CHEE 2331
Chemical Processes
Ch 5: Single Phase Systems

Department of Chemical and Biomolecular Engineering

Finding Physical Properties
(e.g., density, viscosity…)

- Look it up
  - Appendix B in the text
  - Perry's Chemical Engineers Handbook
  - CRC Handbook
  - Databases (e.g., NIST)

- Estimate it (calculate it)
  - Semi-empirical and Empirical correlations based on experimental data.

- Measure it

One, Two or Three Phases

Single phase

- gas
- liquid
- solid

Two-phases

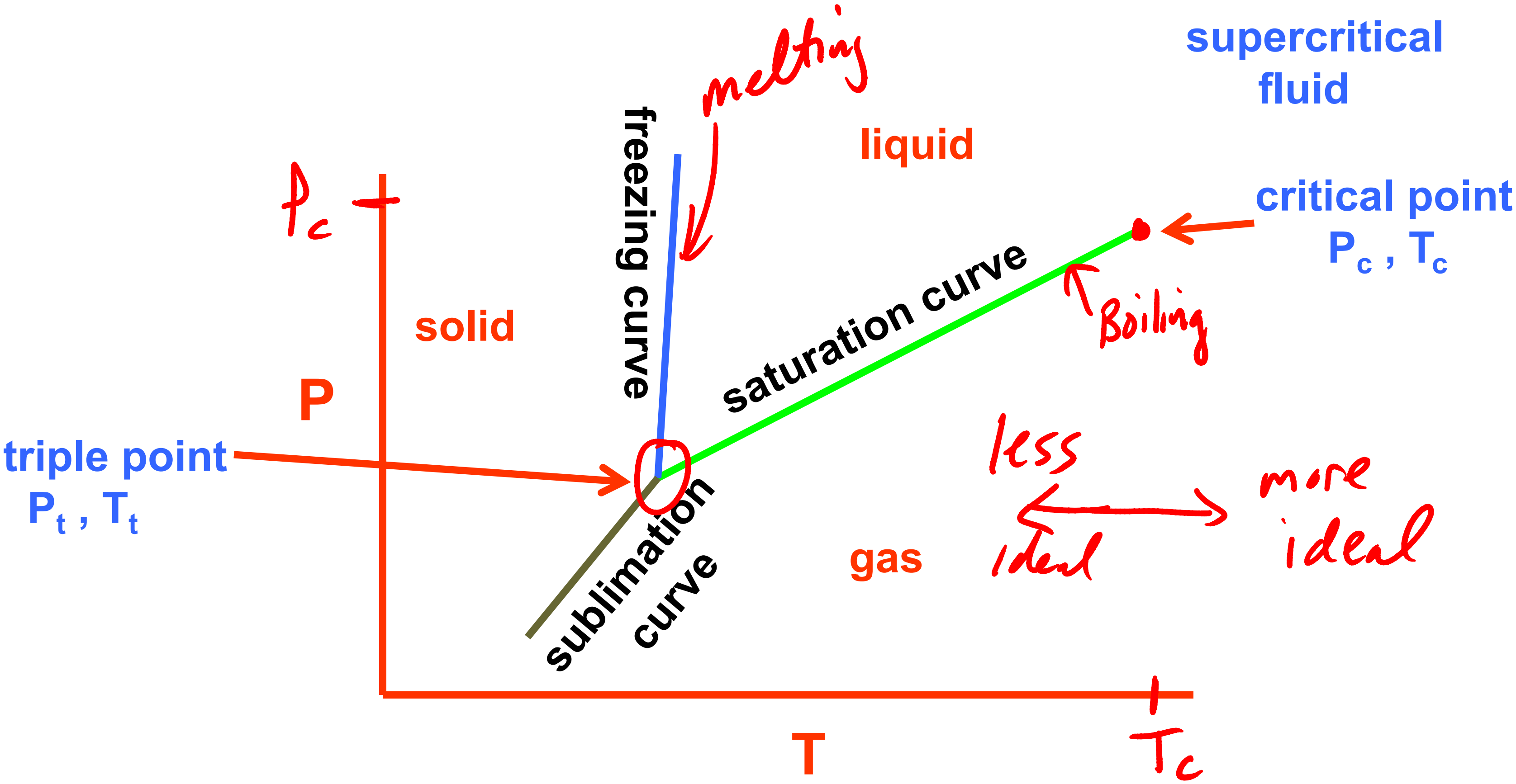
- gas-liquid
- solid-liquid

Three-phases

- gas-liquid-solid

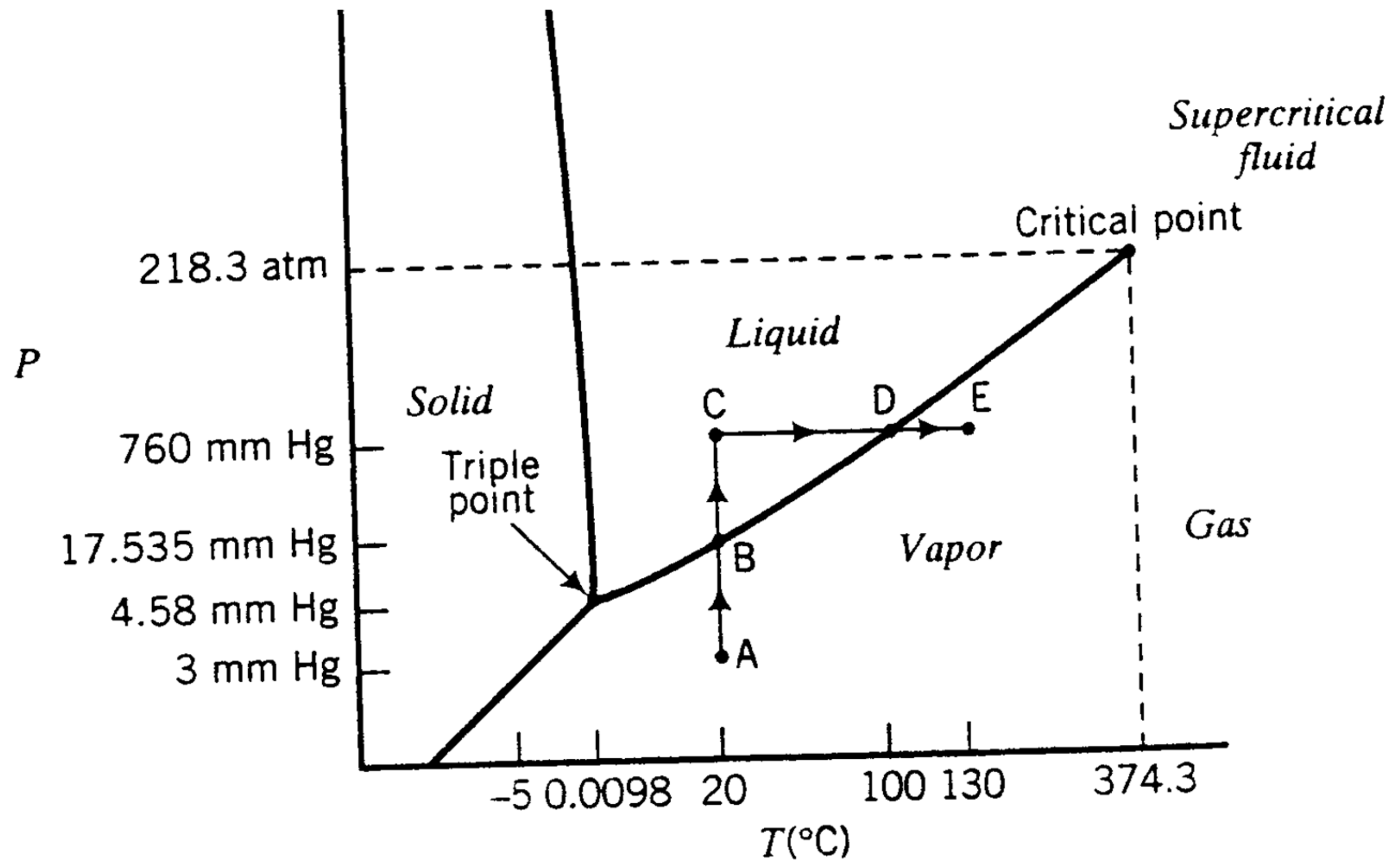
See diagram of next page

Phase diagram (pure substance)



We will discuss the critical point later

Phase Diagram of Water (not drawn to scale)



(a) H_2O

Densities of liquid and solid mixtures

In the absence of data, the density $\bar{\rho}$ of a mixture of n liquids $(A_1, A_2, \ldots, A_n)$ can be estimated from the component mass fractions $[x_i]$ and pure-component densities $[\rho_i]$ in two ways. First, we might assume *volume additivity*—that is, if 2 mL of liquid A and 3 mL of liquid B are mixed, the resulting volume would be exactly 5 mL. Making this assumption and recognizing that component masses are always additive leads to the formula

$$\frac{1}{\bar{\rho}} = \sum_{i=1}^{n} \frac{x_i}{\rho_i} \qquad \textbf{(5.1-1)}$$

Second, we might simply average the pure-component densities, weighting each one by the mass fraction of the component:

$$\bar{\rho} = \sum_{i=1}^{n} x_i \rho_i \qquad \textbf{(5.1-2)}$$

(Equation 5.1-1 calculates the inverse of the mixture density, or the *specific volume* of the mixture, as the weighted average of the pure-component specific volumes.)

Specific Volume

$$\frac{1}{\bar{\rho}} = \sum_{i=1}^{n} \frac{x_i}{\rho_i}$$

More accurate for a mixture of species with similar molecular structure, e.g., alkanes. It is an eq. for additivity of specific volume, 1/ρ.

$$\frac{1}{\rho} = \hat{V} = \text{specific volume} \quad \text{(mass basis)}$$

$$\hat{V}_{mix} = \sum x_i \hat{V}_i$$

Ideal Gases

Assumptions

- molecules have negligible volume.
- no interactions among molecules.
- only elastic collisions with walls.

Valid at dilute concentrations (low pressure, high temperature)

Kinetic theory of gases gives: $PV = nRT$

Calculate the density of an ideal gas:

$PV = nRT = (m/M_W)*RT$

$\rho = m/V = P(M_W)/RT$

Can apply to mixtures of ideal gases using avg MW

M_W=mol. weight

Ideal Gas Test

Table 5.2-1 Standard Conditions for Gases

System	T_s	P_s	V_s	n_s
SI	273 K	1 atm	0.022415 m^3	1 mol
CGS	273 K	1 atm	22.415 L	1 mol
American Engineering	492°R	1 atm	359.05 ft^3	1 lb-mole

$$\hat{V}_s = 22.4 \frac{m^3(STP)}{kmol} \Longleftrightarrow 22.4 \frac{L(STP)}{mol} \Longleftrightarrow 359 \frac{ft^3(STP)}{lb\text{-}mole} \quad \textbf{(5.2-6)}$$

The term **standard cubic meters** (or **SCM**) is often used to denote m^3(STP), and **standard cubic feet** (or **SCF**) denotes ft^3(STP). A volumetric flow rate of 18.2 SCMH means 18.2 m^3/h at 0°C and 1 atm.

$PV = \dot{n}RT$, and $P_s\hat{V}_s = RT_s$ ⇒ $\frac{PV}{P_s\hat{V}_s} = \frac{\dot{n}T}{T_s}$

↑ n=1

Conversion from standard conditions – example 5.2-2

Butane at 360 °C and 3 atm flowing at 1100 kg/h, find $\dot{V}$:

** Example 5.2-4 further shows how/why this is useful

Ideal Gas mixtures

(e.g., gases A, B, C…)

$P_AV = n_ART$ and $P_{total}V = n_{total}RT$

so,

$$\frac{P_A}{P_{total}} = \frac{n_A}{n_{total}} = y_A$$

or

$$P_A = y_AP_{total}$$

P_A is the partial pressure of A in the mixture

For ideal gas mixtures only, mole% composition is the same as volume% composition.

$$\boxed{p_A = y_A P} \tag{5.2-7}$$

That is, *the partial pressure of a component in an ideal gas mixture is the mole fraction of that component times the total pressure.*[4] Moreover, since $y_A + y_B + \cdots = 1$,

$$p_A + p_B + \cdots = (y_A + y_B + \cdots)P = P \tag{5.2-8}$$

or, *the partial pressures of the components of an ideal gas mixture add up to the total pressure (Dalton's law).*

A similar series of calculations can be performed for pure-component volumes:

$$Pv_A = n_A RT$$

$$\Big\Downarrow \text{ Divide by } PV = nRT$$

$$\frac{v_A}{V} = \frac{n_A}{n} = y_A$$

or

$$\boxed{v_A = y_A V} \tag{5.2-9}$$

and

$$v_A + v_B + \cdots = V \qquad \text{(Amagat's law)}$$

The quantity v_A/V is the **volume fraction** of A in the mixture, and 100 times this quantity is the **percentage by volume** (% v/v) of this component. As shown above, *the volume fraction of a substance in an ideal gas mixture equals the mole fraction of this substance.* Stating, for example. that an ideal gas mixture contains 30% CH_4 and 70% C_2H_6 by volume (or 30% v/v CH_4 and 70% v/v C_2H_6) is equivalent to specifying 30 mole% CH_4 and 70 mole% C_2H_6.

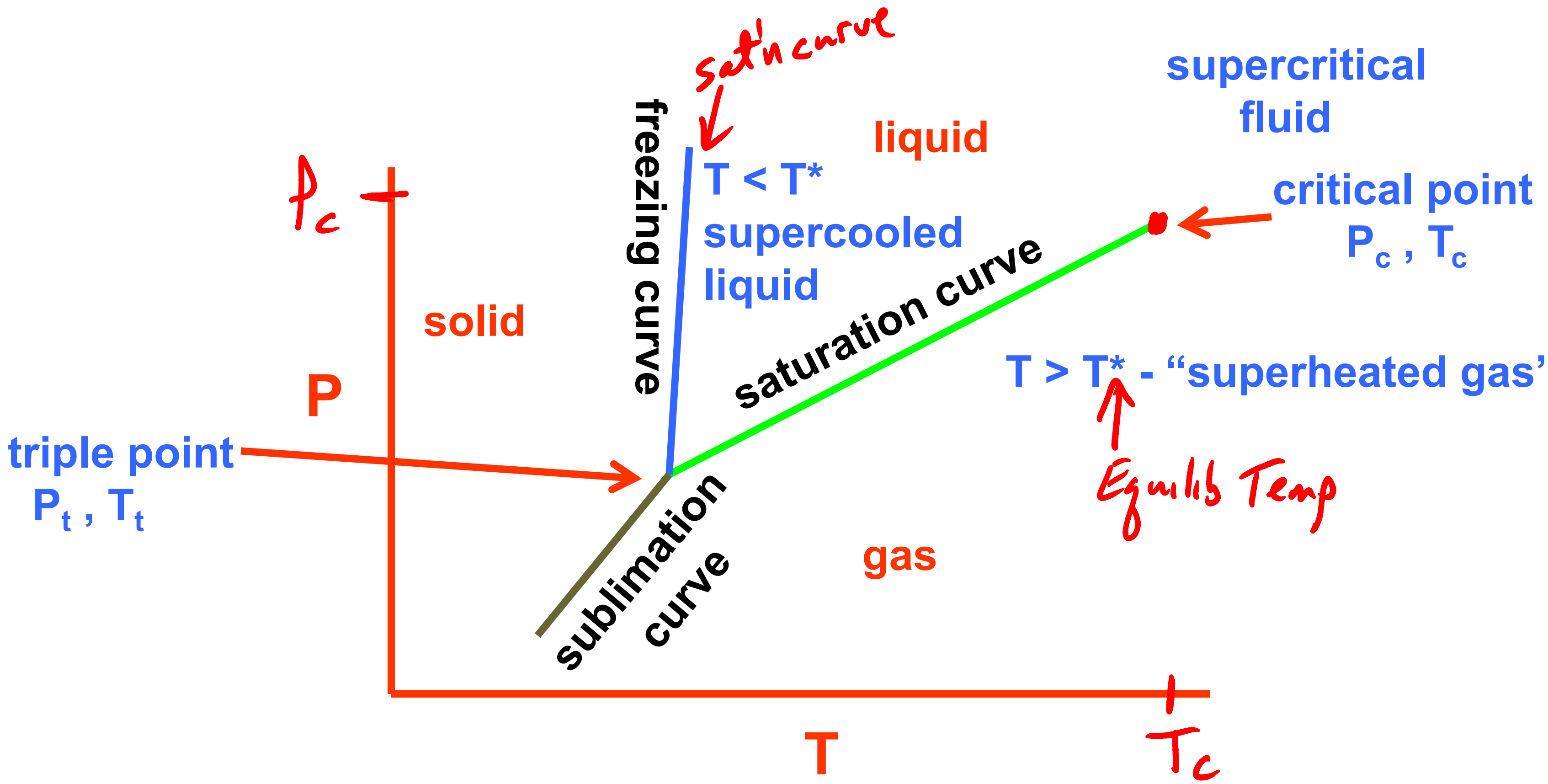
Example 5.2-5 : material balance on an evaporator-compressor

Material Balances on an Evaporator-Compressor

Liquid acetone (C_3H_6O) is fed at a rate of 400 L/min into a heated chamber, where it evaporates into a nitrogen stream. The gas leaving the heater is diluted by another nitrogen stream flowing at a measured rate of 419 m^3(STP)/min. The combined gases are then compressed to a total pressure $P = 6.3$ atm gauge at a temperature of 325°C. The partial pressure of acetone in this stream is $p_a = 501$ mm Hg. Atmospheric pressure is 763 mm Hg.

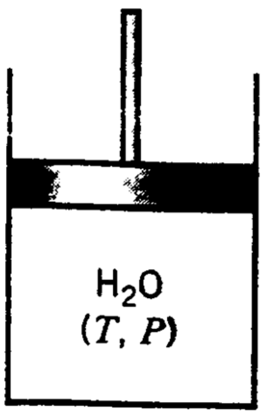
1. What is the molar composition of the stream leaving the compressor?
2. What is the volumetric flow rate of the nitrogen entering the evaporator if the temperature and pressure of this stream are 27°C and 475 mm Hg gauge?

Phase diagram (pure substance)



The Critical Point of a Pure Fluid

Water in a closed piston-cylinder system



Run	T(°C)	P_{cond}(atm)	ρ_v(kg/m^3)	ρ_l(kg/m^3)
1	25.0	0.0329	0.0234	997.0
2	100.0	1.00	0.5977	957.9
3	201.4	15.8	8.084	862.8
4	349.8	163	113.3	575.0
5	373.7	217.1	268.1	374.5
6	374.15	218.3	315.5	315.5
7	>374.15	*No condensation occurs!*		

As T and P increase towards the critical point, The liquid and the gas become increasingly similar. At the critical point, they become indistinguishable from each other. A super critical fluid forms which exhibits properties of both liquid and gas, but is neither !

The **Critical Temperature** (T_c) is the highest temperature at which liquid and vapor of a substance can co-exist. For temperatures above T_c a substance cannot be liquefied, no matter how much it is compressed.

The **Critical Pressure** (P_c) is the pressure corresponding to $T_{c.}$

The **Reduced Temperature** and **Reduced Pressure** are defined as:

$$T_r = T/T_c$$

$$P_r = P/P_c$$

Table B.1 of textbook lists T_c and P_c values.

Non-ideal (real) gases

Theoretical

- Virial equation of state
- Cubic Equations of state:
  - → Van der Waals
  - → SRK

Semi-empirical

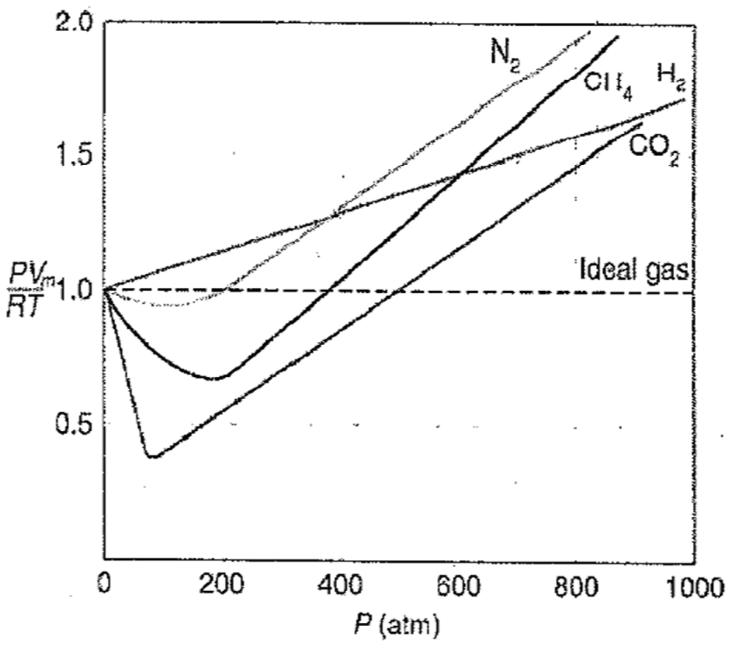
- Compressibility factor

Compressibility factor, Z : deviation from ideality.

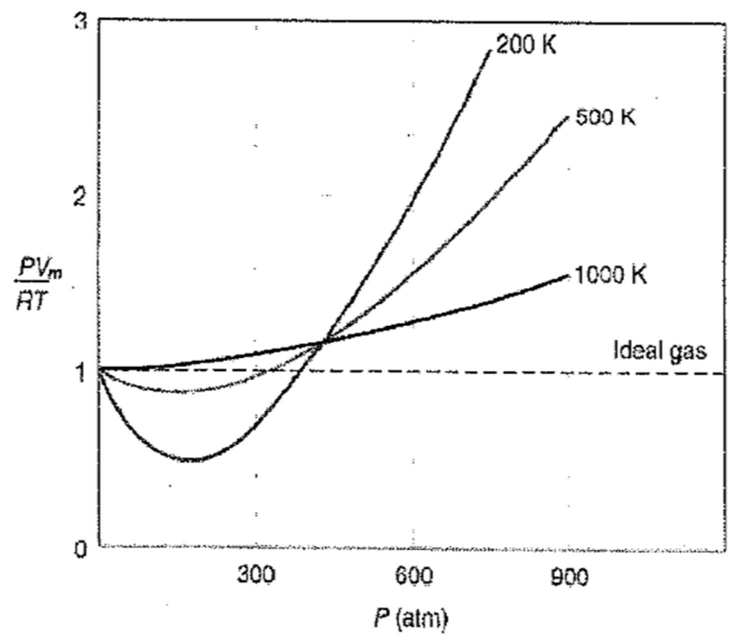
For ideal gases Z=1 !

PV = ZnRT

$$Z = \frac{P\hat{V}}{RT}$$



Z of different gases at 300 K



Z of N_2 gas at various temperatures

Law of Corresponding States

$$Z = f(P_r, T_r)$$

where the "reduced" pressure and temperature is

$$P_r = P/P_c$$

$$T_r = T/T_c$$

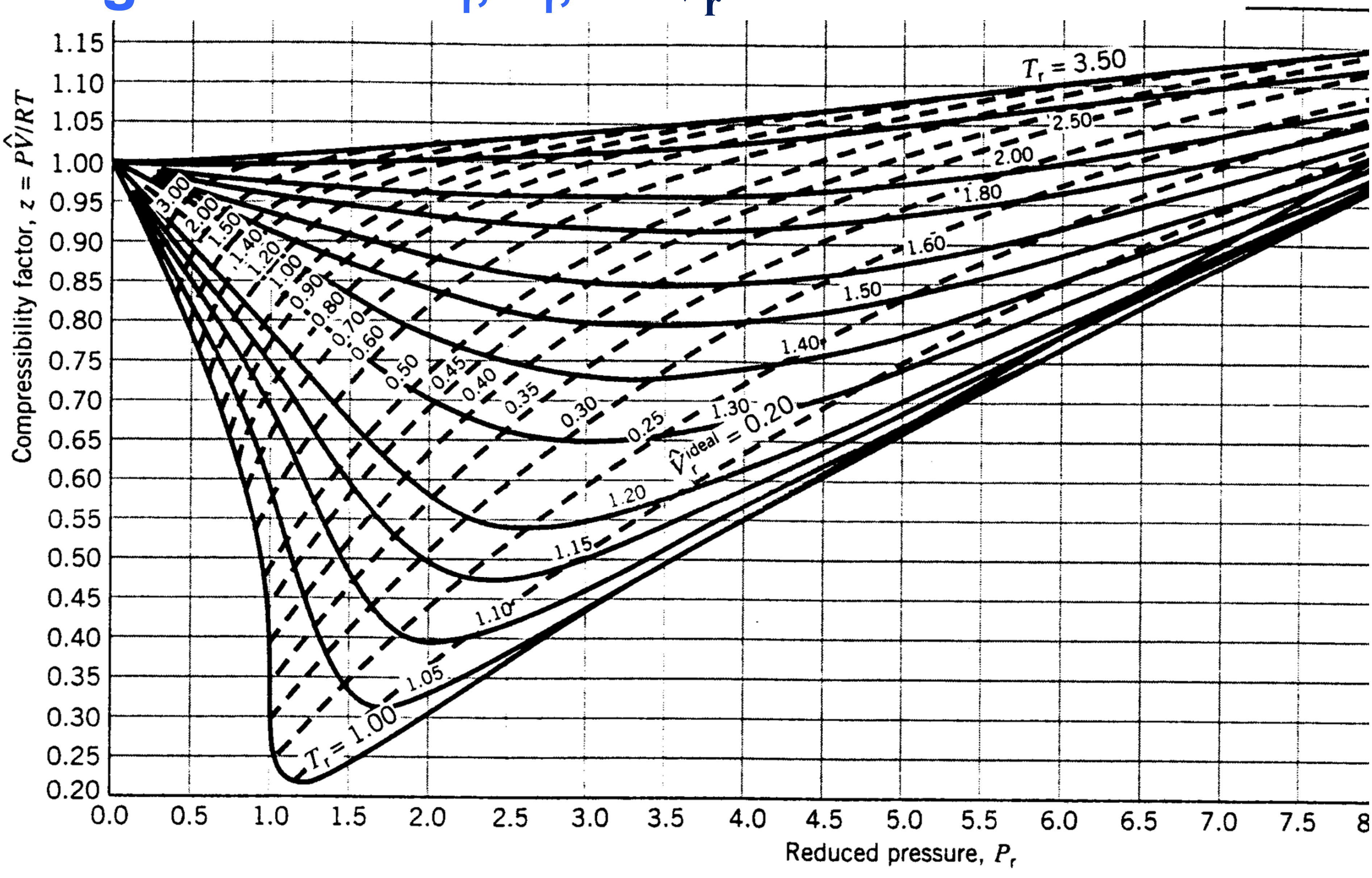
and the function $f(P_r,T_r)$ is found from "generalized compressibility charts."

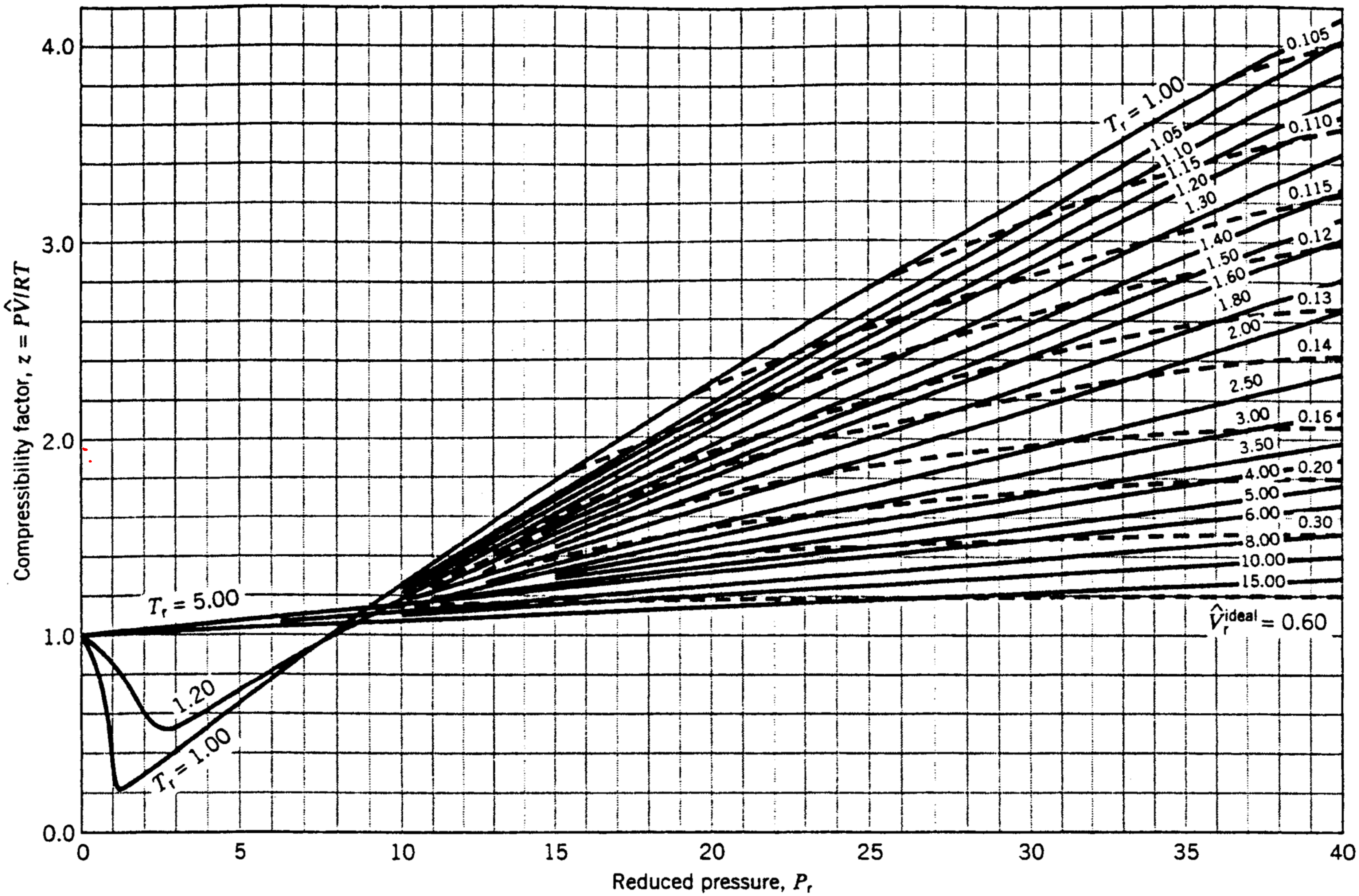
Law of corresponding states: The Z values for different fluids exhibit similar behavior when expressed as a function of T_r and P_r:

All fluids, when compared at the same reduced temperature and reduced pressure have approximately the same Z value, and all deviate from ideal gas behavior to a similar degree.

$$\hat{V}_r^{ideal}$$

Generalized Compressibility Charts: to get Z from P_r, T_r, or $\hat{V}_r^{ideal}$




Compressibility factor, $z = P\hat{V}/RT$
Reduced pressure, P_r
0.0
1.0
2.0
3.0
4.0
0
5
10
15
20
25
30
35
40
$T_r = 5.00$
1.20
$T_r = 1.00$
$T_r = 1.00$
1.05
1.10
1.15
1.20
1.30
1.40
1.50
1.60
1.80
2.00
2.50
3.00
3.50
4.00
5.00
6.00
8.00
10.00
15.00
0.105
0.110
0.115
0.12
0.13
0.14
0.16
0.20
0.30
$\hat{V}_r^{ideal} = 0.60$

The Generalized Compressibility Chart

One hundred gram-moles of nitrogen is contained in a 5-liter vessel at −20.6°C. Estimate the pressure in the cylinder.

Kay's rule estimates *pseudocritical properties* of mixtures as simple averages of pure-component critical constants:[11]

Pseudocritical Temperature: $$T_c' = y_A T_{cA} + y_B T_{cB} + y_C T_{cC} + \cdots \quad \textbf{(5.4-9)}$$

Pseudocritical Pressure: $$P_c' = y_A P_{cA} + y_B P_{cB} + y_C P_{cC} + \cdots \quad \textbf{(5.4-10)}$$

where $y_A, y_B, \ldots$ are mole fractions of species A, B, ... in the mixture. Assuming that the system temperature T and pressure P are known, the pseudocritical properties can be used to estimate the *pseudoreduced temperature and pressure* of the mixture:

Pseudoreduced Temperature: $$T_r' = T/T_c' \quad \textbf{(5.4-11)}$$

Pseudoreduced Pressure: $$P_r' = P/P_c' \quad \textbf{(5.4-12)}$$

The compressibility factor for a gas mixture, z_m, can now be estimated from the compressibility charts and the pseudoreduced properties, and $\hat{V}$ for the mixture can be calculated as

$$\hat{V} = \frac{z_m RT}{P} \quad \textbf{(5.4-13)}$$

→ Don't average the reduced values!

A **virial equation of state** expresses the quantity $P\hat{V}/RT$ as a power series in the inverse of specific volume:

$$\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}} + \frac{C}{\hat{V}^2} + \frac{D}{\hat{V}^3} + \cdots$$

B, C, D are functions of temperature and are the second, third & fourth virial coefficients.

For ideal gases: B = C = D = 0

Truncating to only the second term yields:

$$\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}}$$

See next page on how to estimate B

- Calculate the **reduced temperature,** $T_r = T/T_c$.
- Estimate B using the following equations:

Table 5.3-1 Pitzer Acentric Factors

Compound	Acentric Factor, ω
Ammonia	0.250
Argon	−0.004
Carbon dioxide	0.225
Carbon monoxide	0.049
Chlorine	0.073
Ethane	0.098
Hydrogen sulfide	0.100
Methane	0.008
Methanol	0.559
Nitrogen	0.040
Oxygen	0.021
Propane	0.152
Sulfur dioxide	0.251
Water	0.344

SOURCE: R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th Edition, McGraw-Hill, New York, 1986.

$$B_0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B_1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

$$B = \frac{RT_c}{P_c}(B_0 + \omega B_1)$$

Cubic Equations of State

A number of analytical PVT relationships are referred to as **cubic equations of state** because. when expanded, they yield third-order equations for the specific volume. The **van der Waals equation of state** is the earliest of these expressions, and it remains useful for discussing deviations from ideal behavior.

$$P = \frac{RT}{\hat{V} - b} - \frac{a}{\hat{V}^2} \tag{5.3-7}$$

where

$$a = \frac{27R^2T_c^2}{64P_c} \qquad b = \frac{RT_c}{8P_c}$$

In the van der Waals derivation, the term $a/\hat{V}^2$ accounts for attractive forces between molecules and b is a correction accounting for the volume occupied by the molecules themselves.[5]

Cubic Equations of State
Soave-Redlich-Kwong (SRK)

$$P = \frac{RT}{\hat{V} - b} - \frac{\alpha a}{\hat{V}(\hat{V} + b)}$$

$$a = 0.42747 \frac{(RT_c)^2}{P_c}$$

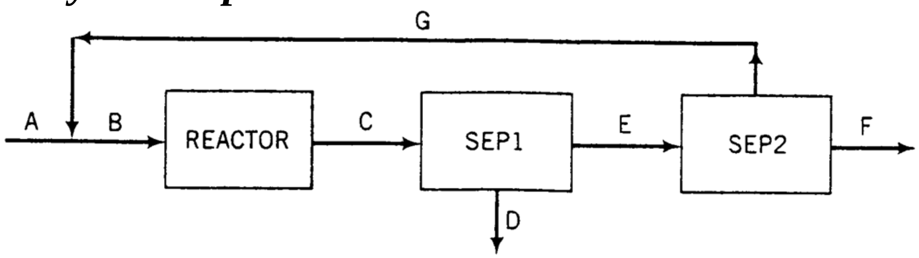
$$b = 0.08664 \frac{RT_c}{P_c}$$

$$m = 0.48508 + 1.55171\omega - 0.1561\omega^2$$

$$T_r = T/T_c$$

$$\alpha = \left[1 + m\left(1 - \sqrt{T_r}\right)\right]^2$$

P5.74: Methanol synthesis process



The following specifications apply to the labeled streams and process units:

A. Fresh feed—a mixture of CO, H_2, N_2, and CO_2
B. Feed to the reactor—30.0 mole% CO, 63.0% H_2, 2.0% N_2, and 5.0% CO_2.
Reactor. Two reactions occur and proceed to equilibrium at 200°C and 4925 kPa absolute:

$$CO + 2H_2 \rightleftharpoons CH_3OH(M), \qquad (K_p)_1 = \frac{p_M}{p_{CO}\,p_{H_2}^2} = 3.49 \times 10^{-6}\ \text{kPa}^{-2}$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad (K_p)_2 = \frac{p_M\,p_{H_2O}}{p_{CO_2}\,p_{H_2}^3} = 5.19 \times 10^{-8}\ \text{kPa}^{-2}$$

C. Reactor effluent—contains all feed and product species at the reactor temperature and pressure. Species partial pressures satisfy the two given equations.

Sep1. Condenses all methanol and water in reactor effluent.
D. Liquid methanol and water. (These species will be separated by distillation in a unit not shown.)
E. Gas containing N_2 and unreacted CO, H_2, and CO_2.
Sep2. Multiple-unit separation process.
F. All of the nitrogen and some of the hydrogen in Stream E.
G. Recycle stream—CO, CO_2, and 10% of the hydrogen fed to Sep2.

(a) Taking 100 kmol/h of Stream B as a basis of calculation, calculate the molar flow rates (kmol/h) and molar compositions of the remaining six labeled streams.
(b) The process is to be used to provide 237 kmol/h of methanol. Scale up the flowchart of part (a) to calculate the required fresh feed rate (SCMH), the flow rate of the reactor effluent (SCMH), and the actual volumetric flow rate of the reactor effluent (m^3/h), assuming ideal gas behavior.
(c) Use the rule of thumb for a diatomic gas given on p. 192 to test the ideal gas assumption at the reactor outlet. If the assumption is invalid, which of the values calculated in part (b) are in error?

EXAM Q (30 points) A 1000-liter steel vessel containing a gas has potentially been mislabeled. It contains either pure methane (MW = 16) or pure ethylene (MW = 28). The pressure in the vessel is measured to be 175 atm (abs). The vessel is placed on a scale, and some of the gas inside is slowly transferred to another tank. After the weight measured by the scale has decreased by 227 pounds, the pressure gauge now reads 49 atm (abs). The temperature is constant at 25°C. What is most likely inside the vessel?

Methane: T_c = 190.7 K, P_c = 45.8 atm

Ethylene: T_c = 283.1 K, P_c = 50.5 atm

$PV = znRT \Rightarrow V, T$ constant

$$\frac{n_1 z_1}{P_1} = \frac{n_2 z_2}{P_2} \qquad n_2 = \left(\frac{n_1 z_1}{P_1}\right)\left(\frac{P_2}{z_2}\right)$$

$$\text{“}-\Delta n\text{”} = n_2 - n_1 = n_1\left(\frac{z_1}{z_2}\frac{P_2}{P_1} - 1\right)$$

Δmass = 227 lbs = 103.2 kg

$$MW = \frac{\Delta \text{mass}}{\Delta \text{moles}}$$

or just calculate n_1 then n_2 get Δn