CEN 202 Thermodynamics

CHAPTER 3: Volumetric Properties of Pure Fluids

The Phase Rule

PVT Behaviour of Pure Substances

PV Diagram

PT diagram does not provide any information about volume. Figure 3.2 shows PV diagrams for a pure substance (a: solid/liquid and gas regions; b: liquid, liquid/vapour and vapour regions with isotherms).

Solid; Liquid; Vapour; Gas;

Critical point;

Fluid;

Subcooled-liquid; Superheated-vapour, Homogenous region, Heterogeneous region,

Critical behaviour

- T_c isotherm
- P_c isobar
- V_c isochore

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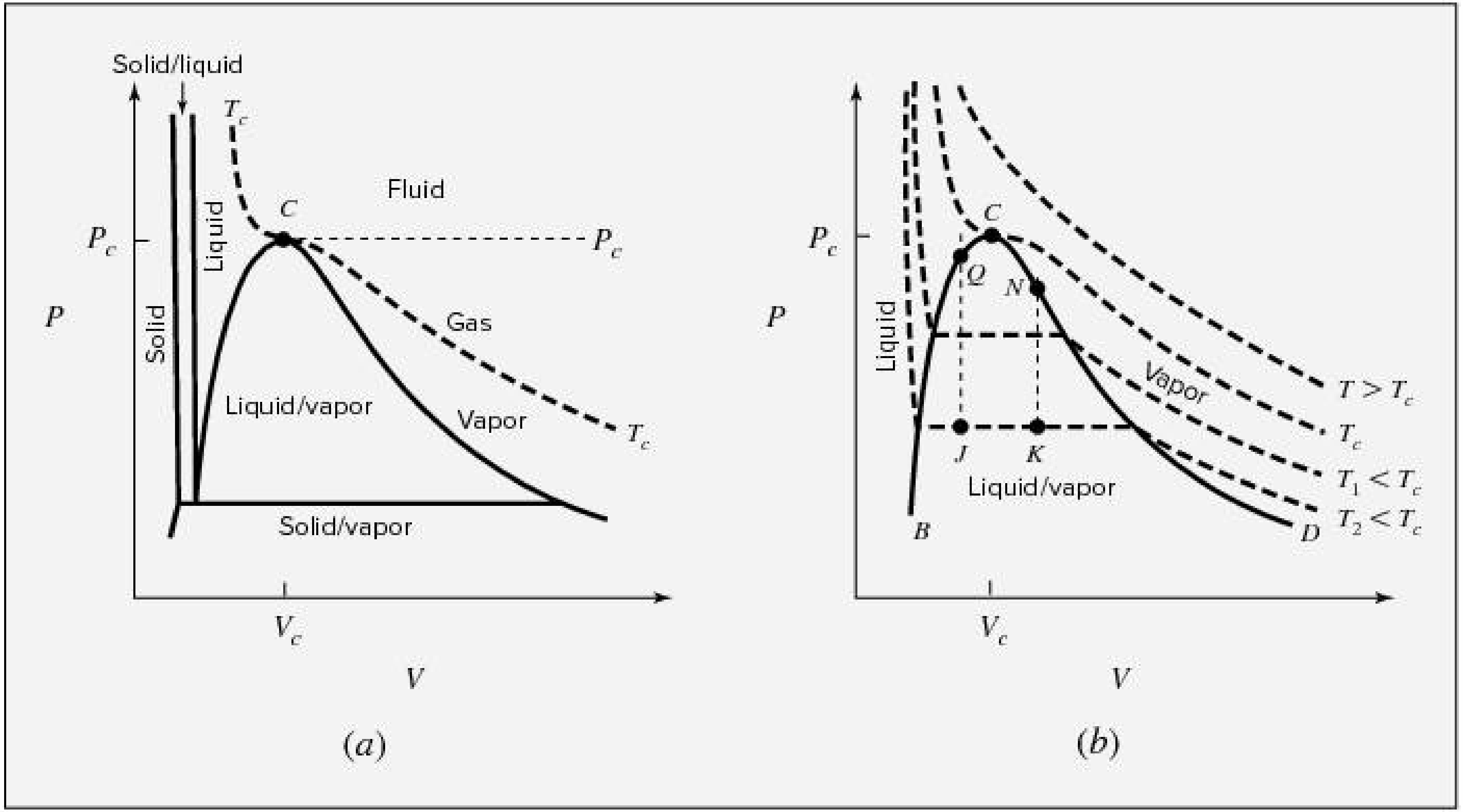

Figure 3.2: *PV* diagrams for a pure substance. (*a*) Showing solid, liquid, and gas regions. (*b*) Showing liquid, liquid/vapor, and vapor regions with isotherms.

Text Book: : J. M. Smith, H. C. Van Ness, M. M. Abbott, M. T. Swihart. "INTRODUCTION TO CHEMICAL ENGINEERING THERMODYNAMICS", EIGHTH EDITION. 2018

Single - Phase Regions

For the single phase regions, there is a unique relation connecting P,V and T. Expressed analytically f(P,V,T)=0, such a relation is known as a PVT equation of state (for example the ideal-gas state, PV=RT).

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

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \qquad 3.2$$

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

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Volume expansivity: $\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

Isothermal compressibility: $\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

Combining these two equations; $\ln\frac{V_2}{V_1} = \beta(T_2 - T_1) - \kappa(P_2 - P_1)$

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Ideal Gas and Ideal-Gas State

Ideal gases are hypothetical gases whose molecules occupy negligible space and have no interaction; consequently, they obeys the gas law exactly. The PVT behaviour of gases at moderate conditions of temperature and pressure is formulised by the gas law:

The equation; PV = RT (V: molar volume, R: universal constant).

Deviations become ever smaller as pressure decrease and temperature increases. This is an ideal gas and called ideal gas law (**valid only for P → 0 and T → infinity**).

The internal energy of a real gas depends on both P and T. In the absence of intermolecular forces, internal energy would depend T only.

- **The equation of state:** $PV^{ig} = RT$ **(ig: ideal gas)**
- **Internal energy:** $U^{ig} = U(T)$

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Ideal Gas and Ideal-Gas State; Property Relations for the Ideal-Gas State

The definition of heat capacity at constant V (function of temperature ONLY),

$$C_V^{ig} \equiv \left(\frac{\partial U^{ig}}{\partial T}\right)_V = \frac{dU^{ig}(T)}{dT} = C_V^{ig}(T)$$

$$H^{ig} \equiv U^{ig} + PV^{ig} = \boldsymbol{U^{ig}(T) + RT = H^{ig}(T)}$$

Heat capacity at constant P (function of temperature ONLY),

$$C_P^{ig} \equiv \left(\frac{\partial H^{ig}}{\partial T}\right)_P = \frac{dH^{ig}(T)}{dT} = C_P^{ig}(T)$$

A useful relation between C_p^{ig} and C_V^{ig} for the ideal gas state comes from differentiation of

$$C_p^{ig} \equiv \frac{dH^{ig}}{dT} = \frac{dU^{ig}}{dT} + R = C_V^{ig} + R$$

From the equations above;

$dU^{ig} = C_V^{ig}\,dT \rightarrow \Delta U^{ig} = \int C_V^{ig}\,dT$	**Functions of temperature only, regardless of the kind of process**
$dH^{ig} = C_P^{ig}\,dT \rightarrow \Delta H^{ig} = \int C_P^{ig}\,dT$	

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Process Calculations for the Ideal-Gas State

For ideal gas; $P = RT/V^{ig}$

$$dQ = C_V^{ig}\, dT + RT\frac{dV^{ig}}{V^{ig}}$$

$$dW = -RT\frac{dV^{ig}}{V^{ig}}$$

$$dQ = C_P^{ig}\, dT - RT\frac{dP}{P}$$

$$dW = -RdT + RT\frac{dP}{P}$$