CH365 Chemical Engineering Thermodynamics

Lesson 10
P-V-T Behavior of Pure Gases

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Objectives

1. For mathematical functions of more than one variable, be able to write the total differential from the partial derivatives.

2. For the molar volume V=V(T,P), be able to write the total differential in terms of the partial derivatives.

3. Be able to qualitatively describe the P-V-T behavior of pure gases using P-T and P-V diagrams.

4. Describe the behavior of a vapor-liquid system between the triple point and the critical point.

5. Explain how the improved equations of state account for non-ideal behavior near the critical point.

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.

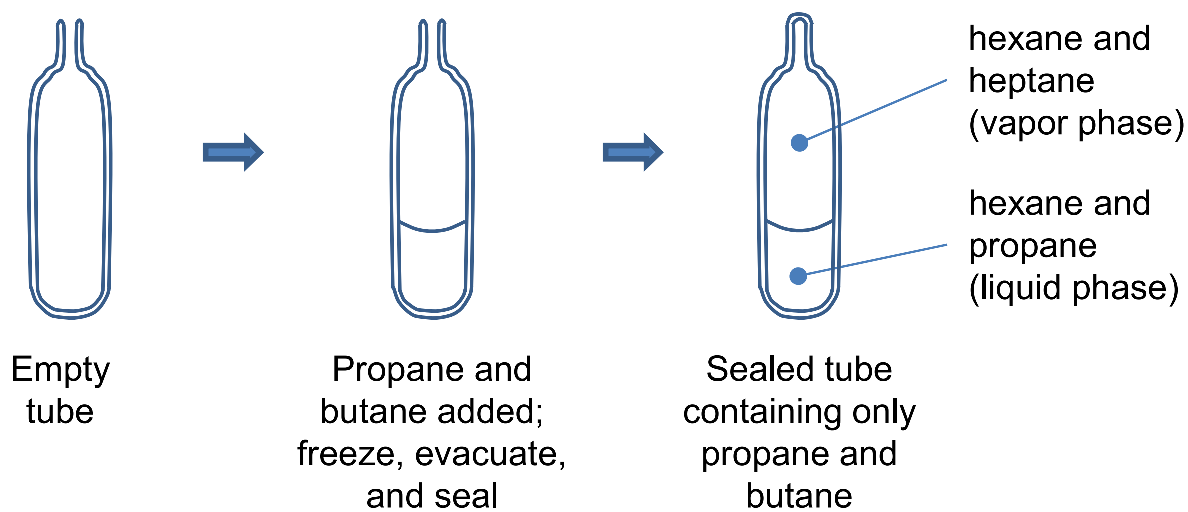
Hidden Material – Take Notes

Gibbs' Phase Rule

$$\boxed{F = 2 - \pi + N}$$ (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.



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

Specifying <u>any</u> two intensive variable allows all other <u>intensive</u> variables to be calculated. For example, specifying T and P allows calculation of V (molar volume).

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.

Hidden Material – Take Notes

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 0.6827 in the vapor phase and about 0.4458 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?

Application of Problem 3.4

Hidden Material – Take Notes

Volume Expansivity & Isothermal Compressibility

Very important definition from calculus:

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

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

This definition will be used in future lessons.

"Equation of State"

Relates molar volume to temperature and pressure.

Ideal Gas Law:

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

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

Liquids and Solids:

Volume expansivity:

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

Isothermal compressibility:

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

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

Important for PS4:

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

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

Problem 3.6

(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, $\kappa = 44.18 \times 10^{-6}$ bar^{-1}.

Hidden Material – Take Notes

Example 3.2, part a

For liquid acetone at 20 °C and 1 bar,

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

For acetone, find

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

Hidden Material – Take Notes

Example 3.2, part b

For liquid acetone at 20 °C and 1 bar,

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

For acetone, find

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

Hidden Material – Take Notes

Example 3.2, part c

For liquid acetone at 20 °C and 1 bar,

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

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

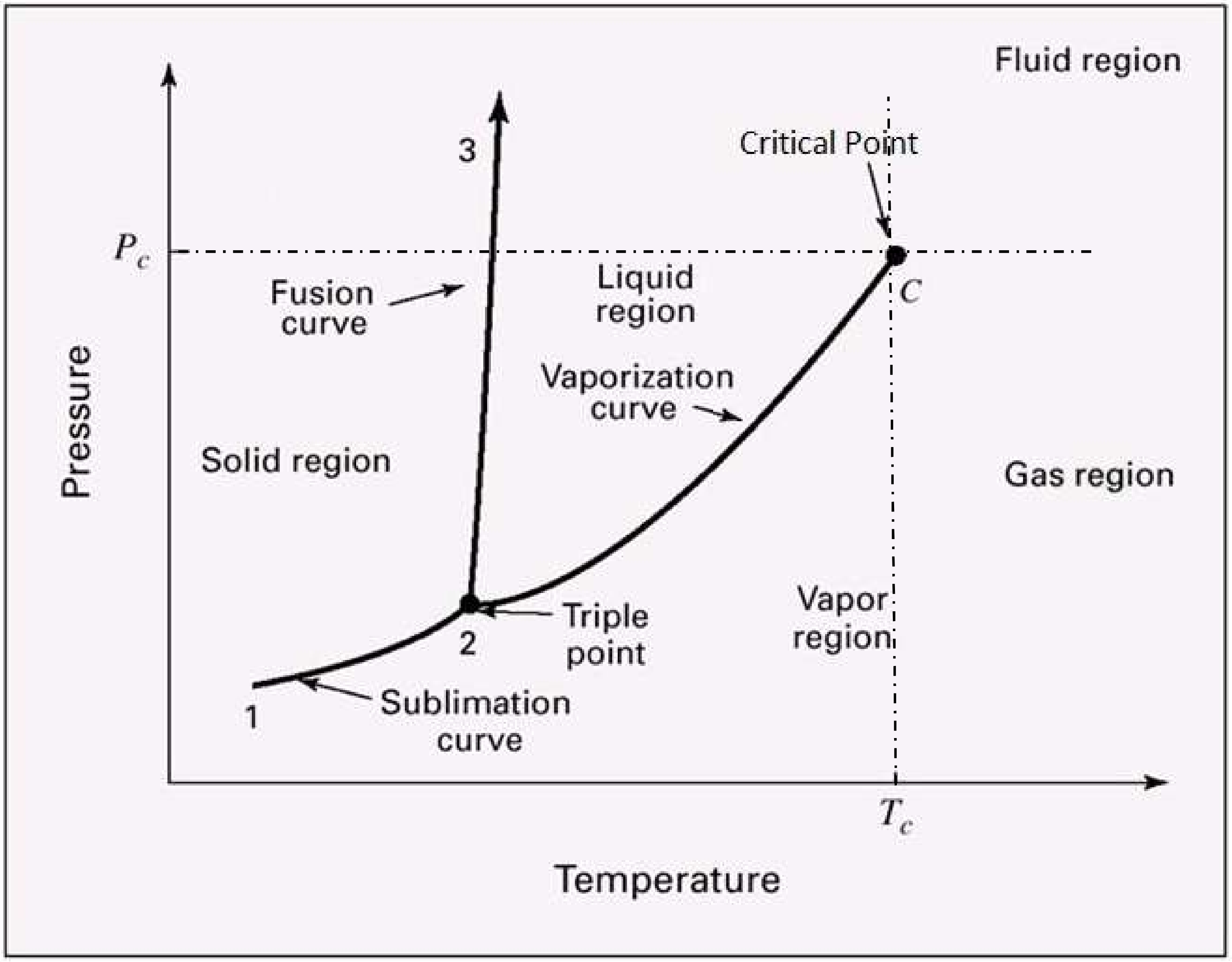


Figure 3.1: *PT* diagram for a pure substance.

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

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

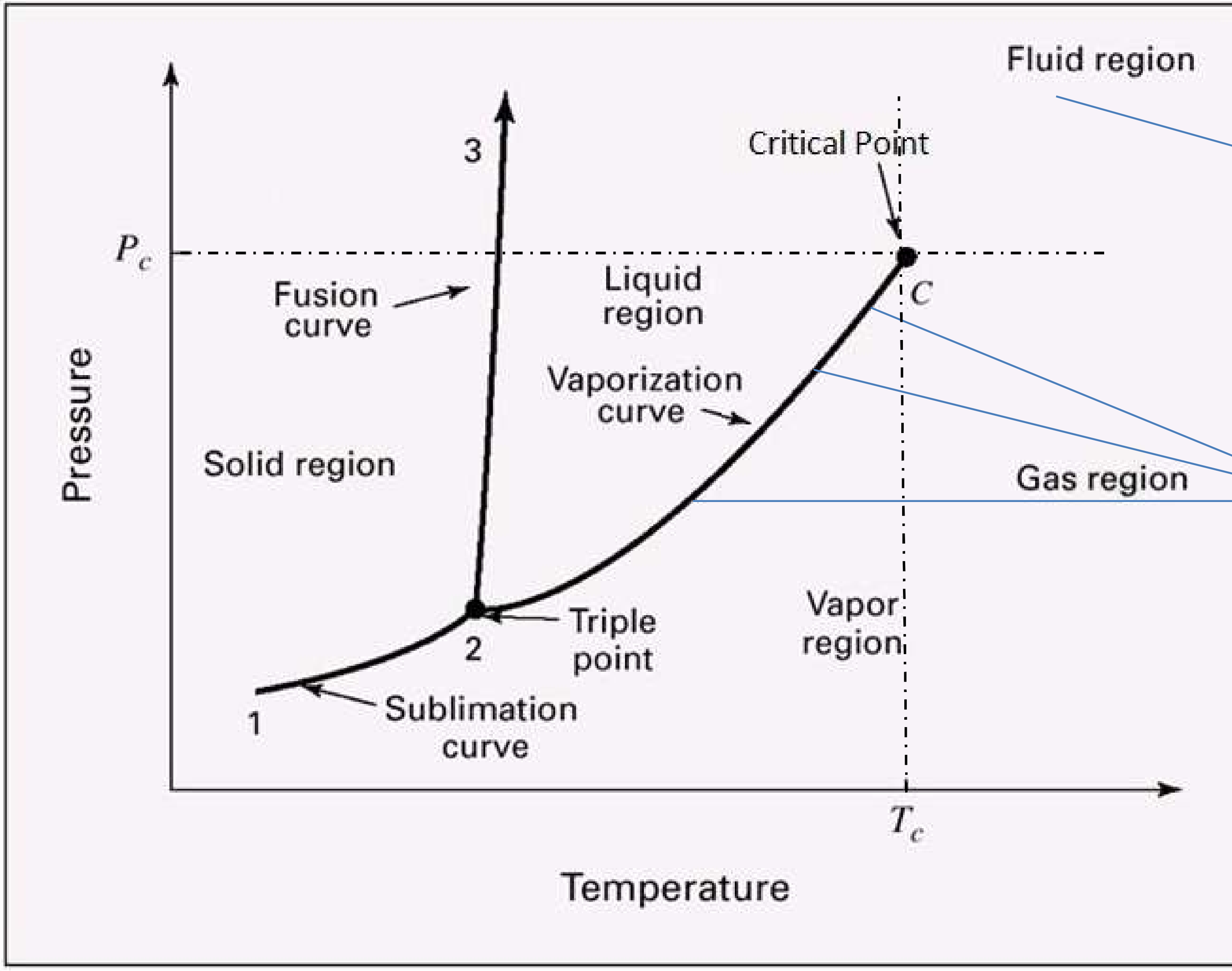
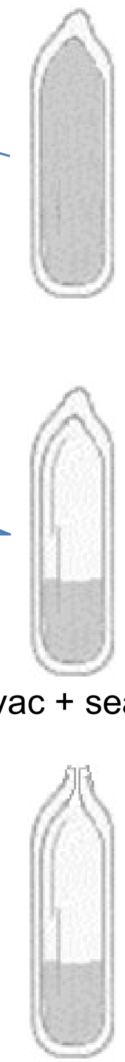


Figure 3.1: *PT* diagram for a pure substance.

N = 1

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

F=2



F=1

evac + seal

open

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?

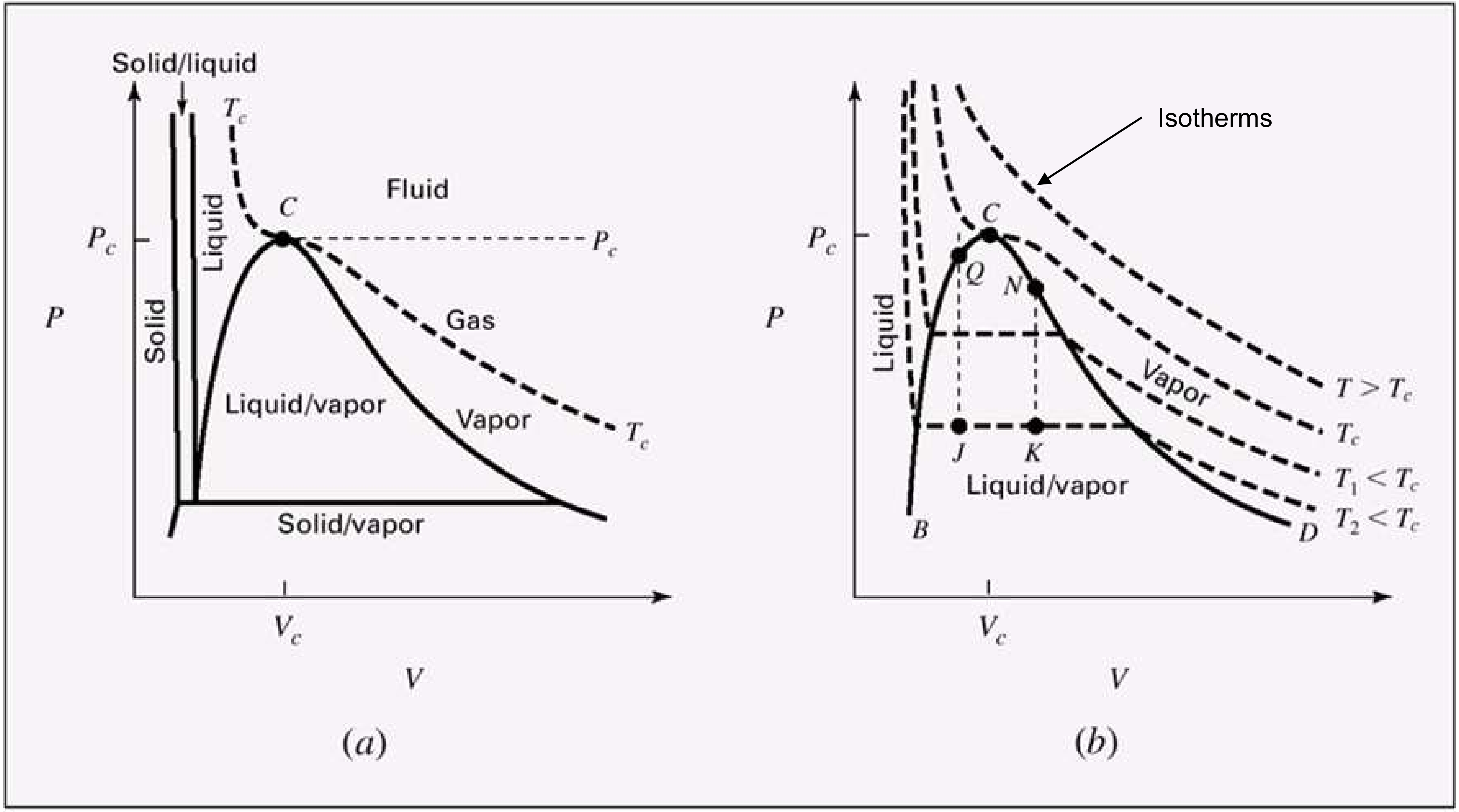
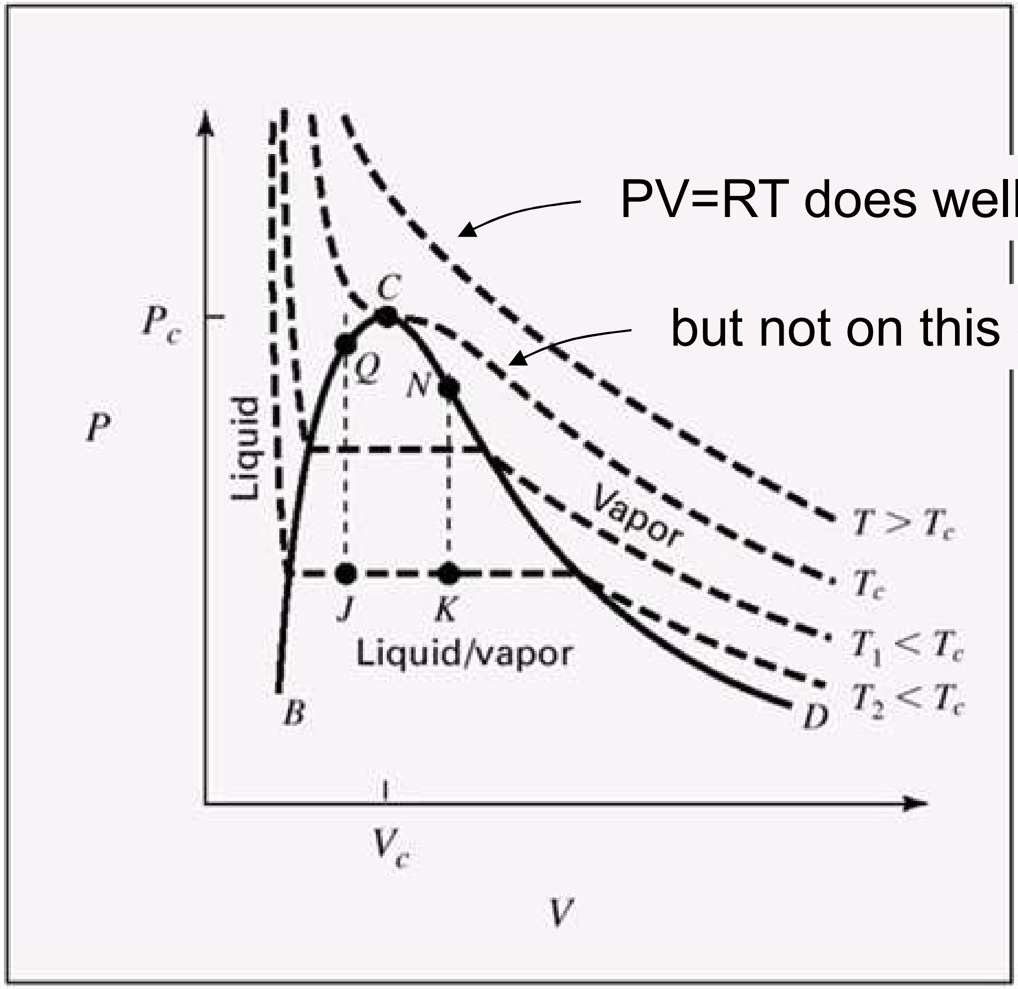


Figure 3.2: PV diagrams for a pure substance. (a) Showing solid, liquid, and gas regions. (b) Showing liquid, liquid/vapor, and vapor regions with isotherms.

Improved Equations of State



PV=RT does well on this curve

but not on this one !

Improved model:

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

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

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

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

Questions?