## ** Single-phase systems:

→ In chapter 4, streams on the flowchart are labeled like:

$$\xrightarrow{100\ \text{mol/s}}$$

0.6 mol A/mol

0.4 mol B/mol

just mass (mole) flowrates (amounts) and compositions information.

→ In this chapter, suppose you have information about T, P ; $Q \equiv \dot{V}$, and/or partial pressures (for gas streams)

### * For solids and liquids streams:

Ex: $\xrightarrow{\dot{n} \text{ or } \dot{m}}$

250 L/s

37 °C

800 mmHg

0.6 mol A/mol

0.4 mol B/mol

what are other equations that relate $\dot{n}$ or $\dot{m}$ with T, P, and Q ?

other equation: $\dot{m} = \rho Q$

$$\dot{n} = \frac{\rho}{Mwt} Q = \frac{Q}{\hat{V}}$$

$\hat{V}$ : specific molar volume [=] $\frac{m^3}{mol}$

$$\frac{1}{\overline{Mwt}} = \sum_{i=1}^{N} \frac{x_i}{Mwt_i} \quad ; \quad \frac{1}{\rho} = \sum_{i=1}^{N} \frac{x_i}{\rho_i}$$

→ For solids and liquids : pick up $\rho_i$ or $SG_i$ from physical properties table at given T and p, such as table B.1 in your textbook

Or use equation of state (EOS) if these densities or specific gravities of pure components are not available at T and p.

– What do we mean by EOS ?

Relationship between T, P, and $\rho$ or $\hat{V}$ :

$$F(T, P, \hat{V} \text{ or } \rho) = 0$$

* For gaseous streams :

$$\dot{n} = \frac{Q}{\hat{V}} \quad \text{or} \quad \dot{m} = \rho Q$$

How to estimate $\rho$ or $\hat{V}$ for gaseous streams ?

① If the stream has pure ideal gas :

$PV = nRT$ "ideal gas law for batch process"

or $P = \hat{V} R T$

Remember that $T$ is absolute temperature in K or °R

$P$ " = pressure .

$R = 8.314 \frac{J}{gmol \cdot K}$

For streams : $P\dot{V} = \dot{n}RT \Rightarrow \boxed{\dot{n} = \frac{P\dot{V}}{RT}}$

(note that ideal gas law is an example of EOS)

Δ properties of ideal gases :

- No attraction forces between molecules ; they move independent of each other.
- Molecules move randomly ; Collisions are perfectly elastic so energy is conserved.
- Molecules of ideal gas have negligible volume

  $V \rightarrow 0 \quad \therefore \rho = \frac{M}{V}$

∆ From where did ideal gas law originally come?

at Constant T and n: $V \propto \frac{1}{P}$ " Boyle's law "

at Constant p and n: $V \propto T$ " Charle's law "

at constant P and T: $V \propto n$

$\therefore \quad V = R\frac{nT}{P}$ R: Constant of proportionality

$$\therefore \quad \boxed{PV = nRT}$$

∆ when can we use ideal gas law?

- For gases at low p and/or high T : low gas densities.
- Do not use ideal gas law for liquids and solids.
- ideal gas law is valid for all gases at:

  $T \geq 0°C$ and $P \leq 1$ atm

- Rule of thumb: ideal gas law works well with small errors if:

  $\frac{RT}{P} > 5 \frac{L}{mol}$ (for diatomic gases such as $N_2$, $H_2$, $O_2$ ... etc)

  or $\frac{RT}{P} > 20 \frac{L}{mol}$ (for other gases)

* standard temperature and pressure (STP): 0 °C
1 atm

at STP: the standard molar volume $\hat{V}_s = \frac{RT}{P}$

$$\hat{V}_s = \frac{RT}{P} = 22.415 \frac{L}{mol} = 22.415 \frac{m^3}{Kgmol} = 359.05 \frac{ft^3}{lbmol}$$

(verify these values)

Ex: A gas stream enters a reactor at rate of 1280 SCFH. what does that mean? find the molar flow rate.

SCFH: standard cubic foot per hour : standard $\frac{ft^3}{hr}$

$\therefore Q = 1280 \frac{ft^3}{hr}$ at STP: 0 °C, 1 atm

$$\Rightarrow \quad \dot{n} = \frac{PQ}{RT}$$

$$\text{or} \quad \dot{n} = \frac{Q}{\hat{V}_s} = \frac{1280\ ft^3}{hr} \left| \frac{lbmol}{359.05\ ft^3} \right. = 3.56 \frac{lbmol}{hr}$$

Ex: A gas enters a reactor at rate of 1280 SCFH, the actual temperature and pressure of this stream are 120 °C and 0.8 atm; respectively. What is the actual flow rate?

State 1: standard : $Q_1 = 1280 \ \frac{ft^3}{hr}$

$T_1 = 0°C = 0 + 273.15 = 273.15 \, K$

$P_1 = 1 \ atm$

State 2: actual : $Q_2 = ?$

$T_2 = 120°C = 120 + 273.15 = 393.15 \, K$

$P_2 = 0.8 \ atm$

note that $\dot{n}_1 = \dot{n}_2 = \dot{n}$ " Constant "

Apply ideal gas law for both states:

$$P_1 Q_1 = \dot{n} R T_1 \qquad \Rightarrow \qquad \frac{P_2 Q_2}{P_1 Q_1} = \frac{T_2}{T_1}$$
$$P_2 Q_2 = \dot{n} R T_2$$

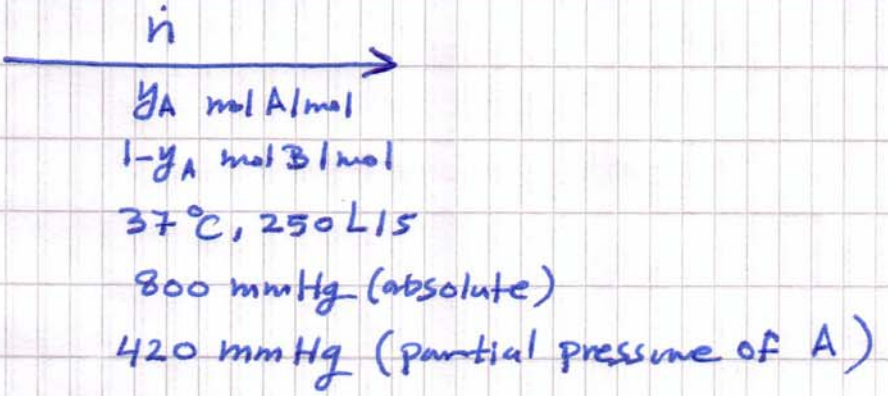
$$Q_2 = \left(\frac{T_2}{T_1}\right)\left(\frac{P_1}{P_2}\right) Q_1 = \left(\frac{393.15}{273.15}\right)\left(\frac{1}{0.8}\right)\left(1280\right)$$

$$= 2303 \ \frac{ft^3}{hr}$$

② If the stream has gas mixture (ideal gas mixture)

For such cases partial pressure information are given or required.

Ex:



Find $\dot{n}$ and $y_A$?

$$PQ = \dot{n}RT \Rightarrow \dot{n} = \frac{PQ}{RT} = 10.34 \text{ gmol/s}$$

How to relate $y_A$ with partial pressure of A; $P_A$?

- Definition of partial pressure of species i in a gas mixture; $P_i$:

$$P_i V = n_i RT$$

$$PV = nRT$$

$$\therefore \frac{P_i V}{PV} = \frac{n_i RT}{nRT} \Rightarrow \frac{P_i}{P} = \frac{n_i}{n} = y_i$$

$$\Rightarrow \boxed{P_i = y_i P} \quad \text{or} \quad \boxed{y_i = \frac{P_i}{P}}$$

In our example $y_A = \frac{P_A}{P} = \frac{420}{800} = 0.525$

Note that $\sum_{i=1}^{N} P_i = \sum_{i=1}^{N} y_i P = P \sum_{i=1}^{N} y_i = P$

$\Rightarrow \quad P = \sum_{i=1}^{N} P_i$ Total pressure equals to the sum of all partial pressures of compounds.

* Sometimes partial volumes of ideal gas mixtures are used:

$$\begin{aligned} PV_i &= n_i RT \\ PV &= nRT \end{aligned} \Rightarrow \frac{V_i}{V} = \frac{n_i}{n} = y_i$$

$$\text{and} \quad \boxed{\begin{aligned} V_i &= y_i V \\ V &= \sum_{i=1}^{N} V_i \end{aligned}}$$

$V_i$ : partial volume of species i in a mixture.

③ If the stream has pure real gas:

$$\text{Real} \Rightarrow \quad P\dot{V} \neq \dot{n} RT$$

$$P\hat{V} \neq RT$$

How P, T, and $\hat{V}$ are related?

They can be related and found using:

(a) Equation of state (EOS):

(b) Compressibility factor: $P\hat{V} = z(T,P)\,RT$

(c) Experimental method.

(a) Equation of State (EOS) method:

- all EOS are based on modifying the ideal gas law.
- EOS are semi-empirical relationships:
  - Modifications are based on thermodynamic theories.
  - some constants are determined based on curve fitting of experimental data.

▵ Most wide used EOS:

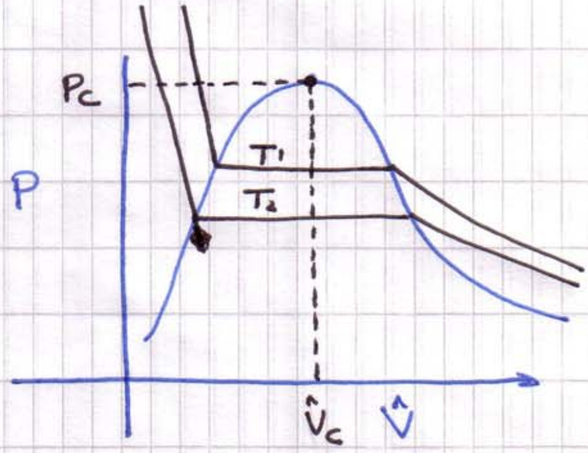
- Van der Waals EOS: $\left(P+\frac{a}{\hat{V}^2}\right)\left(\hat{V}-b\right)=RT$

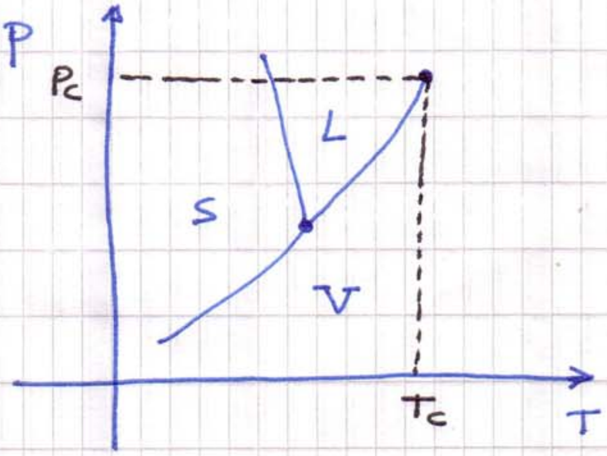
where $a=\frac{27R^2T_c^2}{64P_c}$ ; $b=\frac{RT_c}{8P_c}$

$T_c$: Critical temperature
$P_c$: Critical pressure
} see table B.1

- Redlick-Kwong EOS: see sec. 5.3 in your textbook

Critical state:





Critical state: set of physical conditions at which $\rho$ or $\hat{V}$ and other properties of Liquid and vapor phases become identical.

(b) Compressibility factor method:

$$P\hat{V} = zRT$$

z: Compressibility factor which is function of T and P

z is calculated using Compressibility charts:
Figures 5.4.1 — 5.4.4

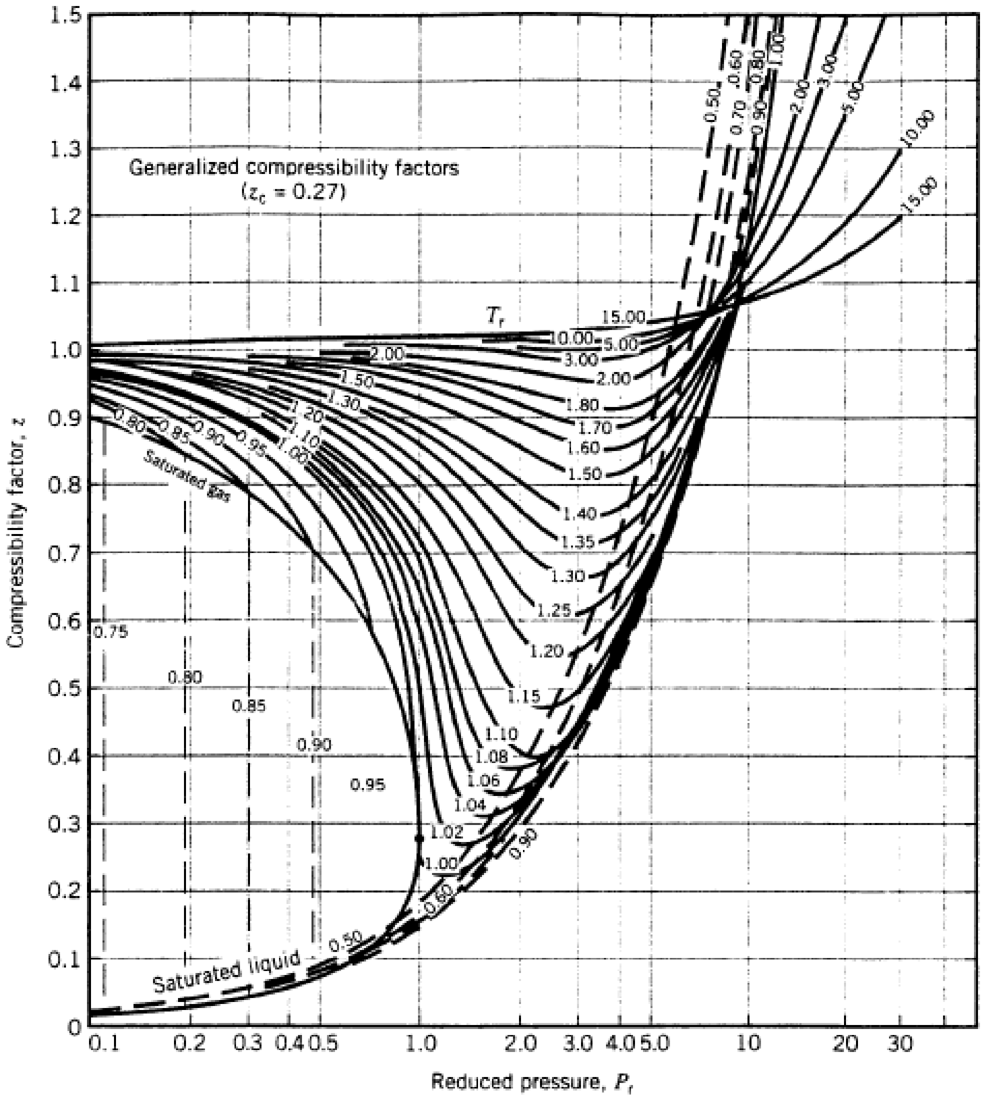


**Figure 5.4-1** (Reprinted with permission from *Chemical Process Principles Charts*, 2nd Edition, by O. A. Hougen, K. M. Watson, and R. A. Ragatz, John Wiley & Sons, New York, 1960.)

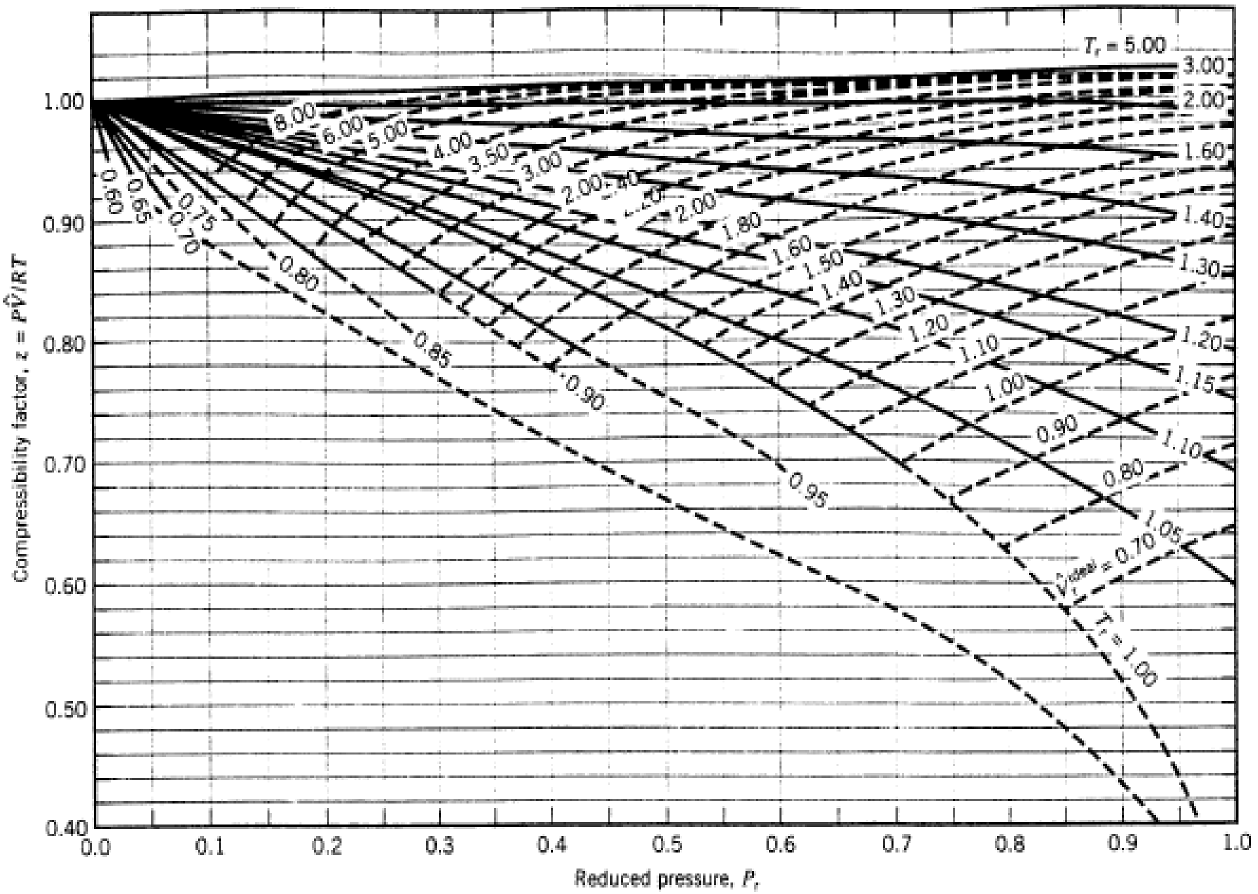


**Figure 5.4-2** Generalized compressibility chart, low pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 175. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

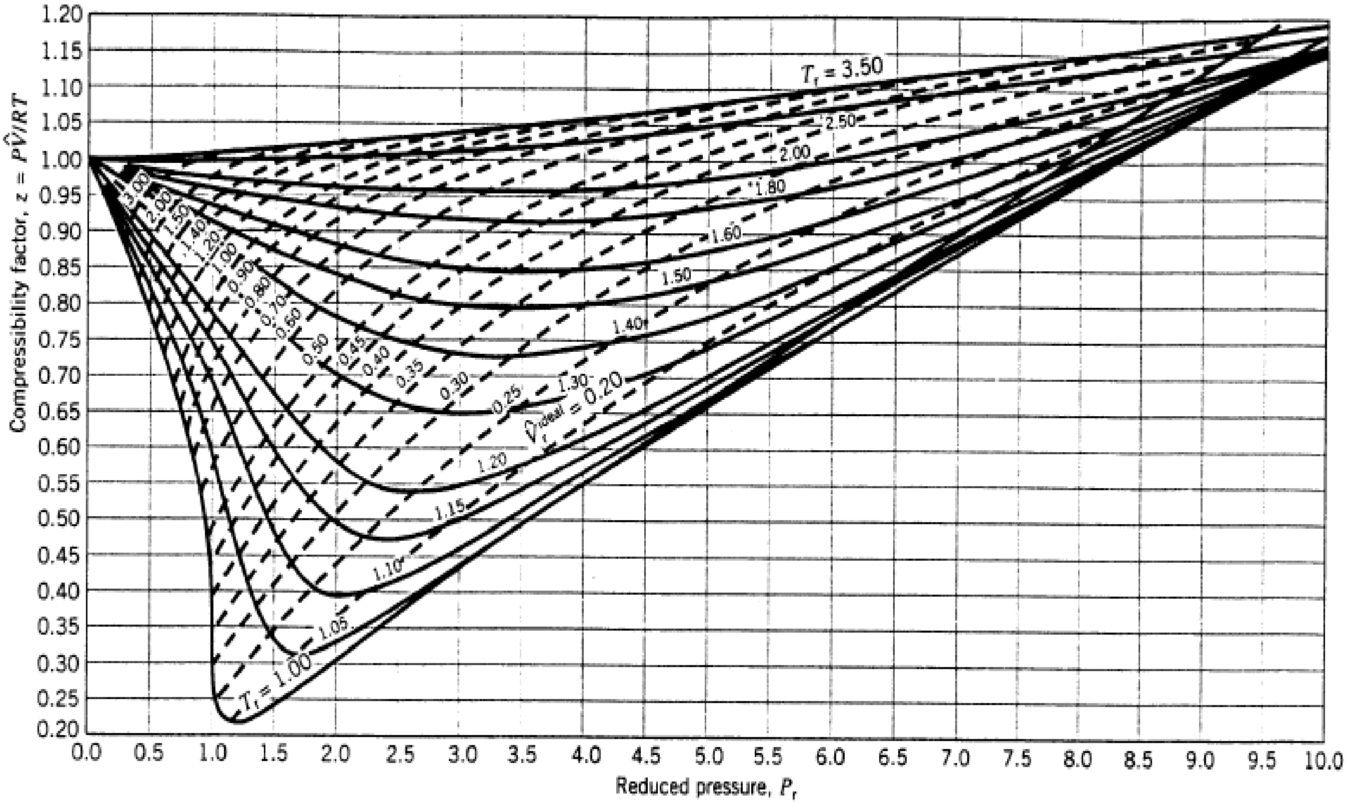


**Figure 5.4-3** Generalized compressibility chart, medium pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 176. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

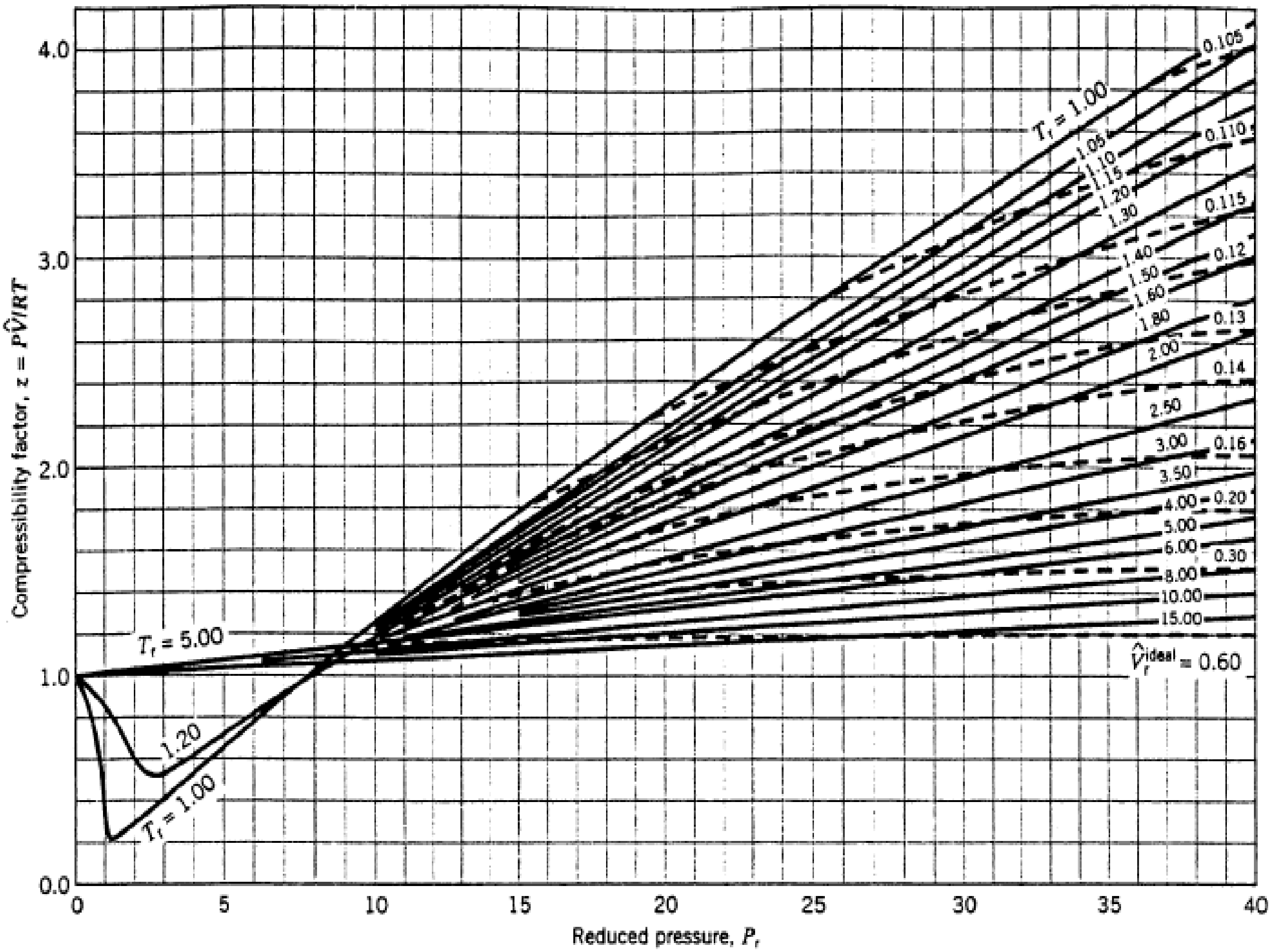


**Figure 5.4-4** Generalized compressibility chart, high pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition. copyright © 1974, p. 177. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

* procedure for using Compressibility Charts :

1. obtain critical values of $T_c$ and $P_c$ for the pure compound from table B.1 in your text book or other handbooks.
2. For $H_2$ and He adjust the critical values using Newton's Corrections:

$$T_c' = T_c + 8\ K$$

$$P_c' = P_c + 8\ atm$$

$\hat{V}_c'$ can be obtained from $\Rightarrow$ $\boxed{\dfrac{RT_c'}{P_c'} = \hat{V}_c'}$

3. Calculate the reduced quantities necessary for using compressibility charts:

$$P_r = \frac{P}{P_c}$$ $P_r$ : reduced pressure

$$T_r = \frac{T}{T_c}$$ $T_r$ : reduced temperature

$$\hat{V}_r = \frac{\hat{V}}{\hat{V}_c} = \frac{\hat{V}}{RT_c/P_c} = \frac{P_c\hat{V}}{RT_c}$$

Remember to use absolute values of T and P.

4. use the suitable chart to determine z or the required reduced quantity.

5. proceed with problem.

③ If the stream has real gas mixture:

There are two ways for dealing of real gas mixtures:

A. Define $z_{mean}$ to solve the problem involving real gas mixture:

$$z_{mean} = \sum_{i=1}^{N} z_i y_i$$

where $y_i$ is the mole fraction of species i

$z_i$ is the compressibility of species i at T and p.

then use: $p\hat{V} = z_{mean} RT$

B. Kay's method: $p\hat{V} = z' RT$

where $z'$ is the pseudo-compresibility factor for a mixture which can be obtained using:

- pseudocritical temperature: $T_c' = \sum_{i=1}^{N} y_i T_{c_i}$
- pseudocritical pressure: $P_c' = \sum_{i=1}^{N} y_i P_{c_i}$
- pseudo-reduced temperature: $T_r' = \frac{T}{T_c'}$
- pseudo-reduced pressure: $P_r' = \frac{P}{P_c'}$

Then use charts to obtain $z'$ at $T_r'$ and $P_r'$

Finally: $\hat{V} = \frac{z' RT}{P}$

Ex: a stream of a mixture of 75% $H_2$ and 25% $N_2$ (molar-basis) at 800 atm and −70 °C. Estimate the specific molar volume of this mixture using

① ideal gas law ?!
② Kay's method.

① ideal gas law : $P\hat{V} = RT$

$$\hat{V} = \frac{RT}{P} = \frac{(8.314)(-70+273.15)}{(800)(101325)}$$

$$= 2.08 \times 10^{-5} \frac{m^3}{mol} = 0.021 \frac{L}{mol}$$

② Kay's method :

- pick up critical values from table B.1 :

For $H_2$: $T_c = 33\ K$ $P_c = 12.8$ atm

these values must be corrected since the gas is $H_2$ :

$$T_c = 33 + 8 = 41\ K$$

$$P_c = 12.8 + 8 = 20.8 \text{ atm}$$

For $N_2$ : $T_c = 126.2\ K$ $P_c = 33.5$ atm

- calculate pseudo-critical values:

$$T_c' = \sum_{i=1}^{2} y_i T_{c_i} = (0.75)(41) + (0.25)(126.2)$$

$$= 62.3\ K$$

$$P_c' = \sum_{i=1}^{2} y_i P_{c_i} = (0.75)(20.8) + (0.25)(33.5)$$
$$= 24.0 \text{ atm}$$

- Calculate reduced values

$$T = -70 + 273.15 = 203.15 \text{ K}$$
$$P = 800 \text{ atm}$$

$$T_r' = \frac{T}{T_c'} = \frac{203.15}{62.3} = 3.26$$

$$P_r' = \frac{P}{P_c'} = \frac{800}{24.0} = 33.3$$

from Chart 5.4.4 at $P_r' = 33.3$ and $T_r' = 3.26$

$$z' = 1.86$$

$$P\hat{V} = z' RT \Rightarrow \hat{V} = \frac{z' RT}{P} = \frac{(1.86)(8.314)(203.15)}{(800)(101325)}$$

$$= 3.9 \times 10^{-5} \frac{m3}{mol}$$

$$= 0.039 \frac{L}{mol}$$

The absolute relative error in estimation $\hat{V}$ using ideal gas law is : $\%\text{ relative error} = \frac{|\hat{V}_{real} - \hat{V}_{ideal}|}{\hat{V}_{real}} * 100$

$$= 46\% \text{ (Large error !)}$$

Hw : - Try to use Van der waals EOS to calculate $\hat{V}$

- Use $z_{mean}$ method to calculate $\hat{V}$.

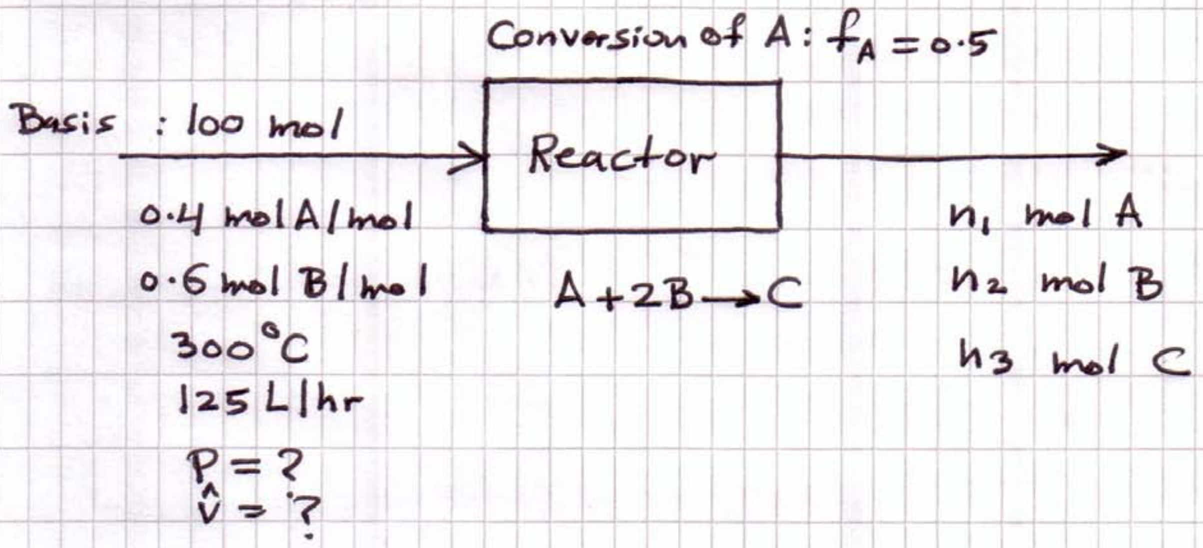
Ex: A gas-phase reaction is used to produce 50 mol/hr of species C according to the reaction:

$$A + 2B \longrightarrow C$$

The gaseous feed stream has a flow rate of 125 L/hr, a temperature of 300°C and molar composition of 40% A and 60% B. Find the pressure of this feed stream if the conversion of A is 50%. The critical values of A and B are: $P_{c,A} = 40$ atm, $P_{c,B} = 30$ atm

$T_{c,A} = 100°C$, $T_{c,B} = 200°C$

- Draw and completely label the flowchart:



Basis: 100 mol of feed stream and let the production rate of C as unknown then we can make scaling to adjust the flow rate of C to be as given (50 mol/hr).

- Degree of Freedom analysis:

For reactive process and using either molecular species balances or extent of reaction method

Degree of freedom is defined as (for material balances)

DF = # of unknowns − # of independent molecular balances − other equations + # of independent reactions.

\# of unknowns = 5 $\quad n_1, n_2, n_3, P, \hat{V}$

\# of indept. molecular balances = 3 $\quad A, B, C$

other equations = 3 :

$$\dot{n} = \frac{Q}{\hat{V}}$$

$$PQ = zRT$$

$$f_A = \frac{n_{A,in} - n_{A,out}}{n_{A,in}}$$

\# of indept. reactions = 1

DF = 5 − 3 − 3 + 1 = 0 ok ✓

- Start with the eq. that give you directly some unknowns:

$$f_A = 0.5 = \frac{(0.40)(100) - n_1}{(0.40)(100)} \Rightarrow \boxed{n_1 = 20 \text{ mol}}$$

Extent of reaction eqns.: $aA + bB \rightarrow cC$

**A** : $n_{out,A} = n_{in,A} - a\,\xi$

**B** : $n_{out,B} = n_{\underset{in}{\cancel{out}},B} - b\,\xi$

C : $n_{out,C} = n_{in,C} + C\,\xi$

our reacton is $A + 2B \rightarrow C$

$a = 1, \quad b = 2 \quad c = 1$

$\underline{A}: \; n_1 = (0.4)(100) - (1)\xi = 20 \Rightarrow \xi = 20 \text{ mol}$

$\underline{B}: \; n_2 = (0.6)(100) - (2)\xi = 60 - (2)(20) = 20 \text{ mol}$

$\underline{C}: \; n_3 = 0 + (1)\xi = (1)(20) = 20 \text{ mol}$

* Scaling to adjust the production of C to be $50 \frac{\text{mol}}{\text{hr}}$

$$SF = \frac{50 \text{ mol/hr}}{20 \text{ mol}} = 2.5 \frac{\text{mol/hr}}{\text{mol}}$$

$$\Rightarrow \dot{n}_0 = (100 \text{ mol}) * 2.5 \frac{\text{mol/hr}}{\text{mol}} = 250 \text{ mol/hr}$$

$\dot{n}_0$ is the molar flowrate of the feed.

$$\dot{n}_1 = (n_1)(SF) = (20)(2.5) = 50 \frac{\text{mol}}{\text{hr}}$$

$$\dot{n}_2 = (n_2)(SF) = (20)(2.5) = 50 \frac{\text{mol}}{\text{hr}}$$

$$\dot{n}_3 = (n_3)(SF) = (20)(2.5) = 50 \frac{\text{mol}}{\text{hr}}$$

$$\dot{n}_0 = \frac{Q}{\hat{V}} \Rightarrow \hat{V} = \frac{Q}{\dot{n}_0} = \frac{125 \text{ L/hr}}{250 \text{ mol/hr}}$$

$$= 0.5 \frac{\text{L}}{\text{mol}}$$

$$= 5 \times 10^{-4} \frac{\text{m}^3}{\text{mol}}$$

$$\hat{V}_r^{ideal} = \frac{\hat{V}}{\hat{V}_c} = \frac{\hat{V}}{RT_c / P_c} = \frac{P_c \hat{V}}{RT_c}$$

Now let us use Kay's method To calculate $z'$

$T_{c,A} = 100 + 273.15 = 373.15$ ; $T_{c,B} = 473.15$

$$T_c' = \sum y_i T_{c_i} = (0.4)(373.15) + (0.6)(473.15)$$

$$= 433.15 \text{ K}$$

$$P_c' = \sum y_i P_{c_i} = (0.4)(40) + (0.6)(30)$$

$$= \frac{34 \text{ atm} \;\big|\; 101325 \text{ Pa}}{\;\big|\; 1 \text{ atm}}$$

$$= 3.445 \times 10^6 \text{ Pa}$$

$$\hat{V}_r^{ideal} = \frac{P_c \hat{V}}{RT_c} = \frac{(3.445 \times 10^6)(5 \times 10^{-4})}{(8.314)(433.15)}$$

$$= 0.48$$

$$T_r = \frac{T}{T_c} = \frac{300 + 273.15}{433.15} = 1.32$$

From Fig 5.4.3 : $z = 0.71$

$$P\hat{V} = zRT$$

$$P = \frac{zRT}{\hat{V}} = \frac{(0.71)(8.314)(573.15)}{5 \times 10^{-4}}$$

$$= 6.766 \times 10^6 \text{ Pa}$$

$$= \frac{6.766 \times 10^6 \text{ Pa} \;\big|\; 1 \text{ atm}}{\;\big|\; 101325 \text{ Pa}}$$

$$= 66.8 \text{ atm}$$