

CH365 Chemical Engineering Thermodynamics

Lesson 10 P-V-T Behavior of Pure Gases

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WPR1 AAR

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Chapter 3 - Overview

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- The equations from chapter 2 allow the calculation of heat and work associated with processes. However, these equations are useless without enthalpy and internal energy values. These are different for each substance and cannot be calculated directly from the laws of thermodynamics. Property values come from experiment or from models validated by experiment.

Hidden Material – Take Notes

Gibbs' Phase Rule

$$F = 2 - \pi + N$$

(3.1, page 69)

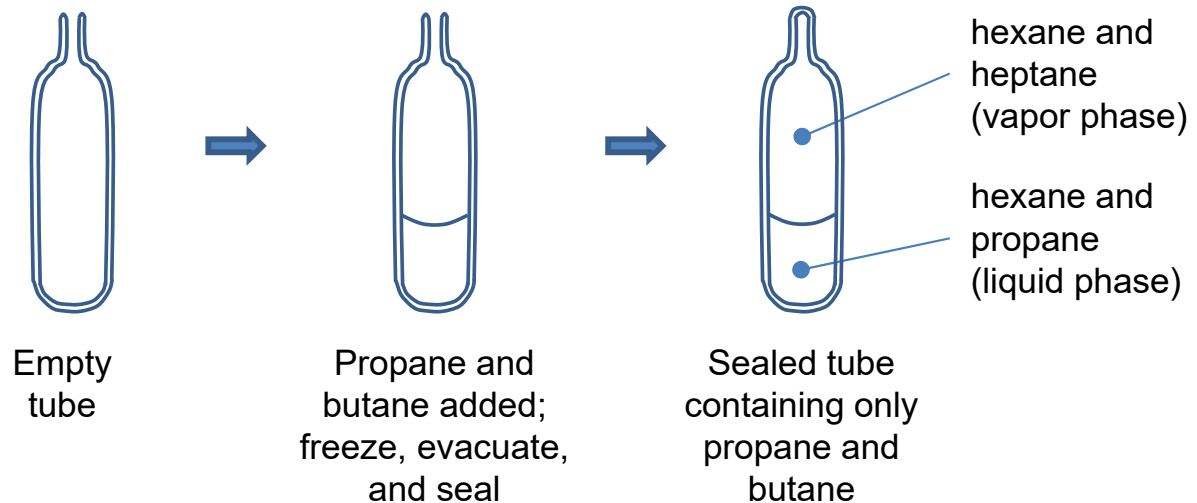
For intensive variables only.
Derived formally in Chapter 12.

Add 50 mol of n-hexane and 50 mol of n-heptane to the tube, freeze it, evacuate and seal it. Allow it to equilibrate at 2 bar and 381.1 K.

Total moles of vapor = ?
Total moles of liquid = ?
Total moles of both = 100

These are all extensive properties. They depend on the "extent" of the system. That is, "how much." The phase rule does not describe these.

Intensive properties do not depend on the size of a system (page 6).



F = degrees of freedom
 π = number of phases
N = number of chemical species

$$\begin{aligned} F &= 2 - \pi + N \\ &= 2 - 2 + 2 \\ &= 2 \end{aligned}$$

Normally specify T and P (2 bar, 381.1 K)

Specifying any two intensive variable allows all other intensive variables to be calculated. For example, specifying T and P allows calculation of V.

Problem 3.2

A renowned laboratory reports quadruple-point coordinates of 10.2 Mbar and 24.1 °C for the four-phase equilibrium of allotropic solid forms of the exotic chemical “ β -maiasmone.” Examine the claim using the Gibbs phase rule and provide a plausible explanation for your results.

Problem 3.4

A system of propane and n-butane exists in two-phase vapor/liquid equilibrium at 10 bar and 323 K. The mole fraction of propane is about 0.67 in the vapor phase and about 0.40 in the liquid phase. Additional pure propane is added to the system, which is brought again to equilibrium at the same T and P, with both liquid and vapor phases still present. What is the effect of the addition of propane on the mole fractions of propane in the vapor and liquid phases?

3.4 Can be Done in CHEMCAD

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Volume Expansivity & Isothermal Compressibility

Very important definition from calculus:

Single-variable function: $y = f(x) \Rightarrow \frac{dy}{dx} = f'(x) \Rightarrow dy = f'(x)dx$

Multi-variable function: $y = f(x, z) \Rightarrow dy = \left(\frac{\partial f}{\partial x} \right)_z dx + \left(\frac{\partial f}{\partial z} \right)_x dz$

This definition will be used in future lessons.

“Equation of State”

Relates molar volume to temperature and pressure.

Ideal Gas Law:

$$PV = RT \Rightarrow V = \frac{RT}{P}$$

Any EoS: $\Rightarrow V = V(T, P) \Rightarrow dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP \quad (3.2)$

Volume expansivity:

$$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (3.3)$$

Isothermal compressibility:

$$\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (3.4)$$

Molar volume V decreases as P increases, so the negative sign makes κ positive.

Important for PS4:

$$\frac{dV}{V} = \beta dT - \kappa dP \quad (3.5)$$

$$\ln \left(\frac{V_2}{V_1} \right) = \beta (T_2 - T_1) - \kappa (P_2 - P_1) \quad (\beta, \kappa \text{ constant}) \quad (3.6)$$

Problem 3.6

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- (1) Express the volume expansivity (β) and isothermal compressibility (κ) as functions of density and its partial derivatives. For water at 50 °C and 1 bar, $\kappa = 44.18 \times 10^{-6} \text{ bar}^{-1}$.

Example 3.2, part a

For liquid acetone at 20 °C and 1 bar,

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

For acetone, find

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

Example 3.2, part b

For liquid acetone at 20 °C and 1 bar,

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

For acetone, find

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

Example 3.2, part c

For liquid acetone at 20 °C and 1 bar,

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

For acetone, find

(c) The change in volume for a change from 20 °C and 1 bar to 0 °C and 10 bar.

Hidden Material – Take Notes

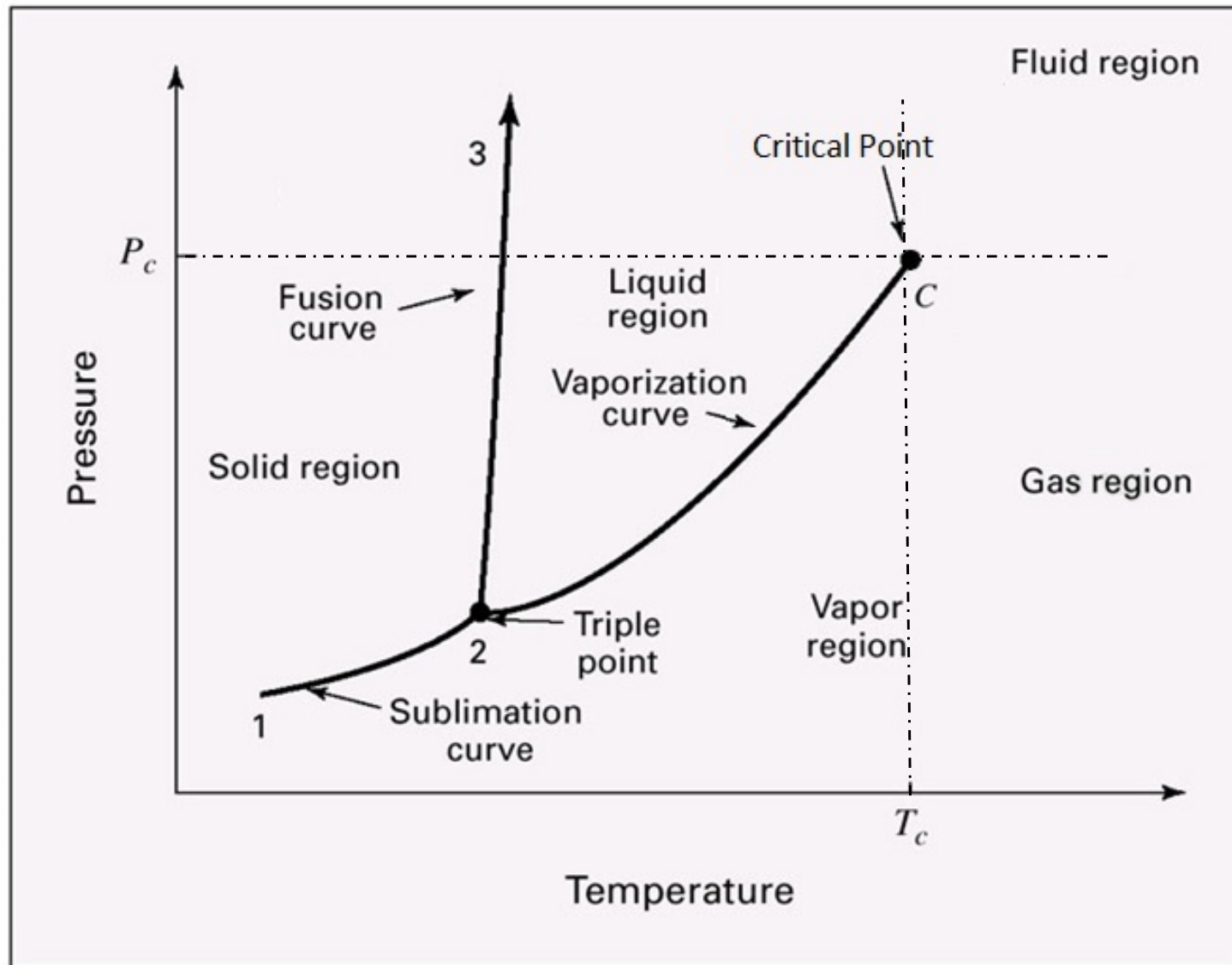


Figure 3.1: PT diagram for a pure substance.

Critical point – (T_c, P_c) - highest T and P at which a pure species is observed to exist in vapor/liquid equilibrium.

Triple point – (T_c, P_c) – All three phases exist in equilibrium. Phase Rule - Invariant

$$F = 2 - \pi + N = 2 - 3 + 1 = 0$$

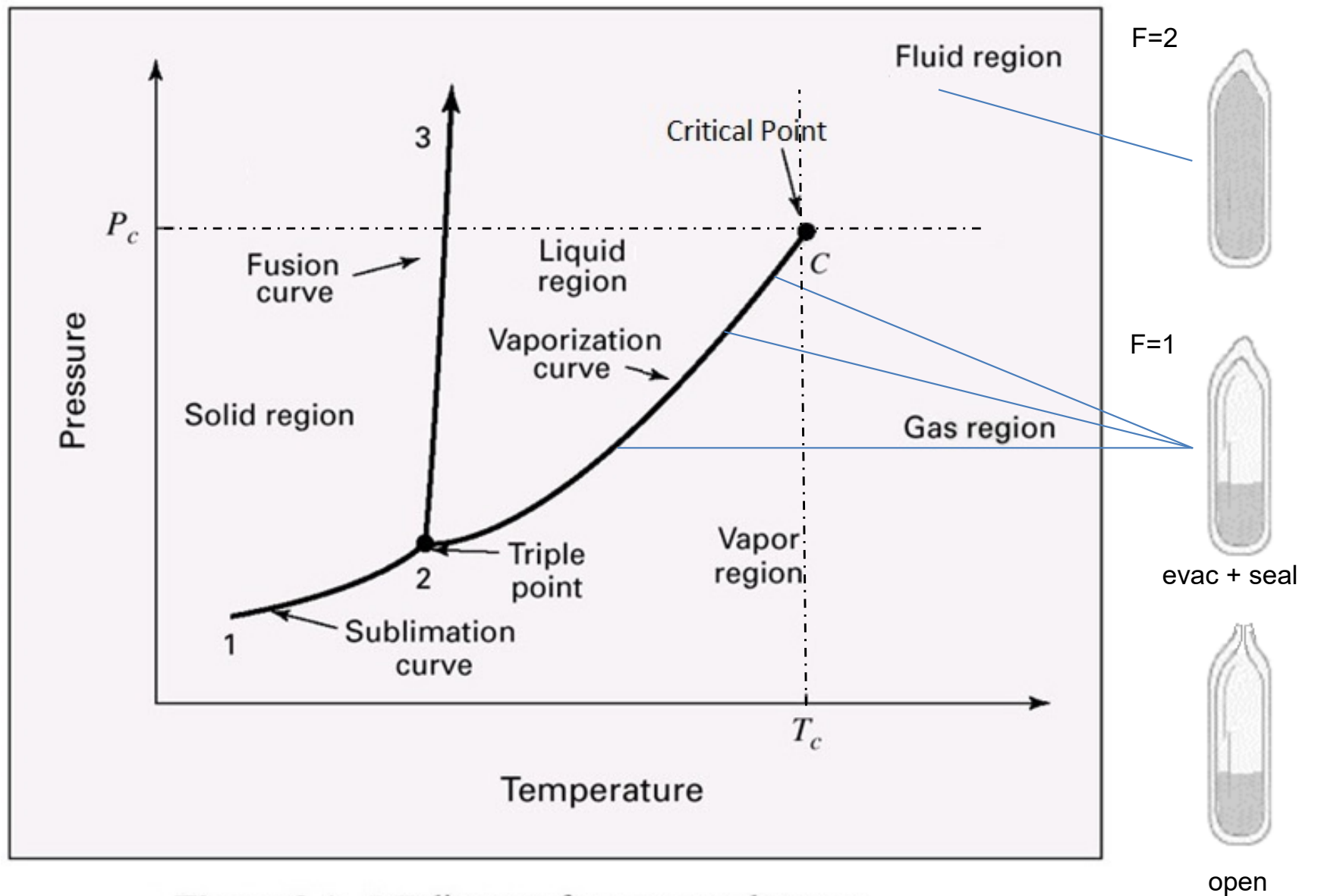


Figure 3.1: PT diagram for a pure substance.

$$N = 1$$

$$F = 2 - \pi + N$$

Place pure fluid
in flask.

Ideal gas: $PV = RT \Rightarrow P = \frac{RT}{V}$

What does the P vs V plot look like at high T ?

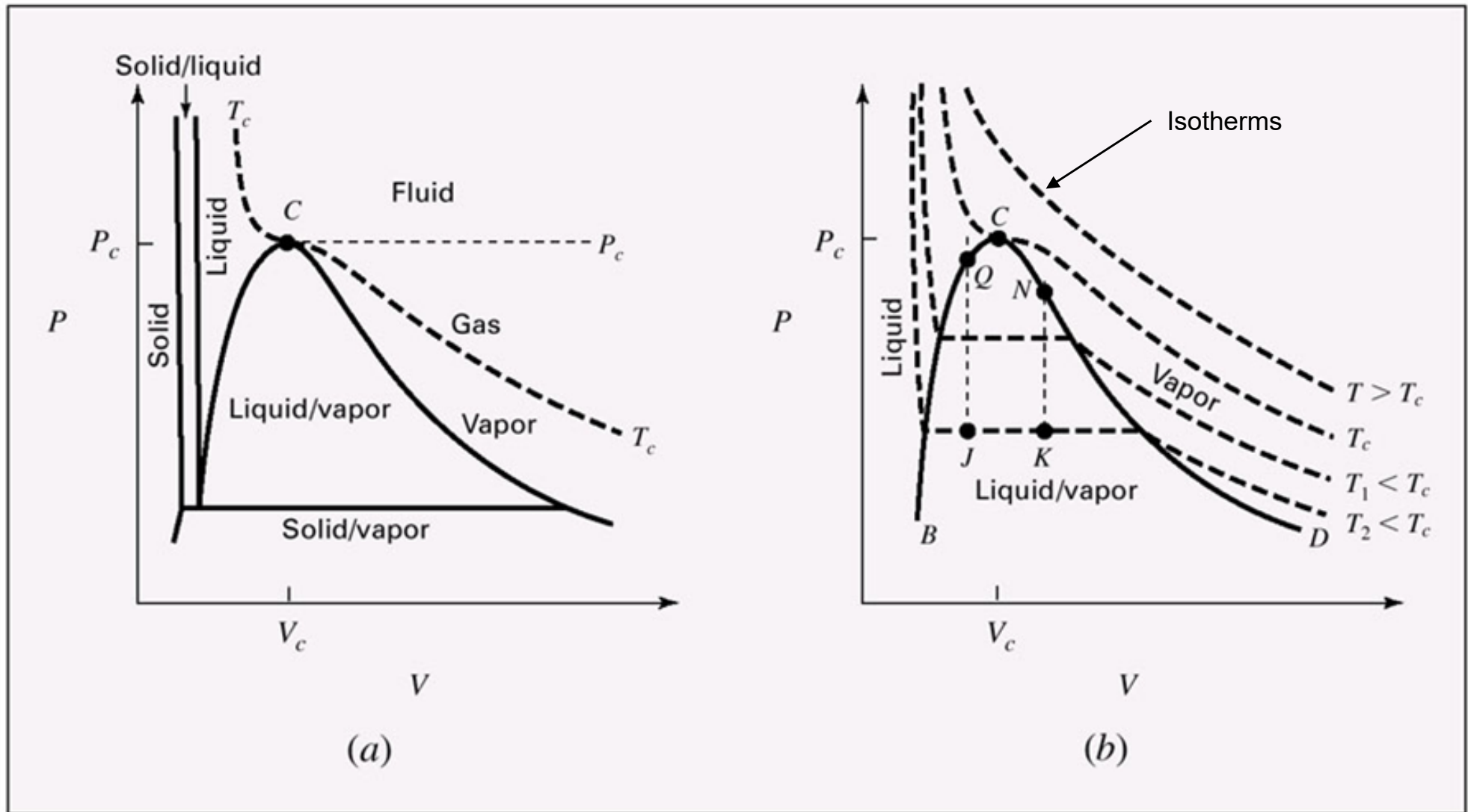
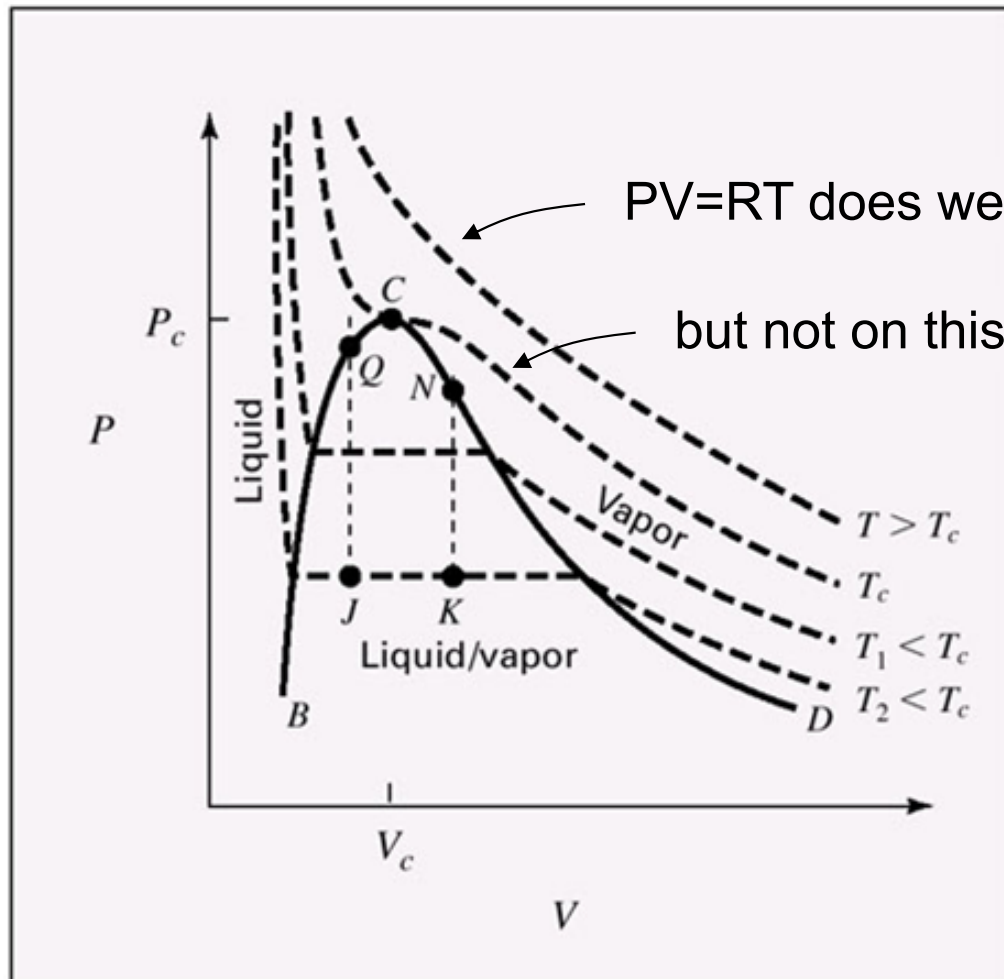


Figure 3.2: P V diagrams for a pure substance. (a) Showing solid, liquid, and gas regions. (b) Showing liquid, liquid/vapor, and vapor regions with isotherms.

Improved Equations of State



$PV=RT$ does well on this curve

but not on this one !

Improved model:

$$PV = a + bP + cP^2 + dP^3 \dots$$

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

$$b = aB', \quad c = aC', \quad d = aD', \quad \text{etc.}$$

Constants b , c , d , etc., are species-dependent and functions of T

“ a ” is found by experiment to be the same function of T for all species

Lesson 10 Homework Problems

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Problem 3.6

Express the volume expansivity (β) and isothermal compressibility (κ) as functions of density and its partial derivatives. For water at 50 °C and 1 bar, $\kappa = 44.18 \times 10^{-6} \text{ bar}^{-1}$. To what pressure must water be compressed at 50 °C to change its density by 1%? Assume κ is independent of P .

$$d\rho = \left(\frac{\partial \rho}{\partial T} \right)_P dT + \left(\frac{\partial \rho}{\partial P} \right)_T dP$$

$$\kappa \equiv \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T$$

$$\beta \equiv -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P$$

$$\kappa \rho = \left(\frac{\partial \rho}{\partial P} \right)_T$$

$$\kappa \equiv +\frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T$$

$$\kappa \rho dP = d\rho \quad (\text{const } T)$$

$$\kappa dP = \frac{d\rho}{\rho} \quad (\text{const } T)$$

$$\frac{d\rho}{\rho} = \beta dT + \kappa dP$$

$$\int_{P_1}^{P_2} \kappa dP = \int_{\rho_1}^{\rho_2} \frac{d\rho}{\rho} \quad (\text{const } T)$$

Problem 3.9

For liquid water the isothermal compressibility is given by

$$\kappa = \frac{c}{V(P + b)}$$

where c and b are functions of temperature only. If 1 kg of water is compressed isothermally and reversibly from 1 to 500 bar at 60 °C, how much work is required? At 60 °C, $b=2,700$ bar and $c=0.125$ cm³ g⁻¹.