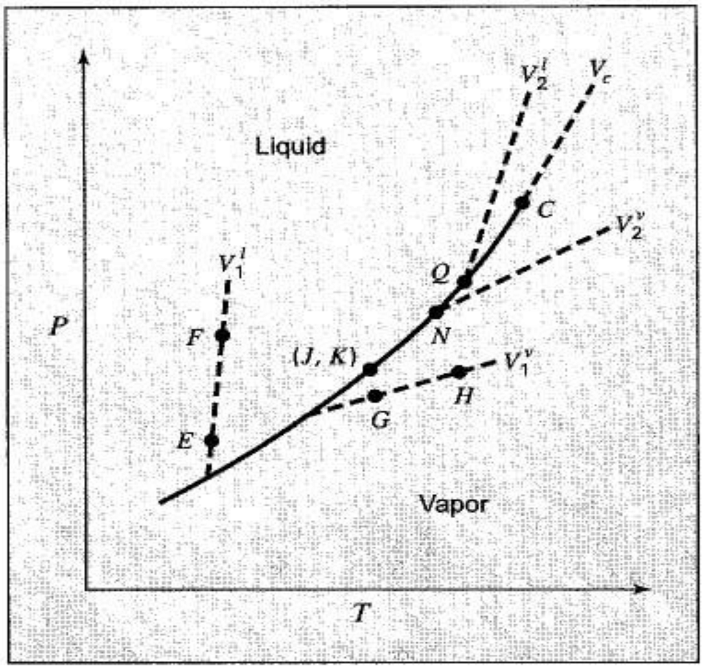

Fig. 3.3: PT diagram for a pure fluid showing the vapor-pressure curve and constant-volume lines in the single-phase regions.

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If the tube is only partially filled with liquid (the remainder being vapor in equilibrium with the liquid), heating at first causes changes described by the vapor-pressure curve (solid line) of Fig. 3.3. For the process indicated by line JQ on Fig. 3.2(b), the meniscus is initially near the top of the tube (point J), and the liquid expands upon heating until it completely fills the tube (point Q). On Fig. 3.3 the process traces a path from (J, K) to Q, and with further heating departs from the vapor-pressure curve along the line of constant molar volume v_2^l.

The process indicated by line KN on Fig. 3.2(b) starts with a lower meniscus level in the tube (point K); heating causes liquid to vaporize, and the meniscus recedes to the bottom of the tube (point N). On Fig. 3.3 the process traces a path from (J, K) to N. With further heating the path continues along the line of constant molar volume V_2^l.

For a unique filling of the tube, with a particular intermediate meniscus level, the heating process follows a vertical line on Fig. 3.2(b) that passes through the critical point C. Physically, heating does not produce much change in the level of the meniscus. As the critical point is approached, the meniscus becomes indistinct, then hazy, and finally disappears. On Fig. 3.3 the path first follows the vapor-pressure curve, proceeding from point (J, K) to the critical point C, where it enters the single-phase fluid region, and follows *V*,, the line of constant molar volume equal to the critical volume of the fluid.

Single-Phase Region

For the regions of the diagram where a single phase exists, Fig. 3.2(b) implies a relation connecting P, V, and T which may be expressed by the functional equation:

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

This means that an equation of state exists relating pressure, molar or specific volume, and temperature for any pure homogeneous fluid in equilibrium states. 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. 3.2(b), and which is discussed in detail in Sec. 3.3. An equation of state may be solved for any one of the three quantities P, V, or T as a function of the 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:*** $$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad (3.2)$$
- ***Isothermal compressibility:*** $$\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right), \qquad (3.3)$$

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

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

The isotherms for the liquid phase on the left side of Fig. 3.2(b) are very steep and closely spaced. Thus both (aV/aT)p and (aV/aP), and hence both @ and K are small. This characteristic behavior of liquids (outside the critical region) suggests an idealization, commonly employed in fluid mechanics and known as the in compressible fluid, for which both ,8 and K are zero. No real fluid is truly incompressible, but the idealization is useful, because it often provides a sufficiently realistic model of liquid behavior for practical purposes. There is no PVT equation of state for an incompressible fluid, because V is independent of T and P.

For liquids β is almost always positive (liquid water between 273.15 K (0°C) and 277.15 K (4°C) is an exception), and K is necessarily positive. At conditions not close to the critical point, β and K are weak functions of temperature and pressure. Thus for small changes in T and P little error is introduced if they are assumed constant. Integration of Eq. (3.4) then yields:

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

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

Example

For liquid acetone at 20°C and 1 bar,

$\beta = 1.487 \times 10^{-3}\ {}^\circ C^{-1}$

κ = 62 × 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.

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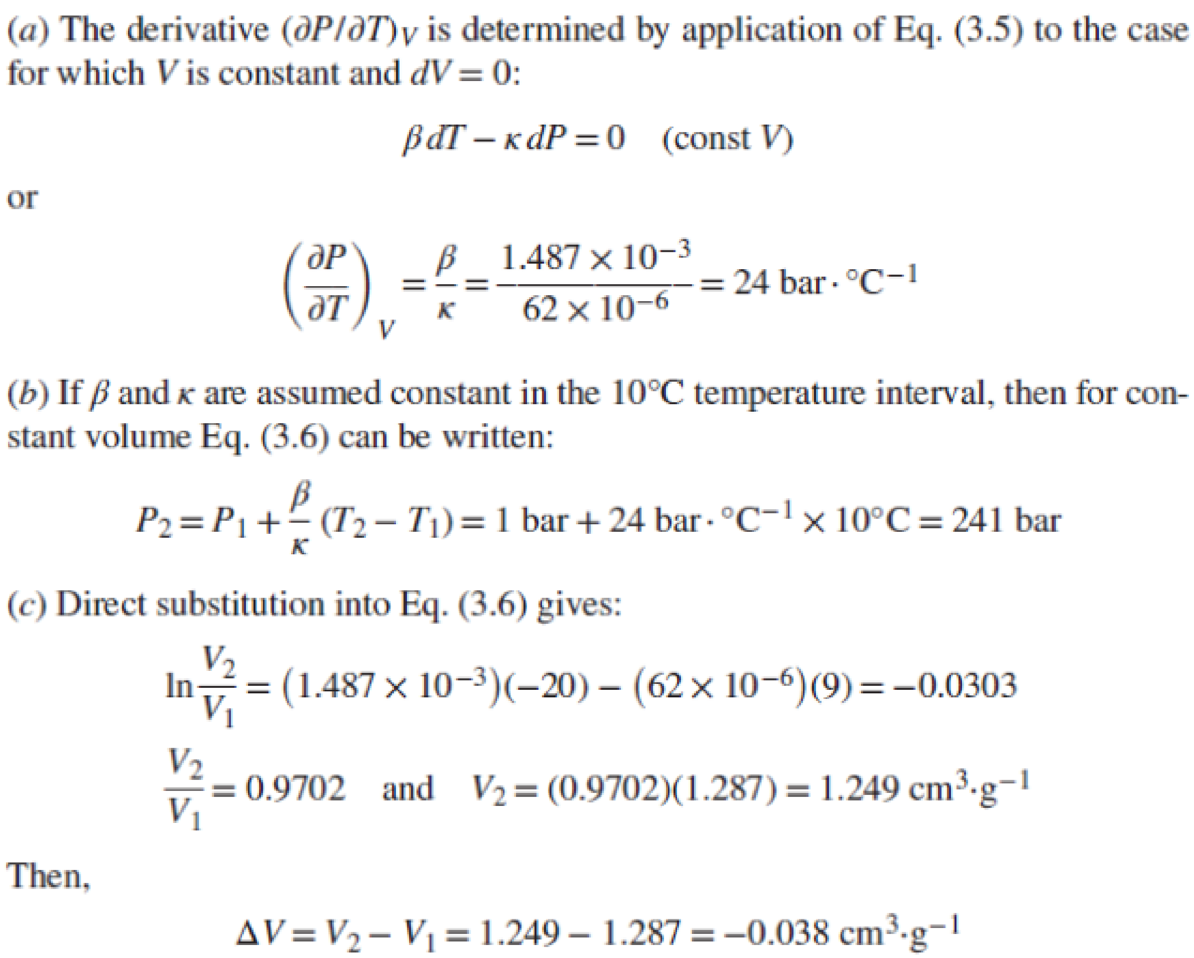
(c) The volume change when T and P go from 20°C and 1 bar to 0°C and 10 bar.

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 $dV = 0$:

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

or

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

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

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

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

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

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

Then,

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

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