

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. Explain how to 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

Slide 3

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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.
- Internal energy and enthalpy cannot be measured directly. These properties are usually evaluated from measurements of molar volume as a function of temperature and pressure, $V=V(T,P)$. These relationships are expressed mathematically as equations of state (EOS). The simplest realistic EOS is the ideal gas law, $PV = RT$.
- **What we will be doing in Chapter 3:**
 - First, look at phase rule.
 - Second, we will describe the general P-V-T behavior of pure fluids.
 - Third, we will discuss the ideal gas behavior in detail.
 - Finally, we will discuss more realistic equations, wrapping up with generalized correlations that give predictions when data is lacking.

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.

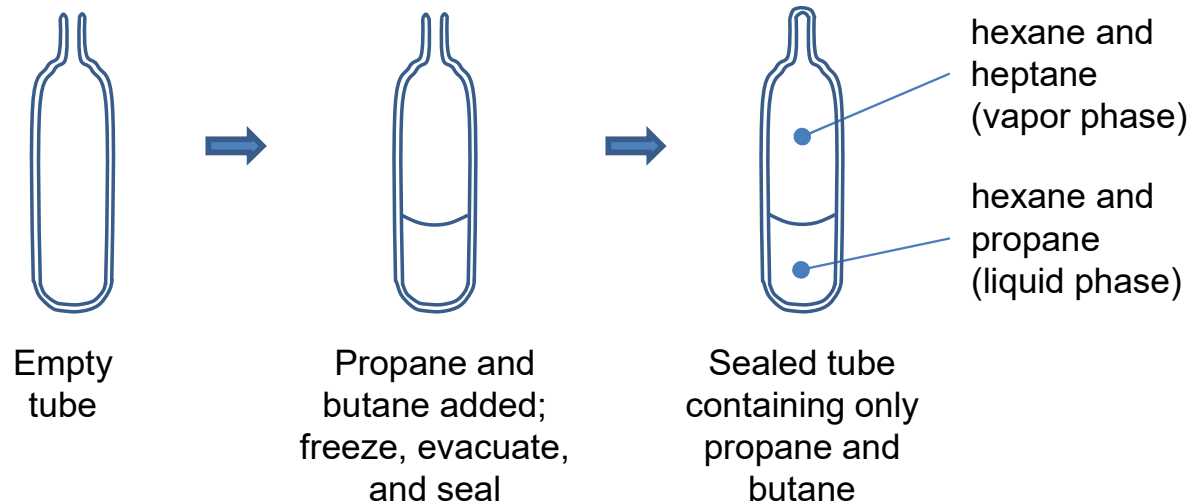
Total moles of both = 100

Total moles of vapor = ?

Total moles of liquid = ?

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) or the amount of substance.



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

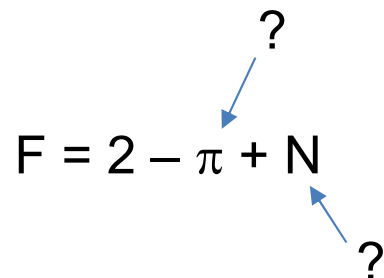
$$\begin{aligned} F &= 2 - \pi + N \\ &= 2 - 2 + 2 \\ &= 2 \end{aligned}$$

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 (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.

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


The diagram shows the Gibbs phase rule equation $F = 2 - \pi + N$. A blue arrow points from a question mark above to the variable π , and another blue arrow points from a question mark to the right to the variable N .

$$F = 2 - 4 + 1 = -1$$

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?

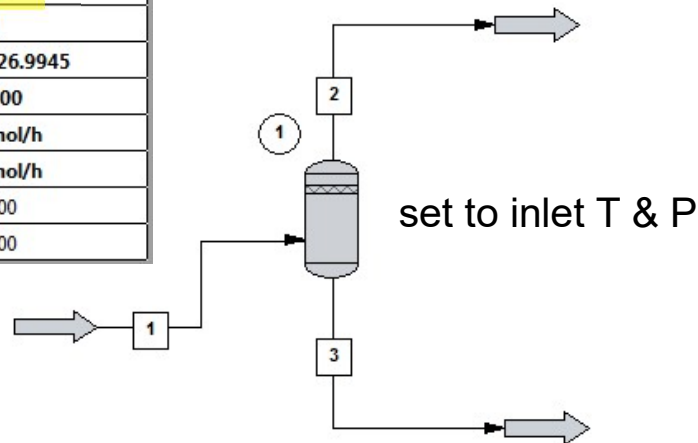
Application of Problem 3.4

Stream No.	1
Stream Name	
Temp K	293.15
Pres bar	10
Vapor Fraction	0
Enthalpy MJ/h	-26.9945
Total flow	200
Total flow unit	mol/h
Comp unit	mol/h
n-Propane	100
N-Butane	100

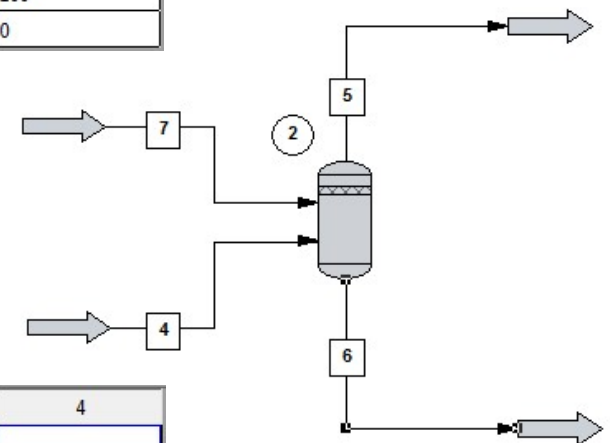
Stream No.	2
Stream Name	
Temp K	323
Pres bar	10
Vapor Fraction	1
Enthalpy MJ/h	-5.06069
Total flow	45.7713
Total flow unit	mol/h
Comp unit	mole frac
n-Propane	0.682747
N-Butane	0.317253

Stream No.	7
Stream Name	
Temp K	293.15
Pres bar	10
Vapor Fraction	0
Enthalpy MJ/h	-12.1565
Total flow	100
Total flow unit	mol/h
Comp unit	mol/h
n-Propane	100
N-Butane	0

Stream No.	5
Stream Name	
Temp K	323
Pres bar	10
Vapor Fraction	1
Enthalpy MJ/h	-30.9187
Total flow	279.644
Total flow unit	mol/h
Comp unit	mole frac
n-Propane	0.682747
N-Butane	0.317253



Stream No.	3
Stream Name	
Temp K	323
Pres bar	10
Vapor Fraction	0
Enthalpy MJ/h	-20.392
Total flow	154.229
Total flow unit	mol/h
Comp unit	mole frac
n-Propane	0.445765
N-Butane	0.554235



Stream No.	4
Stream Name	
Temp K	293.15
Pres bar	10
Vapor Fraction	0
Enthalpy MJ/h	-26.9945
Total flow	200
Total flow unit	mol/h
Comp unit	mol/h
n-Propane	100
N-Butane	100

Stream No.	6
Stream Name	
Temp K	323
Pres bar	10
Vapor Fraction	0
Enthalpy MJ/h	-2.69145
Total flow	20.3559
Total flow unit	mol/h
Comp unit	mole frac
n-Propane	0.445765
N-Butane	0.554235

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

T and P (10 bar, 293.15 K)

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:

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

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

- (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, $\kappa = 44.18 \times 10^{-6} \text{ bar}^{-1}$.
- (2) To what pressure must water be compressed at 50 °C to change its density by 1%? Assume κ is independent of P .

Molar volume is
volume per mole.

Specific volume is
volume per mass.

Density is mass per
volume.

$$\rho = \frac{1}{V \cdot \text{MW}}$$

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

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

Density decreases as T increases, so the negative sign makes β positive.

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

Hint: use this equation for part 2

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

(looks like eq. 3.5)

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.

$$\frac{dV}{V} = \beta dT - \kappa dP = 0 \quad \text{constant } V$$

$$\beta dT = \kappa dP$$

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

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.

$$\frac{dP}{dT} = \frac{\beta}{\kappa}$$

$$dP = \frac{\beta}{\kappa} dT$$

$$\Delta P = \frac{\beta}{\kappa} \Delta T = \left(\frac{1.487 \times 10^{-3}}{62 \times 10^{-6}} \right) 10 = 240 \text{ bar}$$

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.

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

$$\ln\left(\frac{V_2}{V_1}\right) = \beta(T_2 - T_1) - \kappa(P_2 - P_1) = (1.487 \times 10^{-3})(-20) - (62 \times 10^{-6})(9) = -0.0303$$

$$\frac{V_2}{V_1} = 0.9702$$

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

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

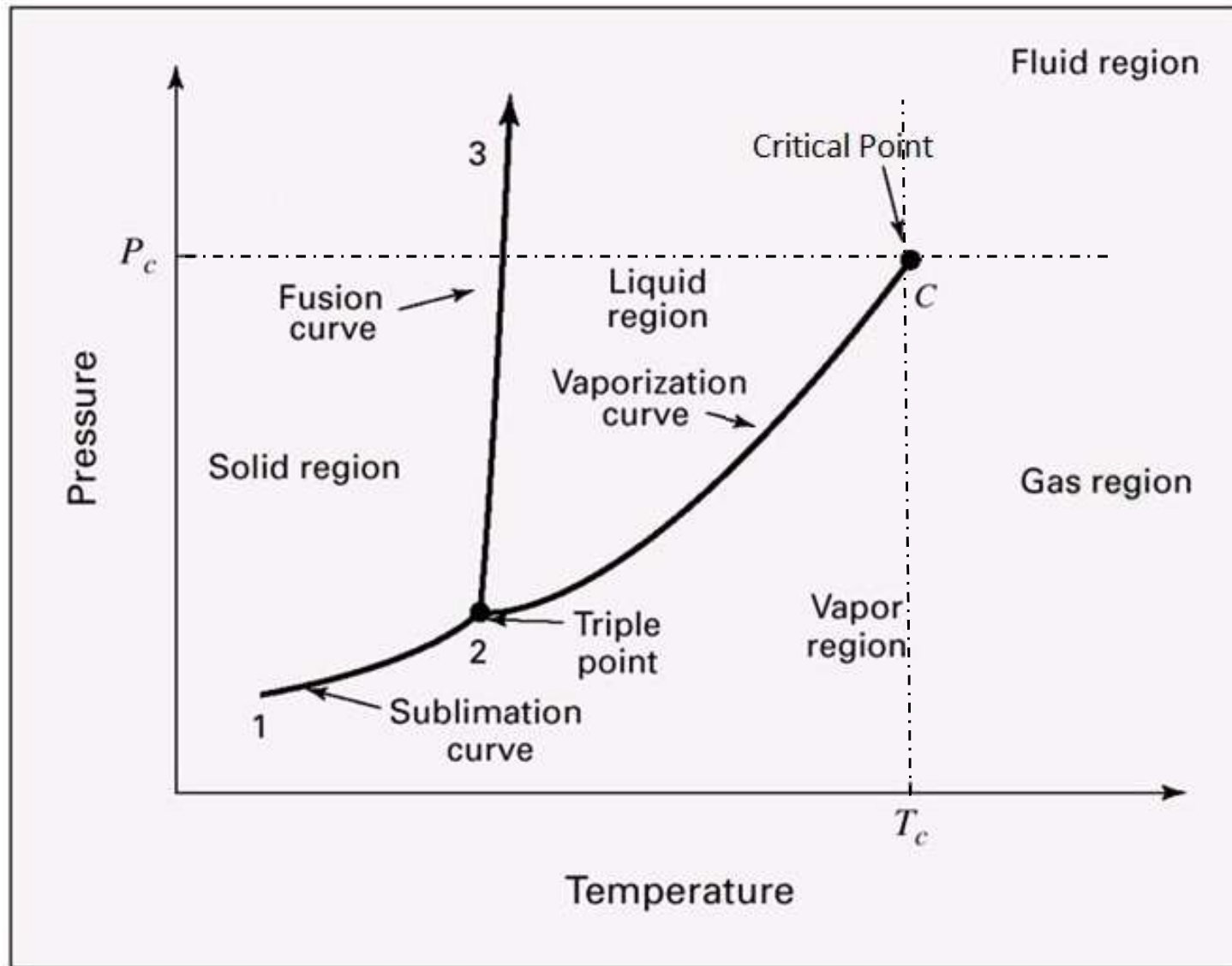


Figure 3.1: PT diagram for a pure substance.

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

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

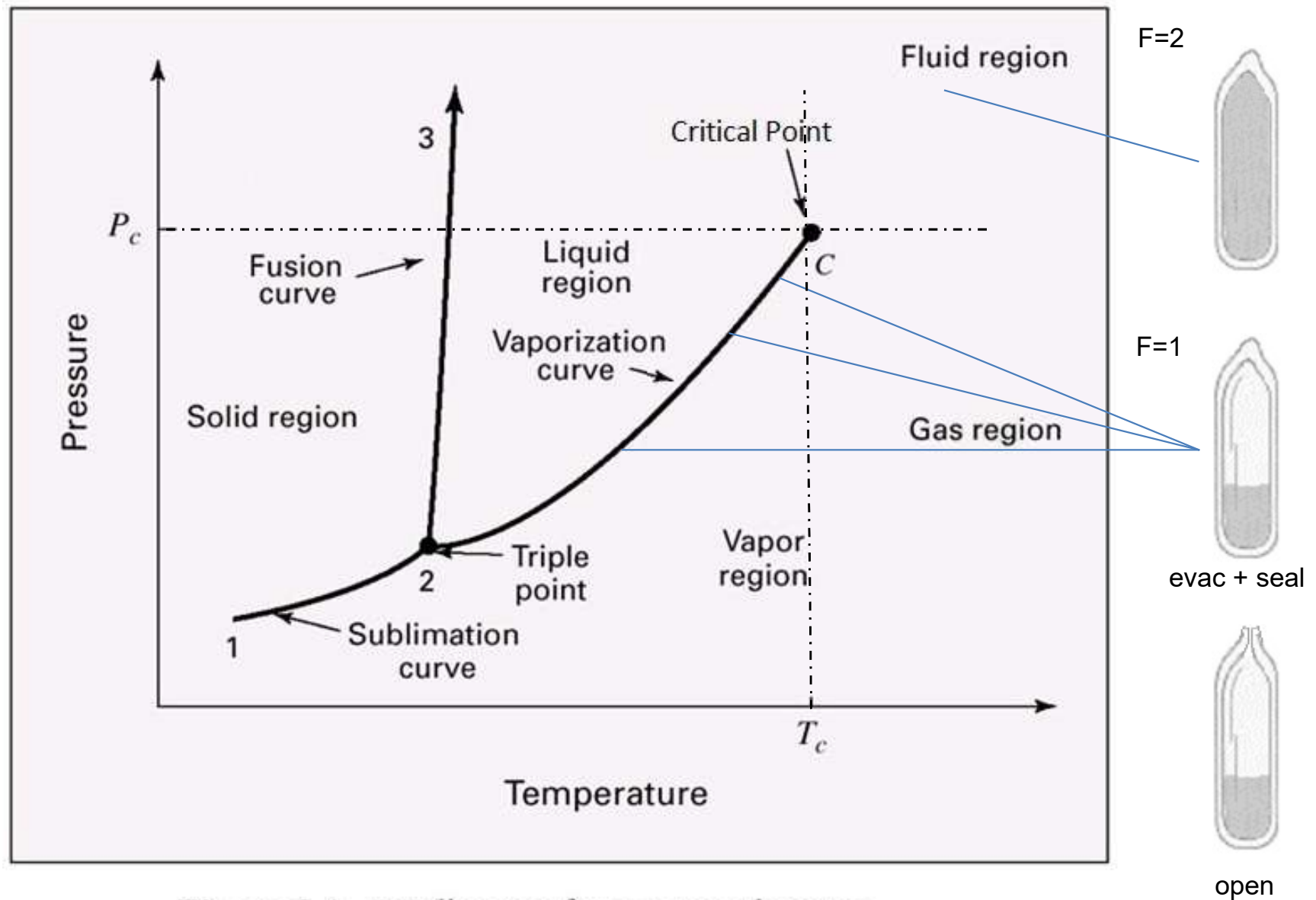


Figure 3.1: PT diagram for a pure substance.

$$N = 1$$

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

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 ?

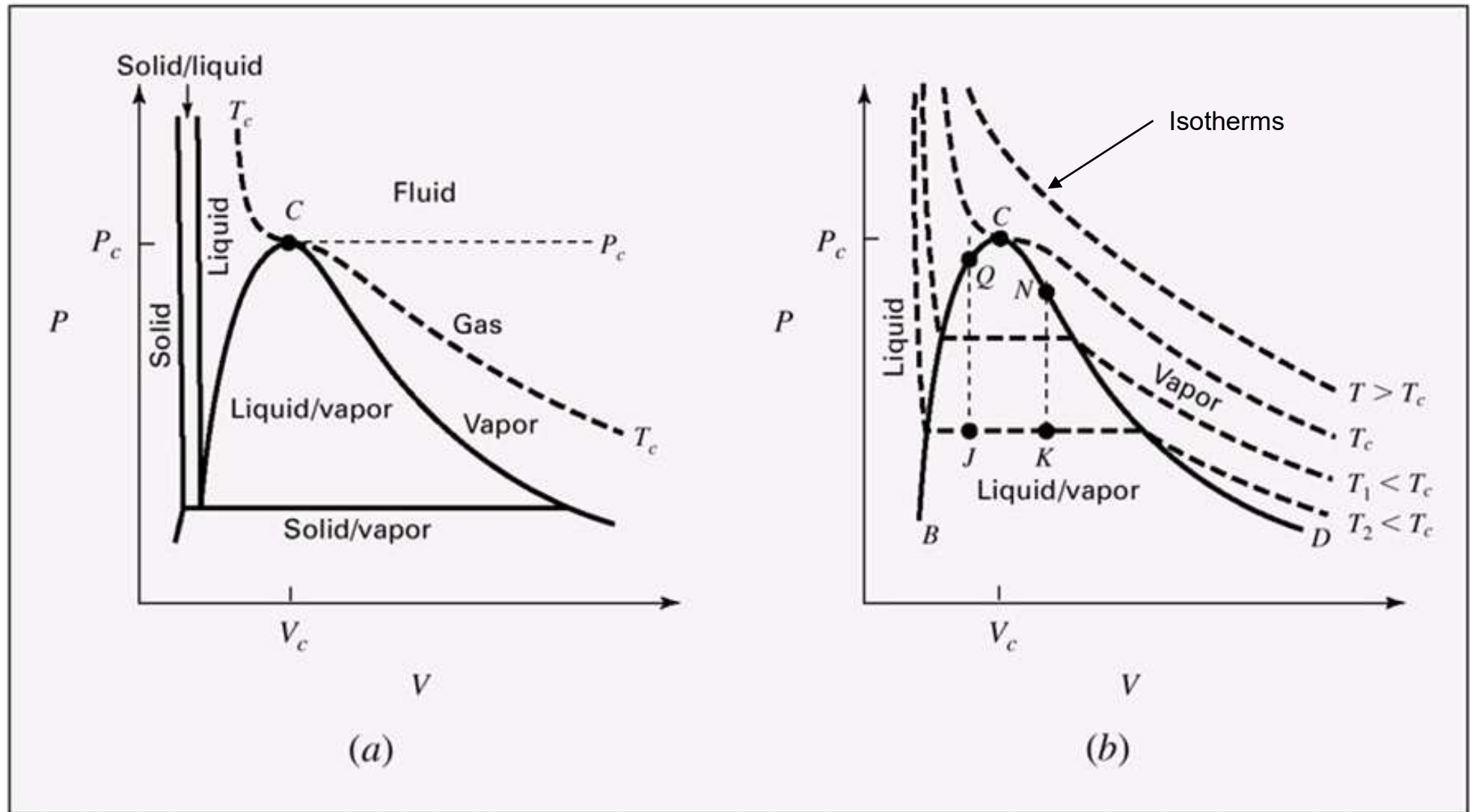
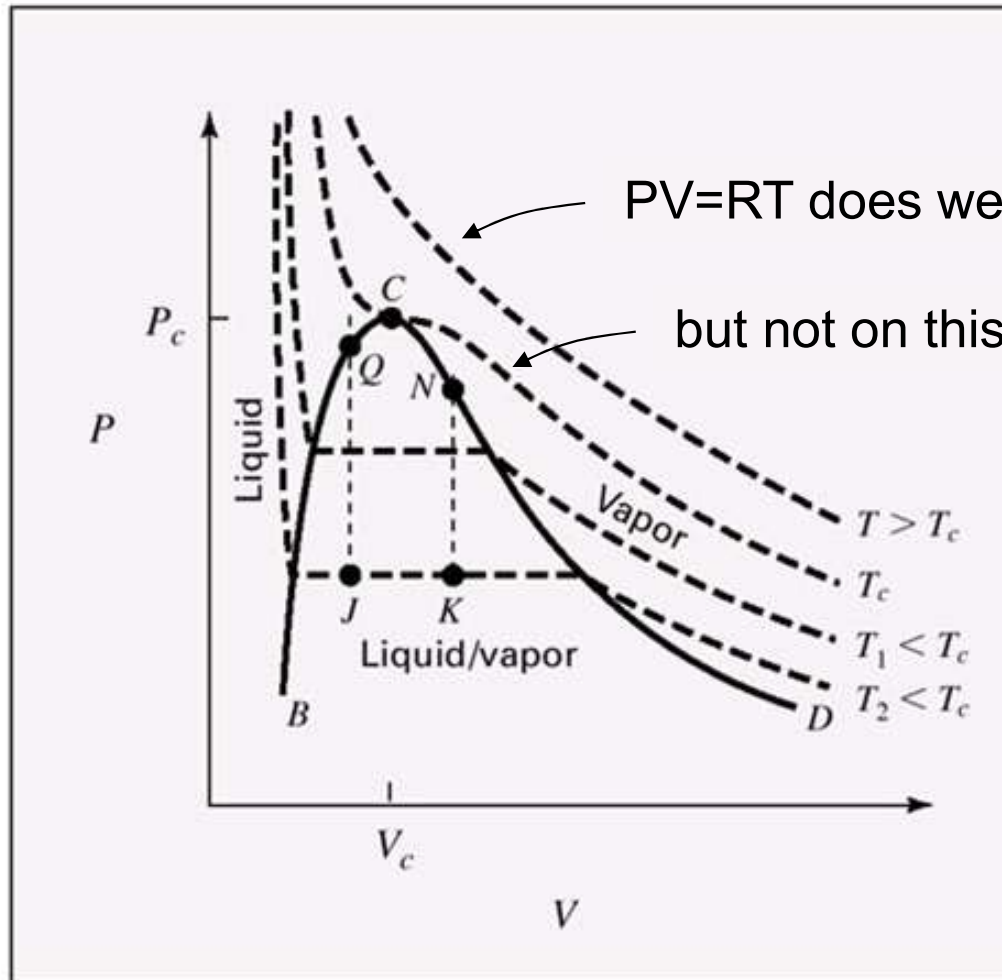


Figure 3.2: P V diagrams for a pure substance. (a) Showing solid, liquid, and gas regions. (b) Showing liquid, liquid/vapor, and vapor regions with isotherms.

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

Questions?