



## **Unit 1**

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# Unit 1: Units and Process Variables

## Process Variables

Def: A value or parameter which can be monitored or controlled in a given system

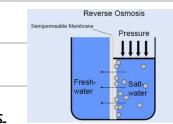
### ① Salt Water Desalination

Large scale thermal distillation may be too energy and cost intensive

SW Reverse Osmosis: Membrane separation process through semi-permeable, selective membrane. Large pressure applied opposite to natural osmosis.

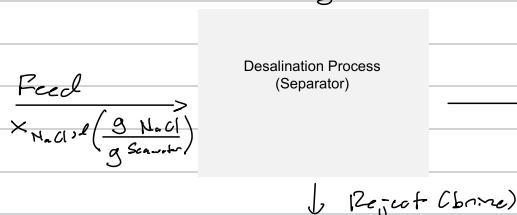
or measured

Tampa Bay Distillation



We simplify to a process flow diagram to allow us to ignore actual machine.

### Process Flow Diagram for desalination



### Flowrate Calculations

The desalination plant produces 25 million gallon per day of drinking water.

$$\dot{V} = 25,000,000 \text{ gal/day}$$

What is the mass flowrate of drinking water?  $\dot{m}$  in  $\frac{\text{lbs}}{\text{day}}$

$$25,000,000 \text{ gal} \times \frac{8.33 \text{ lbs}}{1 \text{ gal}} = 210,000,000 \frac{\text{lbs}}{\text{day}}$$

What is the molar flowrate of drinking water?  $\dot{n}$  in  $\frac{\text{mol}}{\text{day}}$

$$25,000,000 \text{ gal} \times \frac{8.33 \text{ lbs}}{1 \text{ gal}} \times \frac{1 \text{ kg}}{2.2046 \text{ lbs}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 5.3 \times 10^9 \frac{\text{mol}}{\text{day}}$$

Salinity of seawater by mass is 3.5%. What is the mol fraction of salt (NaCl)?

Suppose 100g seawater are present

$$\begin{cases} \rightarrow 3.5 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.04 \text{ g}} \\ \text{Assume Basis} \end{cases}$$

$$\rightarrow 96.5 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g}}$$

• Temperature, T

If calculating and looking up online, truncate as needed but use as many digits as possible. Also, round sigfigs on final answer.

Process Variables  
For systems in right-hand  
for gas/vapor

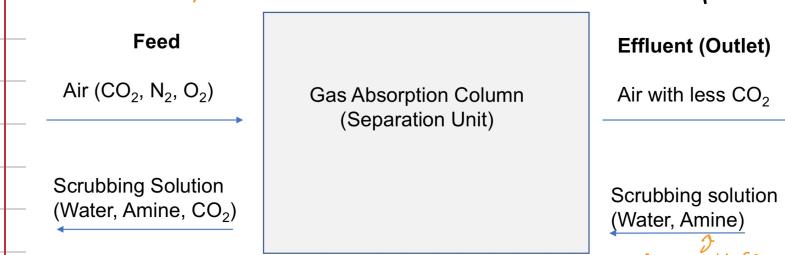
mass fraction:  $x_i = \frac{\text{mass of } i}{\text{mass of mixture}}$  or  $y_i$   
mol fraction:  $\text{mol of } i = \frac{\text{moles of } i}{\text{moles of mixture}} = x_i \text{ or } y_i$

• Pressure, P

Mass flowrate,  $\dot{m}$  ( $\frac{\text{mass}}{\text{time}}$ )  
Volumetric flowrate,  $\dot{V}$  ( $\frac{\text{volume}}{\text{time}}$ )  
Molar flowrate,  $\dot{n}$  ( $\frac{\text{mol/s}}{\text{time}}$ )  
Energy flowrate,  $\dot{H}$  ( $\frac{\text{energy}}{\text{time}}$ )

## ② $\text{CO}_2$ Capture

Chemical Engineers can design pollution control Systems (absorbers/membranes) to remove  $\text{CO}_2$  from industrial waste  
 Gas absorption columns: Use reactions to capture  $\text{CO}_2$  for use in chemical synthesis



Assume our behaviors ideally and consider that absorption with  $i = 1 \text{ mol/min}$ .

Write an equation for  $V_i$ ,

$$PV = n_i RT \quad \text{and} \quad P_i V_i = \bar{n}_i R T \quad \text{is also valid}$$

Be specific about stream which is ideal

$$\rightarrow V_i = \frac{\bar{n}_i R T}{P_i}$$

Consider air is a mixture of  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ . By mass: 76.95%  $\text{N}_2$ , 0.05%  $\text{CO}_2$ , and 23%  $\text{O}_2$ .

Weighted Average Properties of a mixture:  $MW_{\text{air}} (\text{g/mol}) = \sum y_i MW_i$

$y_i$  molar masses of all species  $i$   
 $x_i$  mole fractions of all species  $i$

$$\therefore MW_{\text{air}} (\text{g/mol}) = y_{\text{N}_2} MW_{\text{N}_2} + y_{\text{CO}_2} MW_{\text{CO}_2} + y_{\text{O}_2} MW_{\text{O}_2}$$

Process for Solving

- Look up all MW
  - Convert mass fraction to mol fraction for all species
- Assume a basis for gas calculations, 100 g air

### Relevant Process Variables

- Air Pressure
  - Amine:  $\text{CO}_2$  Reactions
  - ↳ Solution Concentrations
  - Fraction  $\text{CO}_2$  Removed
  - Flowsheet ( $x_i, y_i, v_i, \dot{V}_i$ )  $i = \text{species}$
  - ↳ Total Flowsheet ( $\dot{V}_i$ ) gases
  - Composition of each stream ( $x_i$  vs.  $y_i$ )
  - Energy Flowsheets ( $H_i$ )
  - Temperature and Pressure
- Individual Discussion Group Discussion

## **Unit 2**

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## Unit 2: Fundamentals of Material Balances on Non-Reactive Processes

### Types of Reactors

- Batch:** Reactants fed to reactor at beginning and removed later. No mass crosses system boundary.  
Allows for 'bad batches'  
**Example:** Beverage fermentation, Pharmaceutical, and Food Productions
- Continuous:** Reactants and Products continuously flow in and out of the reactor  
**Example:** Large-scale food production (Blending processes, Polymer extruders)  
Commodity chemical Production  
Faster and 24/7 processes, worker safety due to sealed facilities
- Semi-batch:** Partly batch and partly continuous  
**Example:** Polymerization reactions, Exothermic Reactions (Diluting Reactions)

### Steady-State vs. Transient Processes

- we do  
thus type:  
thus class
- (1) **Steady-State:** Process variables do not change with time with cts. processes
- (2) **Transient:** Process variable change with cts. process  
↳ require differential equations

Material Balance:  $\text{in} - \text{out} + \text{accumulation} - \text{consumption} = 0$

## General problem solving procedure: Material balances on non-reactive systems

1. Draw and label a process flow diagram (PFD)



Material R  
use mostly

- Label All streams with Known process variables ( $T_i, P_i, x_i, y_i$ )
- Label All streams with Unknown process variables
- Identify quantities for which you will solve

2. Perform a degree of freedom analysis on each subsystem

- # unknown process variables
- # independent material balances *\*max will be # of species in your system*
- # additional mathematical relationships

DOF

If  $DOF \leq 0$ , then... *solve!*

If  $DOF > 0$ , then... *Cannot solve...* *This is an unsolvable answer*

3. Convert all quantities to the same basis

4. Determine the "plan of attack" (POA): the order that you will solve the subsystems

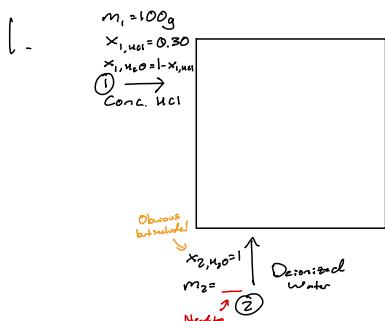
5. Write all material balances for all necessary subsystems

6. Identify the equations you will use to solve for the desired quantities and the order in which you will solve them.

7. SOLVE! Now, you can plug in numbers to calculate quantitative answers

## SINGLE UNITS

**Example 1: Diluting HCl.** In a batch mixing process at a chemical plant, 100g of 30wt% HCl is diluted with deionized water. The final product is 10wt% HCl. How much water is needed for this process?



### 2. Degree of Freedom (DOF) Analysis

Derived from law of cons. of mass:  $\rightarrow$  1 unknown (mass)  $\rightarrow$  1 independent material balance  $\rightarrow$  1 additional eqns.  $\rightarrow$  0 additional eqns.

Can write 2 more as there are 2 species ( $\text{HCl} + \text{H}_2\text{O}$ )

in-out of gen-cons. = accumulation

Mass # species!  $\rightarrow$  2 unknowns  $\rightarrow$  2 material balances  $\rightarrow$  0 additional eqns.

$$2 - 2 - 0 = 0 \text{ DOF } \textcircled{4}$$

3. All Process Variables on same basis?  
Are we dimensionally consistent? ✓

### 4. Material Balances

in - out + generation - consumption = accumulation  
(gen) (cons)

No chemical reaction

Every thing counts  
(not just a batch process!)

$$\rightarrow \text{in} - \text{out} = 0 \quad \text{or} \quad \text{in} = \text{out}$$

5.  $\text{HCl} : m_1 x_{1,\text{HCl}} = m_3 x_{3,\text{HCl}}$

$\text{H}_2\text{O} : m_1 x_{1,\text{H}_2\text{O}} + m_2 x_{2,\text{H}_2\text{O}} = m_3 x_{3,\text{H}_2\text{O}}$

Add up inip and  $\rightarrow$  Total Mass:  $m_1 + m_2 = m_3$

cancel out with mass fractions

$$m_1 x_{1,\text{HCl}} + m_1 x_{1,\text{H}_2\text{O}} + m_2 x_{2,\text{H}_2\text{O}} =$$

$$m_2 x_{3,\text{H}_2\text{O}} + m_3 x_{3,\text{HCl}}$$

$$\rightarrow m_1 (x_{1,\text{HCl}} + x_{1,\text{H}_2\text{O}}) + m_2 (x_{2,\text{H}_2\text{O}} + x_{3,\text{H}_2\text{O}}) =$$

$$m_3 (x_{3,\text{H}_2\text{O}} + x_{3,\text{HCl}})$$

$$\rightarrow m_1 + m_2 = m_3$$

### 6. Plan of Attack (PoA)

- Solve HCl for  $m_3$
  - Solve  $\text{H}_2\text{O}$  for  $m_2$  using (i) result
- For ease, solve  $m_2$  from mass balance

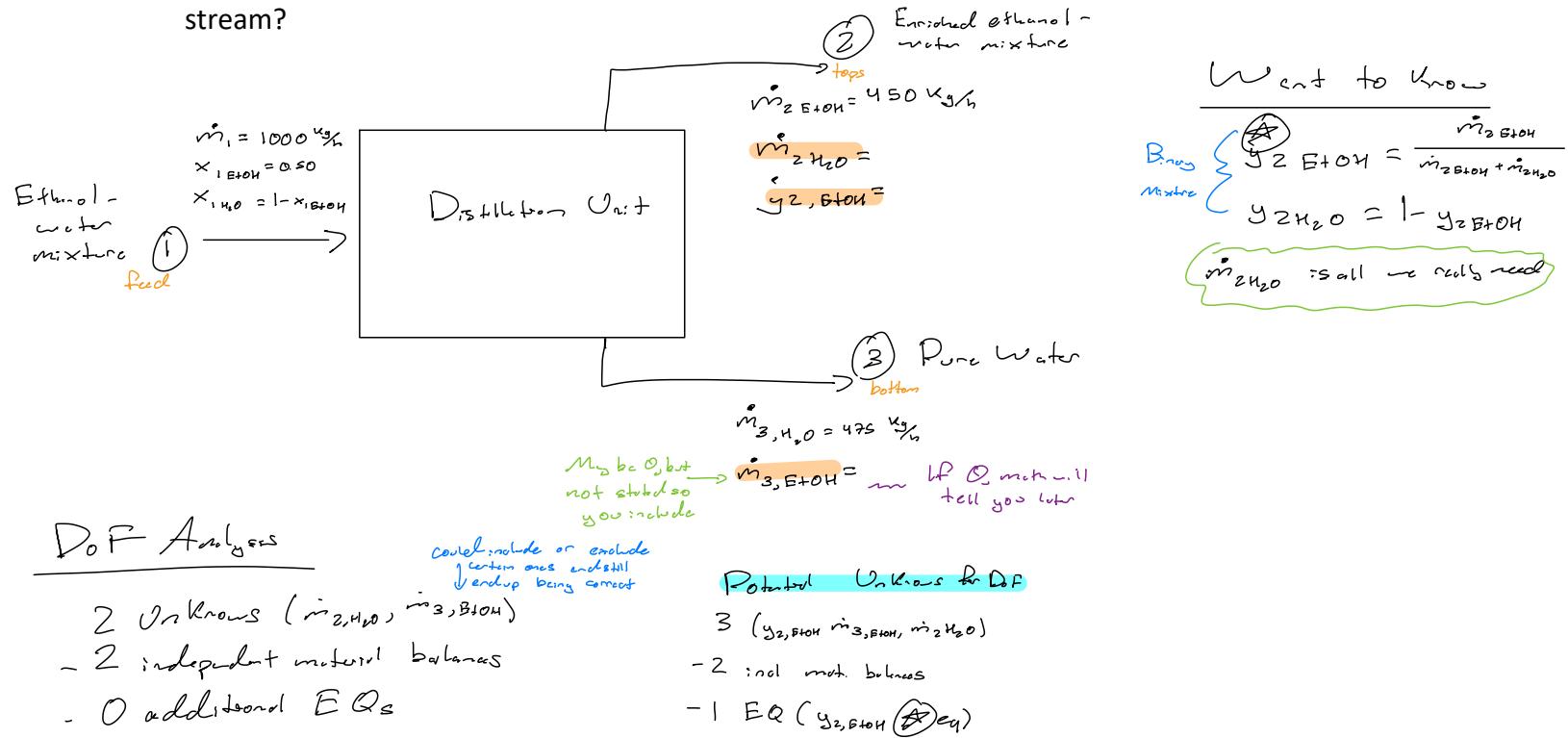
$$7. m_3 = \frac{m_1 x_{1,\text{HCl}}}{x_{1,\text{HCl}}}$$

$$m_1 + m_2 = \frac{m_1 x_{1,\text{HCl}}}{x_{1,\text{HCl}}}$$

$$\rightarrow m_2 = \frac{m_1 x_{1,\text{HCl}}}{x_{1,\text{HCl}}} - m_1$$

Usually stop here or earlier

**Example 2: Continuous Distillation.** In a continuous, steady state process, 1000 kg/h of 50wt% ethanol/water mixture is separated by distillation. Due to the vapor-liquid equilibrium achieved by ethanol and water, the top stream is enriched in ethanol but still contains some water. The mass flowrate of ethanol in the tops stream is 450 kg ethanol/hour. What is the composition (by mass) of the top stream?



O D.o.F  $y_{2,\text{EtOH}}$  ! It's Soluble!

Material Balances

$m_{\text{in}} + \text{generation} - \text{consumption} = \text{accumulation}$   
 No physical separation/reaction occurs

$\rightarrow m_{\text{in}} = m_{\text{out}}$

$$\text{EtOH: } m_1 x_{1,\text{EtOH}} = m_2 x_{2,\text{EtOH}} + m_3 x_{3,\text{EtOH}}$$

$$\text{H}_2\text{O: } m_1 x_{1,\text{H}_2\text{O}} = m_2 x_{2,\text{H}_2\text{O}} + m_3 x_{3,\text{H}_2\text{O}}$$

$$\text{Total: } m_1 = m_2 + m_3$$

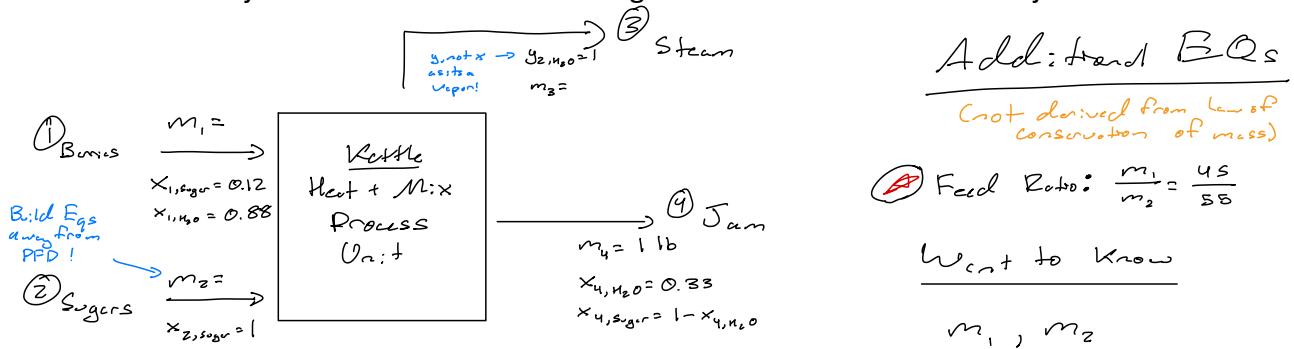
All quantities are on a mass basis

It's steady-state!  
 So there is O  
 accumulated

### Plan of Attack

- Solve  $H_2O$  for  $m_{2,H_2O}$
- Use  $m_{2,H_2O}$  in  $y_{2,EtOH} \neq \text{eq}$

**Example 3: Strawberry Jam.** Strawberries contain 12wt% sugars and 88wt% water. To make jam, crushed strawberries are mixed with additional sugars in a 45:55 mass ratio. Then the mixture is heated until the residue is 1/3 water by mass. How many lbs. of strawberries are needed to make 1 lbs. of jam? How much additional sugar is needed to make 1 lbs. of jam?



### DOF Analysis

- 3 unknowns ( $m_1, m_2, m_3$ )
- 2 independent material balances (two species, sugar & water)
- 1 additional equation ( $\textcircled{1}$ )

$\textcircled{0} \rightarrow \text{DOF} \leq 0 \checkmark$   
Can solve!

Material Balances

Always start with law of conservation of mass!  
in-out + gen = consumption + accumulation  
 $\Rightarrow m_{\text{out}} = m_{\text{in}}$

$H_2O: m_1 x_{1,H2O} = m_2 + m_4 x_{4,H2O}$

Sugar:  $m_1 x_{1,sugar} + m_2 = m_4 x_{4,sugar}$

Total:  $m_1 + m_2 = m_3 + m_4$

Batch process as final quantity is a mass, not flow rate

Independent Balances

Feed Ratio:  $\frac{m_1}{m_2} = \frac{45}{55} \text{ } \textcircled{X}$

To highlight everything you know

### How to Solve

- Solve  $\textcircled{1}$  for  $m_1$
- Plug  $\textcircled{1}$  into sugar balance to solve for  $m_2$
- Plug  $m_2$  into  $\textcircled{1}$  to solve  $m_1$

Solve  $\textcircled{1}$  Not needed on HW unless specified

$$(i) m_1 = \frac{45}{55} m_2$$

$$(ii) \frac{45}{55} m_2 x_{1,sugar} + m_2 = m_4 x_{4,sugar}$$

$$m_2 \left( \frac{45}{55} x_{1,sugar} + 1 \right) = m_4 x_{4,sugar}$$

$$m_2 = \frac{m_4 x_{4,sugar}}{\frac{45}{55} x_{1,sugar} + 1}$$

(iii) ...

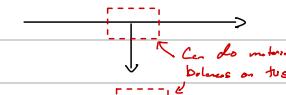
Don't need to do the algebra

Ron LOS

# Multi-Unit Processes w/ Recycle and Bypass Streams

## New Terminology

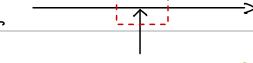
**Splitting Point:** Where 1 stream becomes 2 streams



Note

is a subsystem  
for all pictures  
and PFD here

**Mixing Point:** Where 2 or more streams become 1 Stream



**Purge:** When a portion of the recycle stream is split and leaves the system



## Recycle vs. Bypass

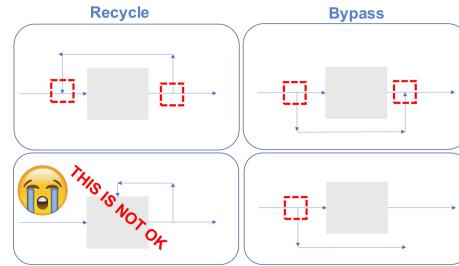
**Recycle:** Dilute a stream

Circulate a working fluid

Recover a catalyst

Reuse unreacted components

**Bypass:** Circumvent a unit operation  
Overflow condition for safety

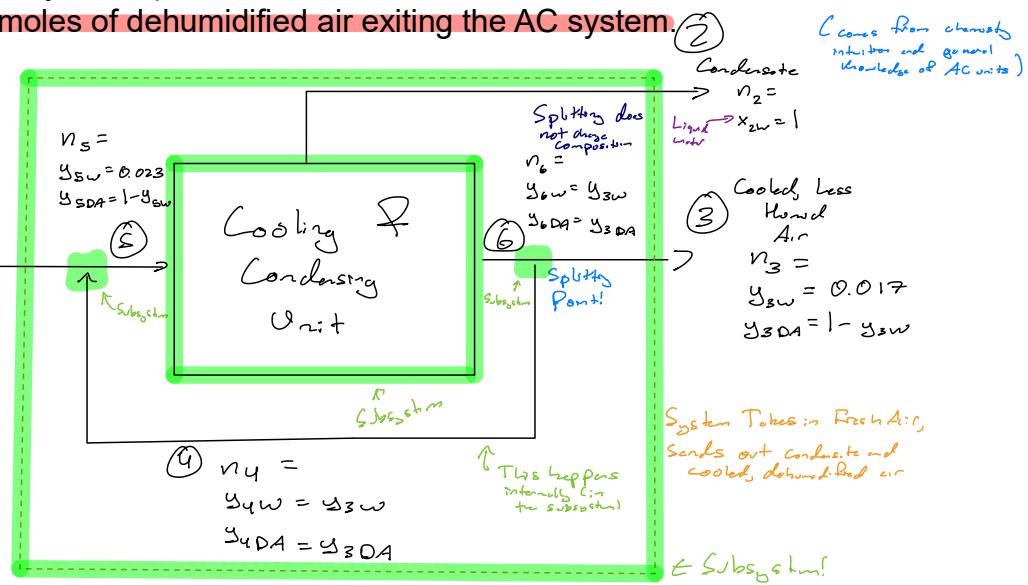


"The stream is  
recycled into the  
reactor" means stream  
going into reactor!

## RECYCLE AND BYPASS (SINGLE AND MULTI UNIT)

**Example 4: Air conditioning.** An air conditioning system takes in fresh air (4 mol% water vapor) and outputs cooled air with lower humidity (1.7 mol% water vapor). A stream of fresh air is combined with a recycled stream of cooled/dehumidified air and is passed through the condenser which lowers the humidity and cools the air. The blended air entering the condenser is 2.3 mol% water vapor. The air conditioning system operates as a continuous, steady state process. Calculate the moles of fresh feed, moles of water condensed, and moles of dehumidified air exiting the AC system.

D.F for total  
Balance



If you are only given compositions, you may assume a basis for your calculation!

Want to know:  $n_1, n_2, n_3$

units constraint ✓  
DoF Analysis: *Can do 1 per subsystem present • Entire System, Splitting Point, do all 4!*

Overall-DoF: 3 unknowns ( $n_1, n_2, n_3$ )

Given only composition information, assume a basis after DoF analysis is completed  
- 2 indep. material balances (W, DA)  
- 0 additional Eqs *From Curr or the PPD*

1 DoF, cannot solve here!

Mixing-DoF: 3 unknowns ( $n_1, n_2, n_3$ )

Given only composition information, assume a basis after DoF analysis is completed  
- 2 indep. material balances (W, DA)  
- 0 additional Eqs *Common one we would be like a mixing ratio*

Splitting-DoF: 3 unknowns ( $n_2, n_4, n_6$ )

W:  $n_6 y_{6w} = n_4 y_{4w} + n_2 y_{2w}$   
DA:  $n_6 y_{6da} = n_4 y_{4da} + n_2 y_{2da}$   
 $\rightarrow n_6 = n_4 + n_2$

~ 1 indep. material balances *May 2 as DA & W, but comp is fine so can only write 1*  
- 0 additional Eqs

2 DoF, cannot solve here!

Cooling/Condensing-DoF: 3 unknowns ( $n_2, n_5, n_6$ )

- 2 indep. material balances (W, DA)  
0 additional Equations

Only can do it when only compositions are given!  
Plan: We have to assume a basis,

look at substreams with DoF!

To avoid assuming basis for what you're looking to find

(i) Go for  $n_s$ , as it allows us to solve 2 substreams  
 $n_s = 100 \text{ mol}$

(ii) Solve cooling/condensing  $\rightarrow$  mixing

(iii) Use Splitting to solve for  $n_3$

## Material Balances

highlight as things are known

### Cooling / Condensing Mat Balances

$$w: n_3 y_{3,w} = n_6 y_{6,w} + n_2$$

$$DA: n_3 y_{3,DA} = n_6 y_{6,DA}$$

$$\text{Total: } n_3 = n_6 + n_2$$

How to Solve:

- (i) Solve (DA) for  $n_6$
- (ii) Solve (Total) for  $n_2$

### Mixing Mat Balances

$$w: n_1 y_{1,w} + n_4 y_{4,w} = n_3 y_{3,w}$$

$$DA: n_1 y_{1,DA} + n_4 y_{4,DA} = n_3 y_{3,DA}$$

$$\text{Total: } n_1 + n_4 = n_3$$

How to Solve:

- (i) Solve (Total) in terms of  $n_1$
- (ii) Plug  $n_1$  into (w) & solve for  $n_4$
- (iii) Plug  $n_4$  into total to calculate  $n_3$

### Splitting Mat Balances

$$w: \quad \quad \quad$$

$$DA: \quad \quad \quad$$

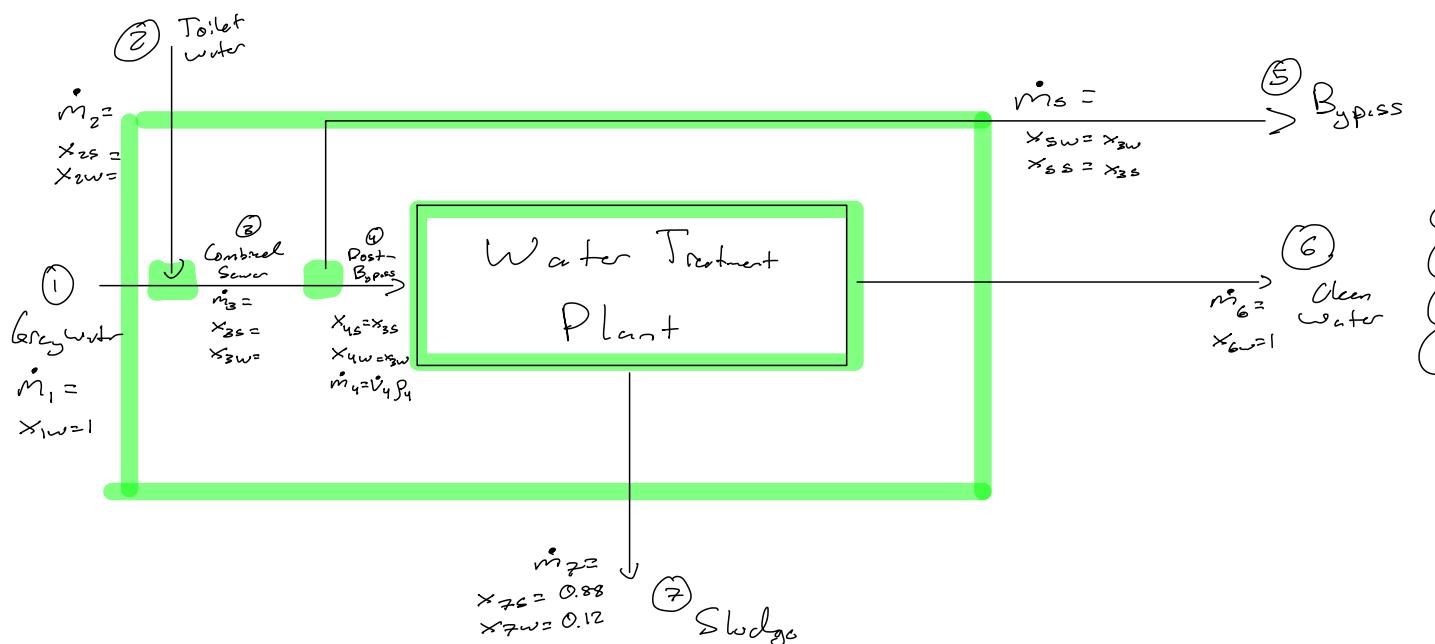
$$\text{Total: } n_6 = n_3 + n_4$$

How to Solve:

- (i) Solve (Total) for  $n_3$

**Example 5: Combined sewers have Lake Erie down in the dumps.** The Easterly Water Treatment Plant in Cleveland, OH treats an average of 100 million gallons of combined sewer water per day and has a maximum capacity of 400 million gallons per day. For the purposes of this exercise, we will model the water treatment plant as a continuous, steady state process. Cleveland's combined sewer systems has two primary sources of water: (1) grey water collected from outdoor sewers (i.e. rain water, water from washing cars, etc.) and (2) toilet water that contains human waste. Grey water is considered pure water. Toilet water can be approximated as a mixture of solids and water. The Easterly Plant intakes the combined sewer stream (mixture of grey water and toilet water) and outputs two streams: (1) treated water that is fed to Lake Erie and (2) sludge which contains mostly solids and some water. When the plant capacity is exceeded (i.e. on very rainy days), some of the combined sewer stream bypasses the Easterly Plant and is fed directly to Lake Erie. On September 7, the combined sewer stream exceeded the Easterly Plant Capacity by 20wt%. The sludge contains 8wt% of the water that was fed to the Easterly Plant. The composition of the sludge is 88wt% solids and the balance is water. The average density of the combined sewer stream is 10 lbs/gallon.

On September 7 (the day of the overflow), how many lbs. of solids were discharged into Lake Erie? What was the volume of clean water discharged into the lake from the water treatment plant (this excludes water in the bypass)?



### Additional Info

$$\dot{V}_4 = 400 \text{ million gallons/day}$$

$$\rho_4 = 10 \frac{\text{lbs}}{\text{gallons}} \quad * \text{ Needs to convert units later}$$

- 8% water in stream 4 exists in stream 7

$$\dot{m}_2 x_{2w} = 0.08 \dot{m}_4 x_{4w} \quad \text{(0.08} x_{4w} = x_{2w})$$

- Combined sewer exceeds capacity by 20 wt%

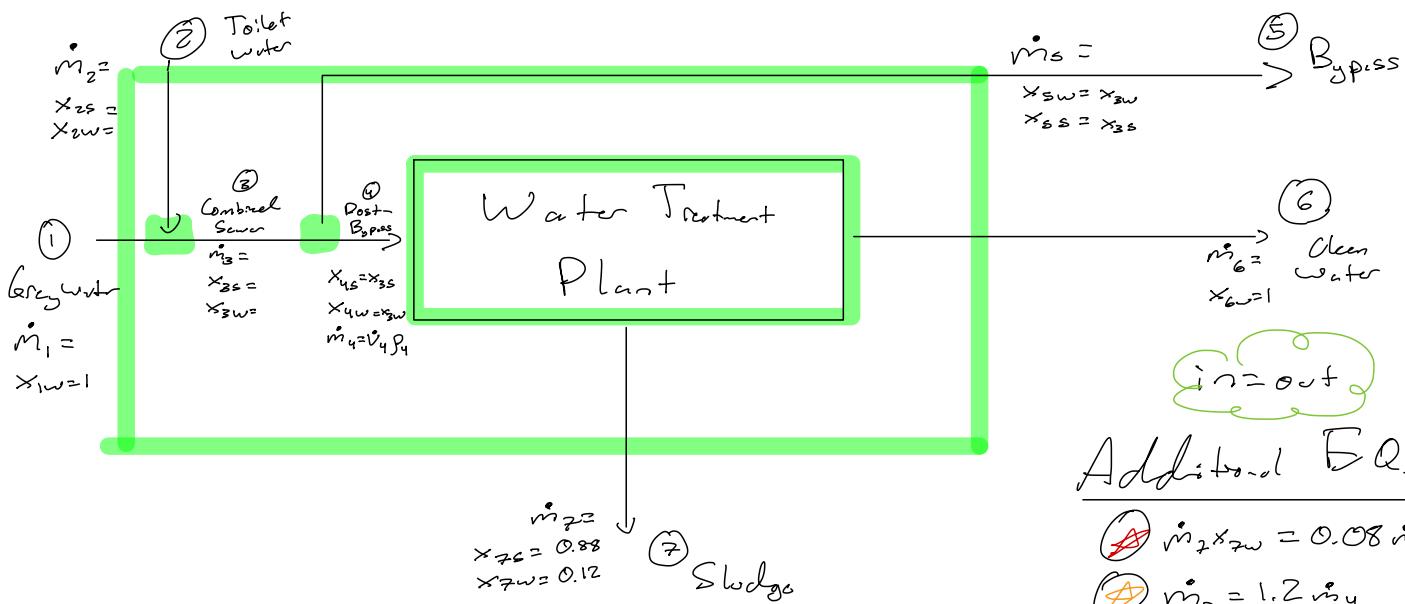
$$\dot{m}_3 = 1.2 \dot{m}_4$$

$$0.2 \dot{m}_4 = \dot{m}_5 \quad \text{This is also valid}$$

### Want to Know

$$\dot{V}_6 = \frac{\dot{m}_6}{\rho_{water}}$$

$$\dot{m}_5 x_{ss}$$



Dof Analysis One per subsystem

### Water Treatment Plant

- 4 unknowns ( $m_6, m_7, x_{3S}, x_{3W}$ )
  - 2 indep. material balances (b/c 2 species)
  - 2 add. transl. Eqs (~~(1)~~, ~~(2)~~)
- 0 Dof Soluble

### Splitting Point

- 4 unknowns ( $m_3, x_{2S}, x_{3W}, m_6$ )
- 1 indep. material balance (Splitting point explained below)
- 2 additional Eqs (~~(1)~~, ~~(2)~~)

1 Dof  $\frac{1}{1}$

$$\text{Si: } m_3 x_{2S} = m_4 x_{2S} + m_5 x_{2S}$$

$$\text{H}_2\text{O: } m_3 x_{3W} = m_4 x_{3W} + m_5 x_{3W}$$

$$\text{Total: } m_3 = m_4 + m_5$$

This is already

### Mixing Point

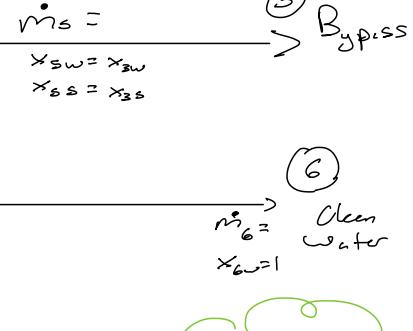
- 7 unknowns ( $m_1, m_2, m_3, x_{2S}, x_{2W}, x_{3S}, x_{3W}$ )
  - 2 indep. balances (2 species)  $\leftarrow$  composition chose @ mixing pt.
  - 2 additional Eqs (~~(1)~~, ~~(2)~~)
- 3 Dof unsolvable

### Overall

- 9 unknowns ( $m_1, m_2, m_3, m_4, m_5, m_6, x_{2S}, x_{2W}, x_{3S}, x_{3W}$ )
  - 2 indep. balances (2 species)
  - 2 additional Eqs (~~(1)~~, ~~(2)~~)
- 5 Dof unsolvable!

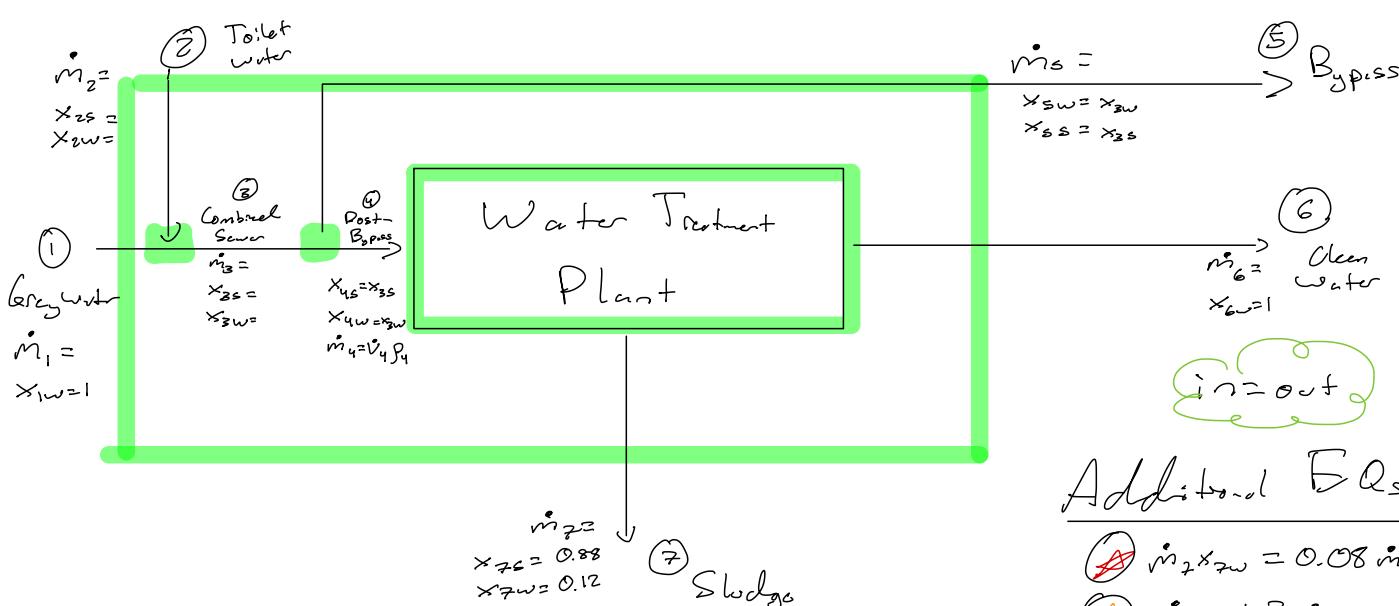
### Plant

- (i) Sole water Treatment Plant  
( $m_6, m_7, x_{3S}, x_{3W}$  will be known)
- (ii) Sole Splitting Point to get  $m_3$



Additional Eqs

$$\begin{aligned} \cancel{(1)} \quad m_2 x_{2W} &= 0.08 m_4 x_{4W} \\ \cancel{(2)} \quad m_3 &= 1.2 m_4 \\ \cancel{(3)} \quad x_{3S} + x_{3W} &= 1 \\ \cancel{(4)} \quad x_{2S} + x_{2W} &= 1 \\ \cancel{(5)} \quad x_{5W} + x_{5S} &= 1 \end{aligned} \quad \begin{array}{l} \text{Build into PFD} \\ \text{into same form} \end{array} \quad \begin{array}{l} \text{Dof. of} \\ \text{mass flow} \end{array}$$



### Material Balances

#### Treatment

$$\text{in-out + gen-cons = accumulation}$$

in-out

$$S: \dot{m}_4 x_{4s} = \dot{m}_7 x_{7s}$$

$$W: \dot{m}_4 x_{4w} = \dot{m}_7 x_{7w} + \dot{m}_6$$

$$\text{Total: } \dot{m}_4 = \dot{m}_7 + \dot{m}_6$$

$$\cancel{\dot{m}_2 x_{2w}} = 0.08 \dot{m}_4 x_{4w}$$

$$\Rightarrow 0.08 \dot{m}_4 (1 - x_{4s}) = \dot{m}_7 (1 - x_{7s}) \quad (y)$$

#### Splitting Point

See SS on Right

Plan: treatment  $\rightarrow$  splitting

MAT Balance - Treatment	in-out+gen-cons=accumulation
S: $\dot{m}_4 x_{4s} = \dot{m}_7 x_{7s}$	norms $x_{4w} + x_{4s} = 1$
W: $\dot{m}_4 x_{4w} = \dot{m}_7 x_{7w} + \dot{m}_6$	Cont. Steady state $0.08 \dot{m}_4 x_{4w} = \dot{m}_7 x_{7w}$
total: $\dot{m}_4 = \dot{m}_7 + \dot{m}_6$	(z) $0.08 \dot{m}_4 (1 - x_{4s}) = \dot{m}_7 (1 - x_{7s})$

#### How to Solve

$$1. \text{ Calculate } \dot{m}_4 = \dot{V}_4 \rho_4$$

$$2. \text{ Solve } (y) \text{ for } \dot{m}_7 \text{ and plug into } S - \text{solve } x_{4s}$$

$$3. \text{ Use } x_{4s} \text{ in } S \text{ balance, solve for } \dot{m}_7$$

$$4. \text{ Use total to calc } \dot{m}_6$$

$$5. \text{ calc } x_{4w} = 1 - x_{4s}$$

#### Splitting Point

$$\dot{m}_3 = \dot{m}_4 + \dot{m}_5 \quad \text{and} \quad \dot{m}_3 = 1.2 \dot{m}_4$$

$$6. \text{ calculate } \dot{m}_5 \text{ from } (y)$$

$$7. \text{ calc } \dot{m}_5 \text{ from mat balance}$$

Now we have  $\dot{m}_6$  and  $\dot{m}_5 x_{5s}$   
because  $x_{3s} = x_{5s}$ .

### Solution Steps

$$(1) \text{ Calculate } \dot{m}_4 = \dot{V}_4$$

$$(2) \text{ Solve } (y) \text{ for } \dot{m}_7 \text{ and plug into } S \text{ balance to solve for } x_{4s}$$

$$(3) \text{ Use } x_{4s} \text{ in } S \text{ balance to solve for } \dot{m}_7$$

$$(4) \text{ Use total to calc } \dot{m}_6$$

$$(5) \text{ Calc } x_{4w} = 1 - x_{4s}$$

## **Unit 3**

---



# Material Balances on Reactive Systems

Stoichiometry: Remember to balance all chemical reactions!

Ex: Haber-Bosch Process combines nitrogen with hydrogen to create ammonia.

See WS/  
Handout

(i) Write a balanced chemical reaction  
(ii) If 100 mol of nitrogen fed to reactor, how many mols ammonia produced?

$$\text{Selectivity} = \frac{\text{moles of desired Product}}{\text{Moles of undesired products}} \times 100$$

$$\text{Yield} = \frac{\text{moles of desired product}}{\text{Theoretical moles of desired product}} \times 100$$

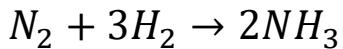
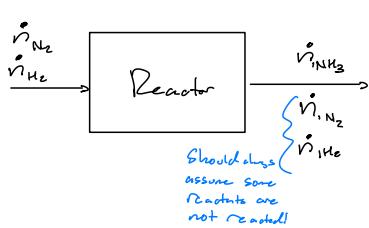
If prop side rxn occurred, what's the max mols that could be produced

Single Pass Conversion: Fractional conversion of reactor

Overall Conversion: Fractional conversion of whole process

## Unit 3: Material Balances on Reactive Systems

Consider the chemical reaction for producing ammonia:



### Jargon for chemical reactions

**Stoichiometric proportion:** Occurs when a ratio of moles present is equal to the ratio of the stoichiometric coefficients in a balanced EQ.

" $H_2$  and  $N_2$  fed in a stoich propn."

$$\Rightarrow \frac{\dot{v}_{N_2}}{\dot{v}_{H_2}} = \frac{1}{3}$$

could be an additional EQ

**Limiting reactant:** A reactant that is present in less than its stoichiometric proportion relative to every other reactant.

"We feed 3 mol  $H_2$  and 0.5 mol  $N_2$ "

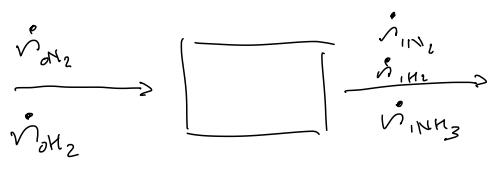
$\Rightarrow N_2$  is the limiting reactant

**Excess reactant:** A reactant that is present in more than its stoichiometric proportion relative to every other reactant.

$\Rightarrow H_2$  is in excess

**Fractional conversion:** Ratio of (moles reacted)/(moles fed) for a given reactant.

$\frac{1}{2} NH_3$  only works  
with a perfect reactor

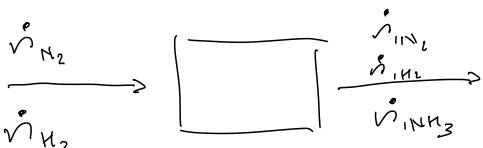


$$f_i = \frac{\dot{v}_{i, \text{reacted}}}{\dot{v}_{i, \text{fed}}}$$

$i = \text{species}$

$$f_{N_2} = \frac{\dot{v}_{N_2} - \dot{v}_{H_2}}{\dot{v}_{N_2}}$$

**Extent of Reaction (extent of conversion):** Indicates how far the reaction proceeds. You can think of this as a combined term that describes the net effect of generation and consumption for a chemical reaction. *You can write one for each reaction*



$$\text{in-out + gen-consum} = \text{accumulation}$$

Batch or Cts. steady state

Keep in mind: chemical rxn. described by "ext of rxn"

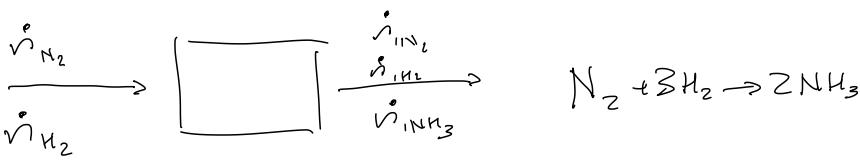
$$\text{Out} = \text{in} + \text{gen/consumption}$$

$$n_{i,i} = n_{i,0} + \sum \gamma_{ij} \bar{z}_j$$

**Extent of Reaction:**

$$\bar{z} = \frac{n_{i,i}}{n_{i,0}} = \frac{\text{out}}{\text{in}}$$

$\gamma_{ij}$  = stoich. coeff. of species  $i$  in rxn  $j$   
 $n_{i,i}$  = moles of  $i$  out  
 $n_{i,0}$  = moles of  $i$  in  
 $\bar{z}_j$  = extent of rxn for reaction  $j$   
+  $\bar{z}$  = when species is generated  
-  $\bar{z}$  = when species is consumed



For single  $R_m$  ( $j=1$ )

$$\dot{n}_{i,s} = \dot{n}_{i,0} + \dot{v}_i \bar{z}$$

Material Balances (for Haber process)

$$N_2: \dot{n}_{N_2} = \dot{n}_{N_2,0} + (-1)\bar{z} \quad \bar{z}_{N_2} = 1 \text{ from EO}$$

$$H_2: \dot{n}_{H_2} = \dot{n}_{H_2,0} + (3)\bar{z} \quad \text{Consuming!} \quad \bar{z}_{H_2} = 3 \text{ from EO}$$

$$NH_3: \dot{n}_{NH_3} = 0 + 2\bar{z} \quad \text{Generating!} \quad \bar{z}_{NH_3} = 2 \text{ from EO}$$

Total? Moles are not conserved (cannot write total balance for reactive systems!!!) No !!

$A \rightarrow 3B$

$\neq 3$

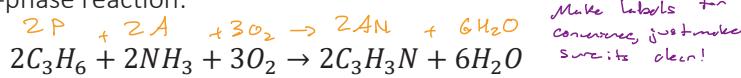
Moles are not conserved!

When working with  
reactor systems,  
you must work  
with moles!!

## Unit 5: Material Balances on Reactive Systems

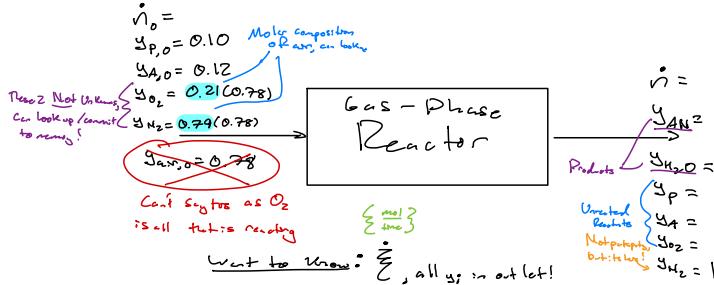
### Example 1: Production of acrylonitrile

Acrylonitrile is an important precursor for many consumer goods! Synthesis of acrylonitrile proceeds according to the following gas-phase reaction:



The feed to the reactor contains 10mol% propylene ( $C_3H_6$ ), 12mol% ammonia ( $NH_3$ ) and 78mol% air. The process has a 30% conversion of the limiting reactant. What are the limiting and excess reactants? What is the extent of reaction? What is the composition of the product stream?

PPD



Addl. Reactn Eqs

$$f_p = \frac{\text{mol P reacted}}{\text{mol P fed}} = \frac{\dot{V}_0 P_{0,0} - \dot{V}_p}{\dot{V}_0 P_{0,0}} = 0.30$$

Alternate Approach

$$\begin{aligned} \dot{V}_{AN} &= \\ \dot{V}_{H_2O} &= \\ \dot{V}_P &= \\ \dot{V}_A &= \\ \dot{V}_{O_2} &= \\ \dot{V}_{N_2} &= \end{aligned}$$

DoF Analysis

Reactn: Assume  $\dot{V}_0 = 100 \text{ mol}$   
 6  $\neq$  Unknowns ( $\dot{V}_0, \dot{V}_p$  is 5  $\dot{V}_i$  from outlet stream)  
 - 6 Indep. Mat. Balances (bc 6 species: AN, H<sub>2</sub>O, P, A, O<sub>2</sub>, N<sub>2</sub>)  
 - 1 Additional Eq (f<sub>P</sub>)  
 +1 Chemical Reaction (1/2)  $\leftarrow$  Extent of P Reaction is added to DoF!

$\partial X$  DoF  $\approx \leftarrow$  Assume a Basis to bring DoF to 0.

Material Balances

Note:  $2P + 2A + 3O_2 \rightarrow 2AN + 6H_2O$

in-out-gain-loss = accumulation

$$G_{out} \rightarrow \dot{V}_i = \dot{V}_{i,0} + \dot{V}_i \frac{1}{2}$$

$$P: \dot{V}_p = \dot{V}_0 \dot{V}_{p,0} + (-2) \frac{1}{2}$$

$$A: \dot{V}_A = \dot{V}_0 \dot{V}_{A,0} + (-2) \frac{1}{2}$$

$$N_2: \dot{V}_N = \dot{V}_0 \dot{V}_{N,0} + 0 \frac{1}{2} \quad \text{No Reactive Species (Inert)} \quad \text{Results in: in-out}$$

$$O_2: \dot{V}_{O_2} = 0 + 6 \frac{1}{2}$$

$$AN: \dot{V}_{AN} = 0 + 2 \frac{1}{2}$$

$$O_2: \dot{V}_{O_2} = \dot{V}_0 \dot{V}_{O_2,0} + (-3) \frac{1}{2}$$

Cannot write a total balance as moles are not a conserved quantity!!!

Addl. Reactn Eqs

$$f_p = \frac{\text{mol P reacted}}{\text{mol P fed}} = \frac{\dot{V}_0 P_{0,0} - \dot{V}_p}{\dot{V}_0 P_{0,0}} = 0.30$$

How to Solve

(i) Solve  $f_p$  for  $\dot{V}_p \rightarrow$  Plug into P balance  $\rightarrow$  solve  $\frac{1}{2}$

(ii) Solve A balance for  $\dot{V}_{AN} \left( \frac{\text{moles A}}{6} \right)$

(iii) Solve N<sub>2</sub> balance for  $\dot{V}_{N,0}$

(iv) Solve H<sub>2</sub>O balance for  $\dot{V}_{H_2O}$

(v) Solve AN for  $\dot{V}_{AN}$

(vi) Solve O<sub>2</sub> for  $\dot{V}_{O_2}$

(vii) Calculate  $\dot{V}_p$  from  $f_p$

(viii) Calculate mol fraction of each species in outlet stream

$$y_i = \frac{\dot{V}_i}{\sum \dot{V}_i} = \frac{\text{moles of } i}{\text{total moles}} \quad \leftarrow \text{Given generic definition in terms of what you solved for}$$

### **Additional Jargon for Chemical Systems with Chemical Reactions**

For systems with multiple chemical reactions...

**Selectivity:**

$$\text{Selectivity, } \alpha_D = \frac{\text{moles of desired product}}{\text{moles of undesired product(s)}}$$

**Yield:**

$$\text{Yield} = \frac{\text{moles of desired product}}{\text{theoretical moles of desired product}}$$

**Theoretical moles:** If no side reaction occurred, this is the maximum number of moles that could be produced in the given reactor

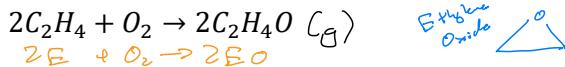
For reactive systems that include a recycle stream...

The **single-pass conversion** is the fraction conversion in a reactor

The **overall conversion** is the fraction conversion of the whole process

## Example 2: Synthesis of ethylene oxide

Ethylene oxide is produced by the catalytic oxidation of ethylene:

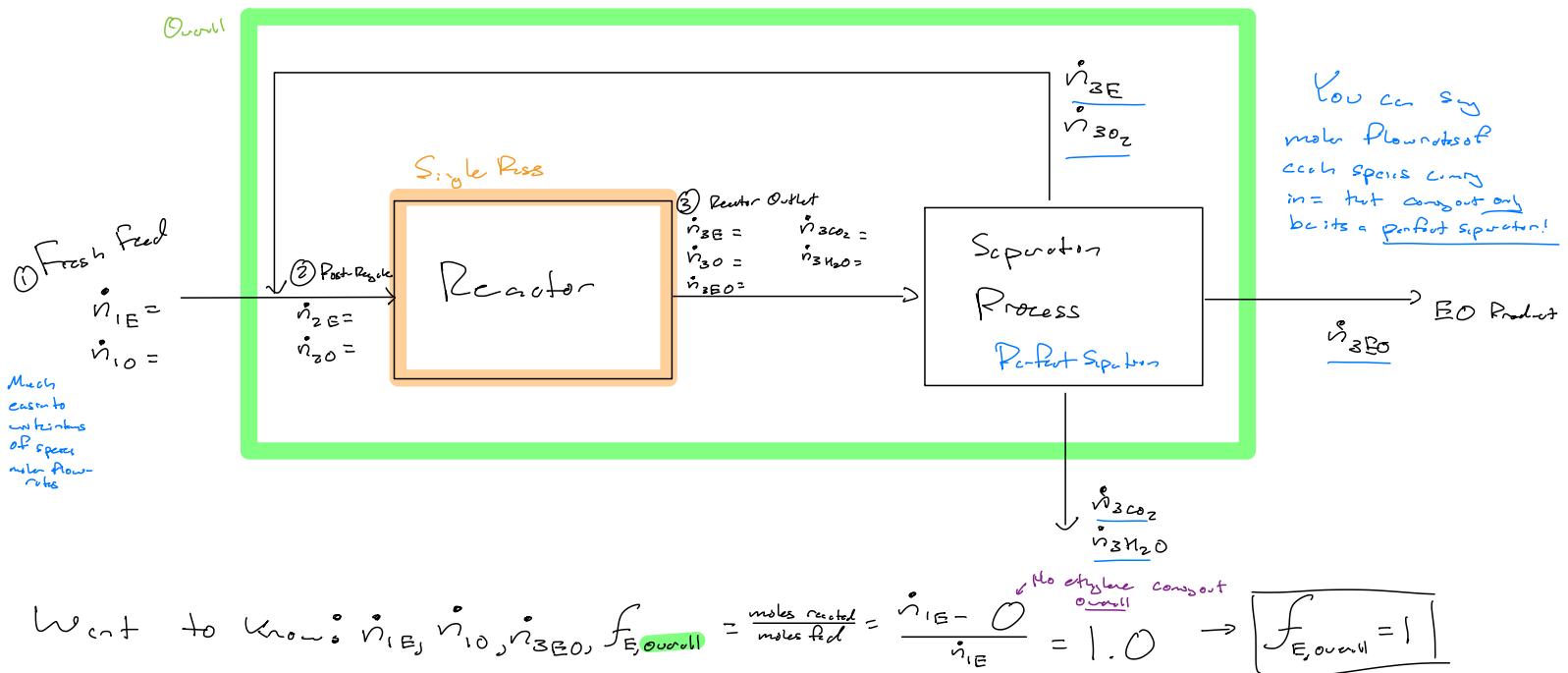


An undesired competing reaction is the combustion of ethylene:



The feed to the reactor contains 3 moles of ethylene per mole of oxygen. The single-pass conversion of ethylene is 20% and for every 100 moles of ethylene consumed in the reactor, 90 moles of ethylene oxide emerges in the reactor products. A multiple-unit process is used to separate the products: ethylene and oxygen are recycled to the reactor, ethylene oxide is sold as a product, and carbon dioxide and water are discarded.

Calculate: Molar flowrates of ethylene and oxygen in the feed, production rate of ethylene oxide and overall conversion of ethylene.



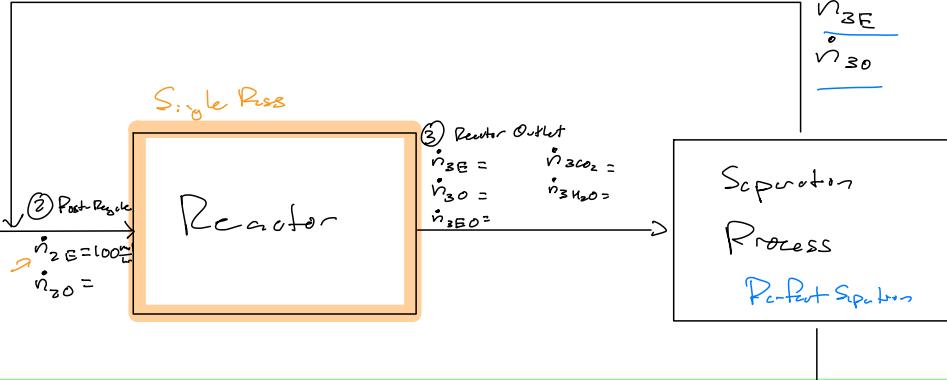
Additional Eqs

$$\textcircled{A} \quad \dot{n}_{2E} = 3\dot{n}_{2O} \quad \leftarrow \quad \frac{\dot{n}_{2E}}{\dot{n}_{2O}} = \frac{3}{1}$$

$$f_{E, \text{single}} = \frac{\dot{n}_{2E} - \dot{n}_{3E}}{\dot{n}_{2E}} = 0.20 \quad \text{r} \quad \begin{matrix} \text{D.P. from} \\ \text{molar conversion} \end{matrix}$$

$$\textcircled{B} \quad \frac{\dot{n}_{2E} - \dot{n}_{3E}}{\dot{n}_{2EO}} = \frac{100}{40} \quad \leftarrow \quad \frac{100 \text{ moles E reacted}}{40 \text{ moles BO produced}}$$

Overall



You can say  
molar flowrates of  
each species coming  
in = that coming out only  
because it's a perfect separator!

## DOF Analysis

### Reactor

6 DOFs (UnKnowns ( $\dot{n}_{2E}, \dot{n}_{2O}, \dot{n}_{3E}, \dot{n}_{3O}, \dot{n}_{3EO}, \dot{n}_{3CO_2}, \dot{n}_{3H_2O}$ ))  
Assume as basis:  $\dot{n}_{2E} = 100 \frac{\text{mol E}}{\text{hr}}$

- 5 Indep Mat Balances (5 species)
- 3 Additional Eqs ( $\dot{n}_E, f_{E,\text{overall}}, \dot{n}_O$ )
- + 2 Indep. Cheml Reacs ( $\dot{E}_1, \dot{E}_2$ )

0 DOF  $\Downarrow$

### Mixing

No rxns take place  
in mixing part

- 5 UnKnowns ( $\dot{n}_{1E}, \dot{n}_{1O}, \dot{n}_{2O}, \dot{n}_{3E}, \dot{n}_{3O}$ )  
- 2 Indep Mat Balances (2 species E & O)  
- 2 Additional Eqs ( $\dot{n}_E, f_{E,\text{overall}}$ )  $\leftarrow$  But useful as  
0 Cheml Reacs (mixing part)  $\leftarrow$  Separation is  
perfect

1 DOF  $\Downarrow$  Constitute  $\dot{n}_E$  as + mols EO

### Overall

Extent of reaction is tied to  
Reactant conversion

- 5 UnKnowns ( $\dot{n}_{1E}, \dot{n}_{1O}, \dot{n}_{2E}, \dot{n}_{3CO_2}, \dot{n}_{3H_2O}$ )  
- 5 Indep Material Balances (5 species crossing the boundary)  
- 0 Additional Eqs (None or relevant)  
+ 2 Chemical Reactions ( $\dot{E}_1, \text{overall}, \dot{E}_2, \text{overall}$ )  $\leftarrow$   $\dot{E}_1, \dot{E}_2$  &  $\dot{E}_{\text{overall}}$

2 DOF  $\Downarrow$

We went into separator, as it is perfect!

## Plan of Attack

- Solve Reactor for  $\dot{n}_3$
- Solve mixing part to win!!

### Material Balances

#### Reactor

in-out generation consumption = accumulation  
out = in + (gen - const term)  
 $\Rightarrow \dot{n}_i = \dot{n}_{in} + \sum \dot{n}_j \dot{E}_j$

$$\begin{aligned} E: \quad \dot{n}_{2E} &= \dot{n}_{2E} - 2\dot{E}_1 - 1\dot{E}_2 \\ O: \quad \dot{n}_{3O} &= \dot{n}_{2O} - 1\dot{E}_1 - 3\dot{E}_2 \\ EO: \quad \dot{n}_{3EO} &= 0 + 2\dot{E}_1 + 0\dot{E}_2 \\ CO_2: \quad \dot{n}_{3CO_2} &= 0 + 0\dot{E}_1 + 2\dot{E}_2 \\ H_2O: \quad \dot{n}_{3H_2O} &= 0 + 0\dot{E}_1 + 2\dot{E}_2 \end{aligned}$$

No totally mole not conserved, can also drop the O atoms, just here for completeness

### Mixing

in = out

$$\begin{aligned} E: \quad \dot{n}_{1E} + \dot{n}_{2E} &= \dot{n}_{2E} \\ O: \quad \dot{n}_{1O} + \dot{n}_{3O} &= \dot{n}_{2O} \end{aligned}$$

- Solve E balance for  $\dot{n}_{1E}$
- Solve O balance for  $\dot{n}_{1O}$

We have now solved for  $\dot{n}_{1E}, \dot{n}_{1O}, \dot{n}_{3EO}$ , and  $f_{E,\text{overall}}$ , as required.

### Overall

Want molar flowrates instead of total mol  
Composition for simplicity.  
Different separation processes  
may change total limiting species,  
but it's OK if units are  
the same dimensional homogeneity

$i = \text{row #}$   
 $i = \text{species}$   
 $\dot{n}_i = \text{stoch coef of}$   
species  $i$  in row  $i$

## How to Solve

- Use  $\textcircled{1}$  to solve for  $\dot{n}_{2O}$
- Use  $f_{E,\text{overall}}$  to solve for  $\dot{n}_{3EO}$
- Use  $\textcircled{3}$  to solve for  $\dot{n}_{3CO_2}$
- Solve EO Balance for  $\dot{n}_{3EO}$
- Solve E Balance for  $\dot{n}_{1E}$
- Solve O Balance for  $\dot{n}_{1O}$
- Solve CO<sub>2</sub> Balance for  $\dot{n}_{3CO_2}$
- Solve H<sub>2</sub>O Balance for  $\dot{n}_{3H_2O}$

## How to Solve

- Solve E balance for  $\dot{n}_{1E}$
- Solve O balance for  $\dot{n}_{1O}$

## **Unit 4**

---



# Equations of State & Single Phase Systems

**Single Phase Systems** Components exist in one single phase (solid, liquid, g.s.)

Usually refers to a specific stream

Solids & Liquids are generally incompressible



If we want to convert  $\rho$  to  $\rho_s$  for an incompressible fluid

$$\rho_s = \rho \left( \frac{m}{m_L} \right)$$

Good Sources  
of values

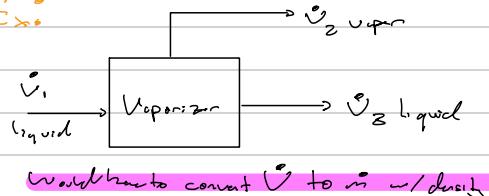
- Go to NIST chemical webbook
- Perry's chemical handbook
- Appendix B (in textbook)
- Wolfram Alpha

Bad Sources  
of values

- Google AI
- Wikipedia (directly)
- ChatGPT
- Look @ sources on textbook

When would we use these properties?

Ex:



Wouldn't convert  $V$  to  $m$  w/density

Value is not a conserved quantity  
we cannot write Mass Balances w/ them  
alone!

↳ moles & volume not conserved  
but mass is conserved by

$$P_{\text{species}} = P_{\text{H}_2\text{O}} \cdot SG_{\text{species}}$$

Tables sometimes give  
SG values can be used  
to get  $P_{\text{species}}$

$$SG_{\text{species}} = \frac{P_{\text{species} @ 20^\circ\text{C}}}{P_{\text{H}_2\text{O} @ 40^\circ\text{C}}}$$

**Equations of State:** A function that relates the molar quantity and volume of a gas to temp and pressure. ( $n$ ,  $P$  and  $V$  are process variables)

↳ Derived under specific conditions, only usable under such conditions

## Ideal Gas Law

**Assumptions:** Large # of molecules in random motion

↑ Volume of individual molecules << volume of gas

**Expected to know** No intermolecular forces btwn molecules

Perfectly elastic collisions if they bump (lose no energy)

Temperature of gas depends on KE of the molecules

Conditions for which • "High" Temperature (above 0°C)

Ideal Gas Law Applies • "Low" Pressure (around 1 atm)

$$PV = nRT$$

but no gas is truly ideal!

How do we know?

$$(i) \text{ Calculate } \frac{RT}{P} = V \quad \frac{L}{\text{mol}}$$

(ii) Assess  $V$ ! Can use ideal gas law when...

$$V = \frac{RT}{P} > 5 \frac{\text{L}}{\text{mol}} \text{ for diatomic gases} \quad \leftarrow \text{contrast air (N}_2/\text{O}_2\text{) as diatomic}$$

$$V = \frac{RT}{P} > 20 \frac{\text{L}}{\text{mol}} \text{ for other gases}$$

Caveat: 'STP' number from AP exams is only valid under specific conditions, use in ESI

## Equation of State

If the ideal gas law does not apply...

- Virial EoS
- Van der Waals EoS
- Compressibility Factor EoS

- Soave-Redlich-Kwong (SRK) EoS
- So many others!

## Van der Waals EoS

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

where  $V = \frac{v}{n}$

Accurate for volume occupied by molecule

Accurate for intermolecular attractions

$V$  is equivalent to little  $v$  in ECHB225  
class E

where  $a = \frac{27R^2T^2}{64Pc}$  and  $b = \frac{RTc}{8Pc}$  Look up quantum factors

## Compressibility Factor EoS

$$PV = zRT \text{ where } z = f(T_r, P_r) \text{ and } T_r = \frac{T}{T_c}, P_r = \frac{P}{P_c}$$

Look up

## Almost All EoSs Reference critical $T \& P$

- $T_c$  and  $P_c$ : highest temp and corresponding pressure at which species can coexist in two phases (liquid & vapor)
- $T_c$  and  $P_c$ : certain physical properties of a gas strongly depend on the proximity of the gas to its critical state

$$\hookrightarrow T_c = \frac{T}{T_c}$$

$\leftarrow$  critical state temp

$$P_c = \frac{P}{P_c}$$

$\leftarrow$  critical state pressure

We want to choose an EoS that works for our system

$\hookrightarrow$  "works"  $\rightarrow$  Allows us to predict properties ( $T, V, P$ , composition) reliably

**Law of corresponding states:** All gases behave similarly when compared at the same  $T_r$ ,  $P_r$ ,  $V_r$  meaning that they all deviate from ideal behavior to a similar extent or degree.

**Compressibility factor equation of state:**  $P\hat{V} = zRT$  where:  $z = f(T_r, P_r, V_r^{ideal})$

When  $z=1$ , ideal gas law!

↑ How far a gas deviates from ideality

**How do we find  $z$ ?**

[Table B.1  
Wolfram Alpha  
NIST]

1. Look up the  $T_c$  and  $P_c$  for all species in the stream.
2. Was there only one species? If yes, proceed to 2. If not multiple species, calculate the critical properties of the mixture according to Kay's Law Rule then proceed to 3.

In mixture:  $T_c' = \sum y_i T_{ci}$  and  $P_c' = \sum y_i P_{ci}$  Kay's Rule

3. Calculate any 2 of the 3 the reduced properties (e.g.  $T_r$  for pure,  $T_r'$  for a mixture)

$$T_r = \frac{T}{T_c} \quad \begin{matrix} T \\ \leftarrow \\ \text{Process Variables} \end{matrix} \quad P_r = \frac{P}{P_c} \quad V_r^{ideal} = \frac{\hat{V} P_c}{R T_c} \quad \begin{matrix} \hat{V} \\ \leftarrow \\ \frac{V}{y} \left( \frac{L}{mol} \right) \end{matrix}$$

4. Use 2 of the 3 reduced properties ( $T_r$ ,  $P_r$  or  $V_r$ ) to look up  $z$  using the generalized compressibility chart

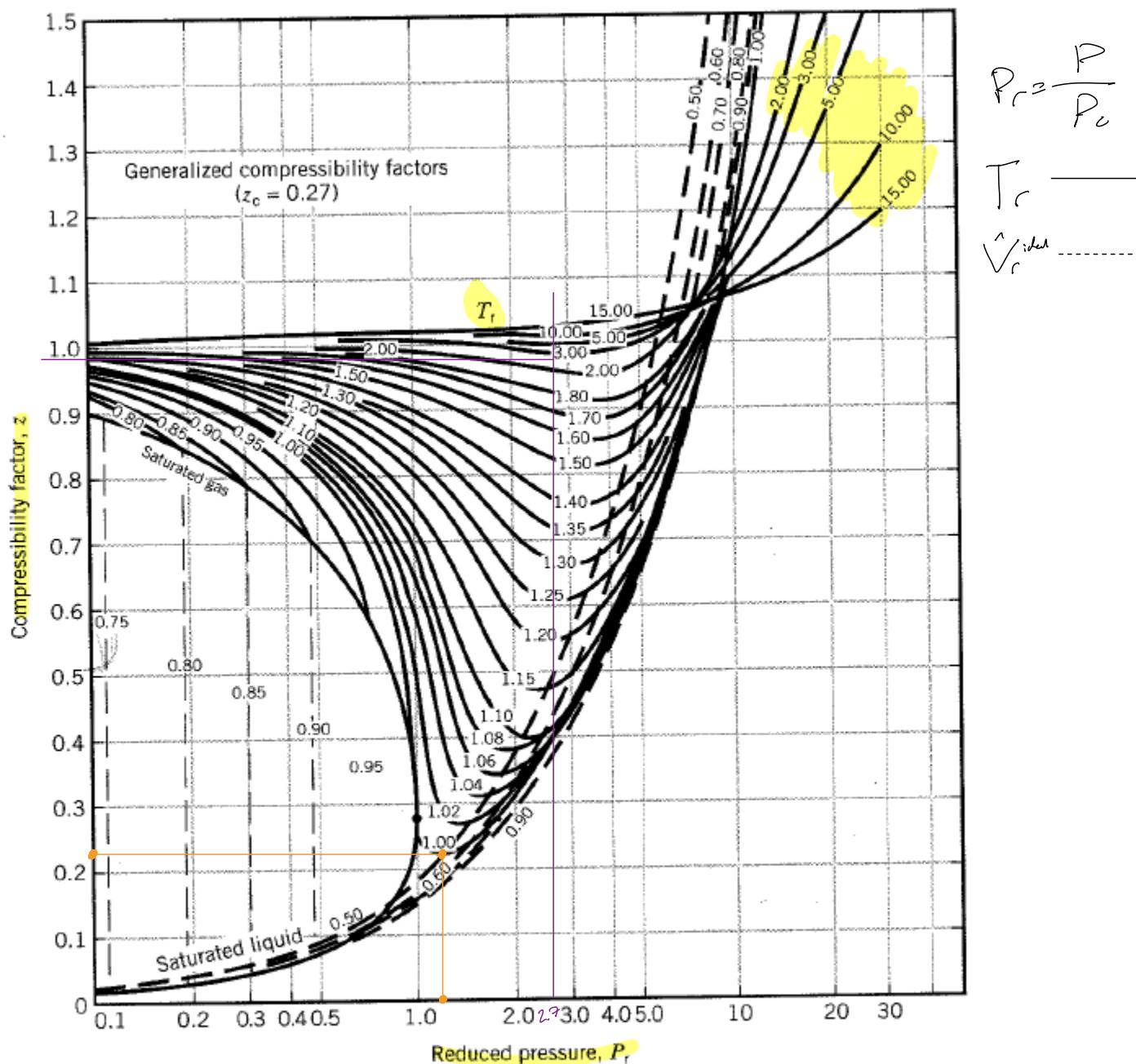
### Examples

1)  $T_r = 1.0$ ,  $P_r = 1.2$ ,  $z = ?$   $z \approx 0.23$

2)  $P_r = 5.0$ ,  $\hat{V}_r^{ideal} = 0.8$ ,  $z = ?$   $z \approx 1.05$

3)  $T_c = 1.50$ ,  $P_r = 30$ ,  $z = ?$   $z \approx 2.5$

Compressibility charts taken from: Felder and Rousseau. *Elementary Principles of Chemical Processes*, 3<sup>rd</sup> edition. Chapter 5, pages 208-211

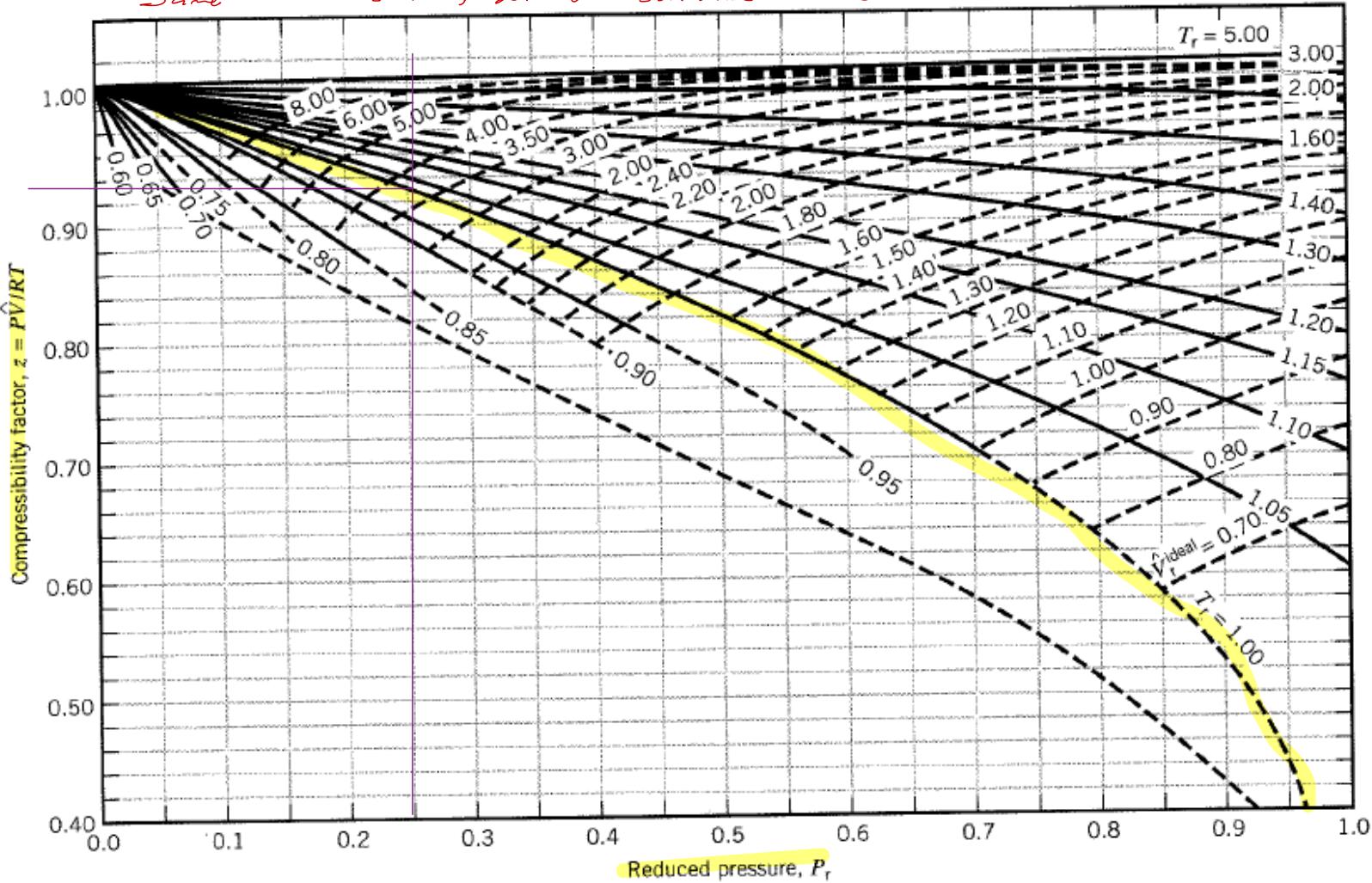


**Figure 5.4-1** (Reprinted with permission from *Chemical Process Principles Charts*, 2nd Edition, by O. A. Hougen, K. M. Watson, and R. A. Ragatz, John Wiley & Sons, New York, 1960.)

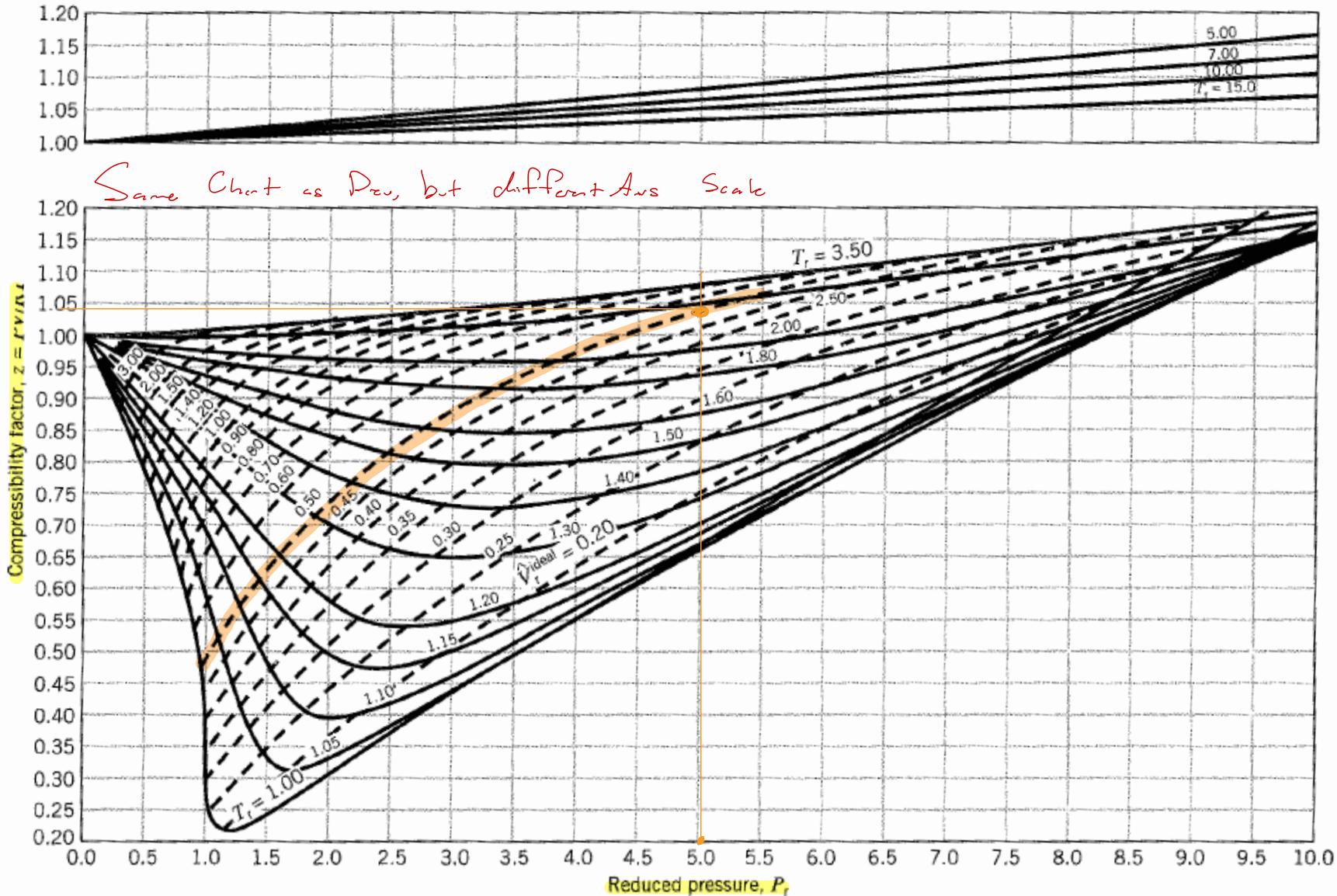
Compressibility charts taken from: Felder and Rousseau. Elementary Principles of Chemical Processes, 3<sup>rd</sup> edition.  
Chapter 5, pages 208-211

$T_r$  —  
 $\sqrt{V_r}$  —

Same Chart as  $P_{cr}$ , but different Ans Scale



**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.)

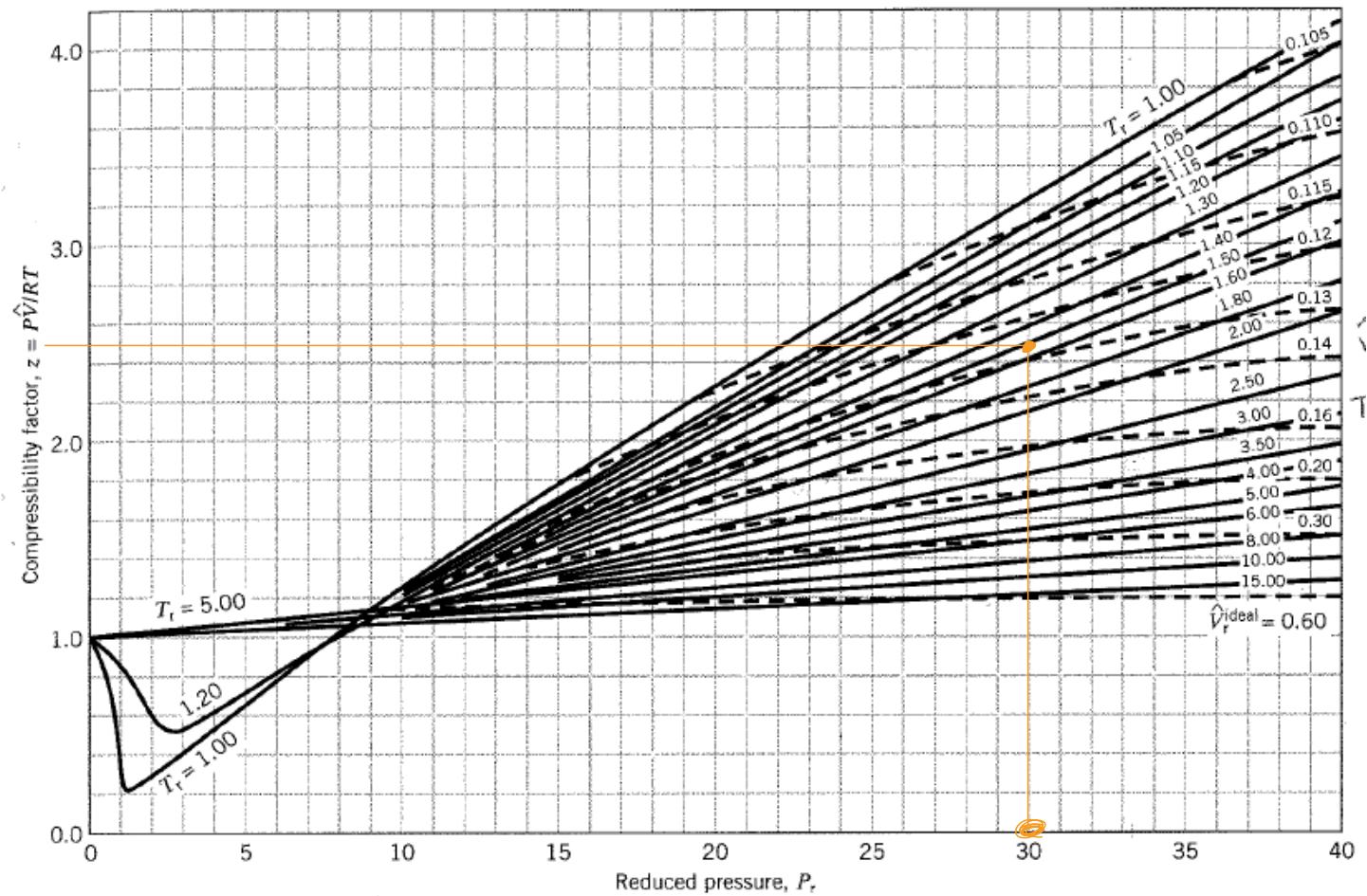


**Figure 5.4-3** Generalized compressibility chart, medium pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 176. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

$T_r$  —————  
 $\sqrt{V_r}$  -----

*Same Chart as Prev, but diff P + Ans Scale*

Compressibility charts taken from: Felder and Rousseau. *Elementary Principles of Chemical Processes*, 3<sup>rd</sup> edition. Chapter 5, pages 208-211

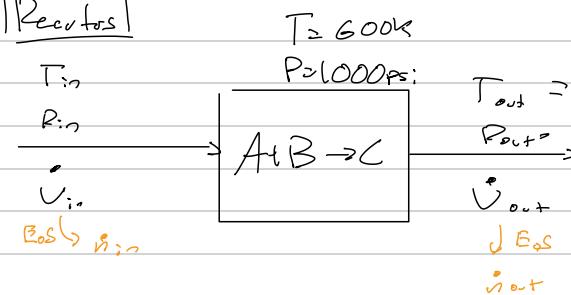


**Figure 5.4-4** Generalized compressibility chart, high pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 177. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

Where do you see EoS of r. t. g.s takes?

EoS can relate  $P, V, T$  to each other in a given system (tank)

### Reactor



$T_{in} + \Delta T$

$P_{in} = P_{out}$

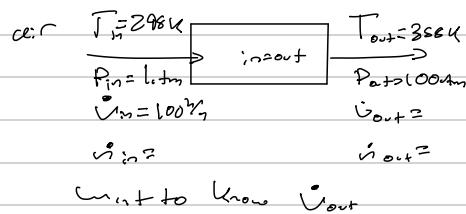
$V_{in} = V_{out}$

$J_{EoS}$   
 $\dot{m}_{out}$

Fully isolated PFD with heat.

$T, P, \text{Flowrate, composition, or species molar flowrate}$

### Compressor



Mol. Balances:  $\dot{m}_{in} = \dot{m}_{out}$

Apply  $V^2$  law to determine

EoS for inlet & outlet

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

: If  $V > 8 \frac{L}{mol}$  compressible  $\Rightarrow$  (ideal)  
If  $V > 20 \frac{L}{mol}$  others  $\Rightarrow$  (ideal)

$$V = \frac{(10.08 \frac{L \cdot atm}{mol \cdot K})(358K)}{100 \text{ atm}}$$

$$= 0.2 \frac{L}{mol}$$

Not ideal!

How to Solve

(i) Use ideal G.s to calculate  $\dot{m}_i$ ,  $P_i V_i = n_i RT_i$

(ii) Use total Balance to calculate  $\dot{m}_2$  as  $\dot{m}_1 = \dot{m}_2$  for compressors

(iii) Use  $P_2 V_2 = n_2 R T_2 Z$

$$\text{a) Calculate } T_r' = \frac{T_2}{T_1} \quad \& \quad R_r' = \frac{R_2}{R_1}$$

implies mixtures

$$T_c = \sum y_i T_{ci} \quad \left[ \begin{array}{l} \text{Kays rule for} \\ \text{mixtures (ideal)} \end{array} \right]$$

$$P_c = \sum y_i P_{ci} \quad \left[ \begin{array}{l} \text{Kays rule for} \\ \text{mixtures (ideal)} \end{array} \right]$$

Calculate  $T_c'$  for air

$$T_c' = y_{N_2} T_{c,N_2} + y_{O_2} T_{c,O_2}$$

$$= 0.79(126K) + 0.21(154K)$$

$$T_{c,N_2} = 126K$$

$$T_{c,O_2} = 154K$$

Molar Balance

Only written in either mass or moles!

Calculate  $P_r'$  for air

$$P_r' = y_{N_2} P_{c,N_2} + y_{O_2} P_{c,O_2}$$

$$= 0.79(33.5 \text{ atm}) + 0.21(49.7 \text{ atm})$$

$$P_{c,N_2} = 33.5 \text{ atm}$$

$$P_{c,O_2} = 49.7 \text{ atm}$$

Calculate Reduced Properties,  $T_r$  and  $P_r$

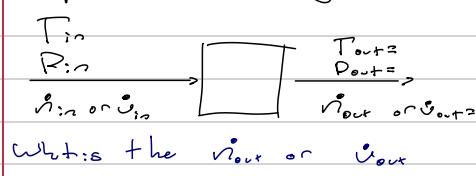
$$T_r = \frac{T_2}{T_c'} = \frac{358K}{126K} = 2.7$$

$$P_r = \frac{P_2}{P_r'} = \frac{100 \text{ atm}}{37 \text{ atm}} = 2.7$$

$Z = 0.95$  read from compressibility charts

Plug  $Z = 0.95$  into compressibility EoS to calculate  $V_2$

### Expansion or Throttling



EoS will depend  
based on Additional  
Equations

Observe not  
limited to any  
expansion processes

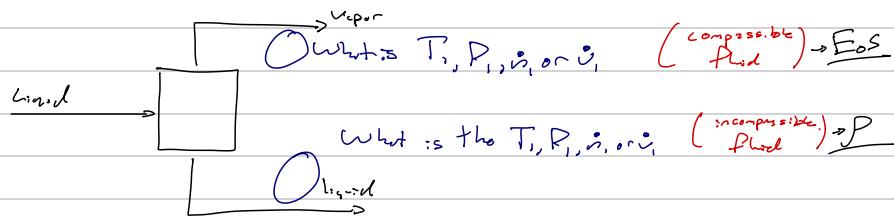
### Additional Equations

$$PV = nRT \quad V \leftarrow \text{constant} \quad \text{molar volume}$$

$$PV = zRT \quad V \leftarrow \text{constant} \quad \text{volume}$$

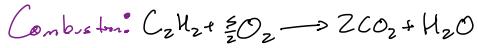
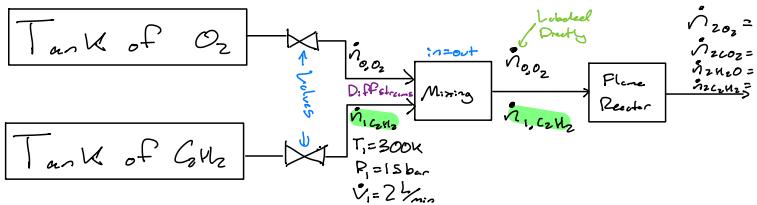
$$P \bar{V} = zRT \quad V \leftarrow \text{constant} \quad \text{volume}$$

### Evaporator or Distillation Column



Douit doesn't usually count  
 $z$  as unknown for D/F assist  
 $\Rightarrow$  found from tables based on values

# Example: Combustion of Acetylene



Want to calculate  $n_{C_2H_2}$  for usc:n reactor molar balance

1.  $C_2H_2$  is a compressible or incompressible fluid

↪ EOS can be used as it is compressible

2. Choose EOS: ideal g.s. or factor?

↪ Test: !

$$\text{Eqn: } V = \frac{RT}{P} = \frac{(0.082 \frac{\text{L}_{\text{atm}}}{\text{mol}\cdot\text{K}})(300\text{K})}{15\text{ atm}} = 1.6 < 2.0$$

1 atm ≈ 1 bar

Cannot use ideal g.s.!

3. Use  $P_1 V_1 = z n_{C_2H_2} RT_1$       we need to read z-value  
from generalized compressibility chart

$$\begin{aligned} T_r &= \frac{T_1}{T_c} & P_r &= \frac{P_1}{P_c} \Rightarrow T_r &= \frac{300\text{K}}{309.5\text{K}} \approx 1 \\ T_c &= 309.5\text{K} & P_c &= 61.6 \text{ atm} & P_r &= \frac{15\text{ atm}}{61.6 \text{ atm}} = 0.25 \end{aligned}$$

$\left. \right\} z \approx 0.93$

Calculate  $n_{C_2H_2}$  using found  $z = 0.93$

## **Unit 5**

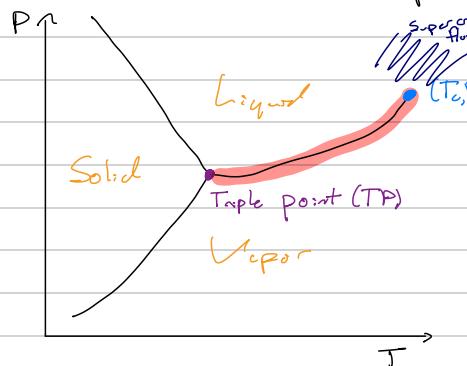
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# Multiphase Systems

• Evaporator, Distillation Unit, Condenser *watch out for these in problem statements*

• Most commonly known separator processes rely on liquid-vapor systems



$P_c, T_c$  - Point above which liquids & gases cannot coexist  
above  $(T_c, P_c)$  we have supercritical fluids

Triple Point: All 3 phases of matter can coexist b

■ = vapor-liquid equilibrium line

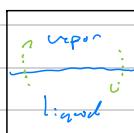
↳ steam tables (For given  $T$ , state, what is  $P$ ?)

↳ COX chart

↳ Antoine Equation

## Vapor-Liquid Equilibrium (VLE)

Def: Occurs when a gas is in equilibrium with a liquid and that gas is saturated with the volatile component of the liquid



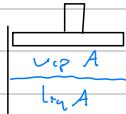
Rate of condensation = Rate of evaporation

Volatile Species: a species that can vaporize, volatilize, or otherwise enter the vapor phase in a given set of conditions ( $T, P$ )

Vapor: Gas from a species that is typically a liquid

$H_2O$  liquid vs.  $N_2$  gas

Saturated Vapor: Cannot hold any more of the species; it is saturated with a fixed conditions



Vapor phase is saturated with A

Add 1 more molecule of A to vapor

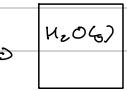
phase → 1 molecule of A must condense

What happens if we increase  $P$ ?

Concen A, increase fraction of A in the liquid phase

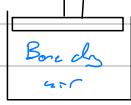
What happens if we decrease  $T$ ?

VLE



Saturated vapor

Superheated vapor: A vapor that is present in less than its saturation amount



Inject 1 droplet... what happens? It evaporates!

↪ repeat,  $H_2O$  evaporates

$H_2O(l)$  and  $H_2O(g)$



Superheated

Saturation Pressure: Partial pressure of a vapor when it is saturated

$P_i^s$  = partial pressure of species i

$P_i^s$  = function of the temperature in the system. It is the maximum quantity that can exist in the vapor phase for species i

If you have a superheated vapor:  $P_i < P_{i,sat}$

Ideal Gases

$$P_i = y_i P_{tot}$$

Nonideal Gases

$$P_i = y_i P_{tot} \phi$$

Dew Point Temperature ( $T_{dew}$ ): temperature at which the first droplet of liquid forms when condensing a saturated vapor

Bubble Point Temperature ( $T_{bp}$ ): temperature at which first bubble forms when vaporizing a saturated liquid

**Raoult's Law:**

$$y_i P = x_i P_i^{\text{sat}}$$

Annotations:

- ↑ System Pressure
- ↑ Saturated pressure of species  $i$  at process Temp
- ↑ Upper phase mol fraction of species  $i$
- ↑ Liquid phase mol fraction of species  $i$

**Conditions:**

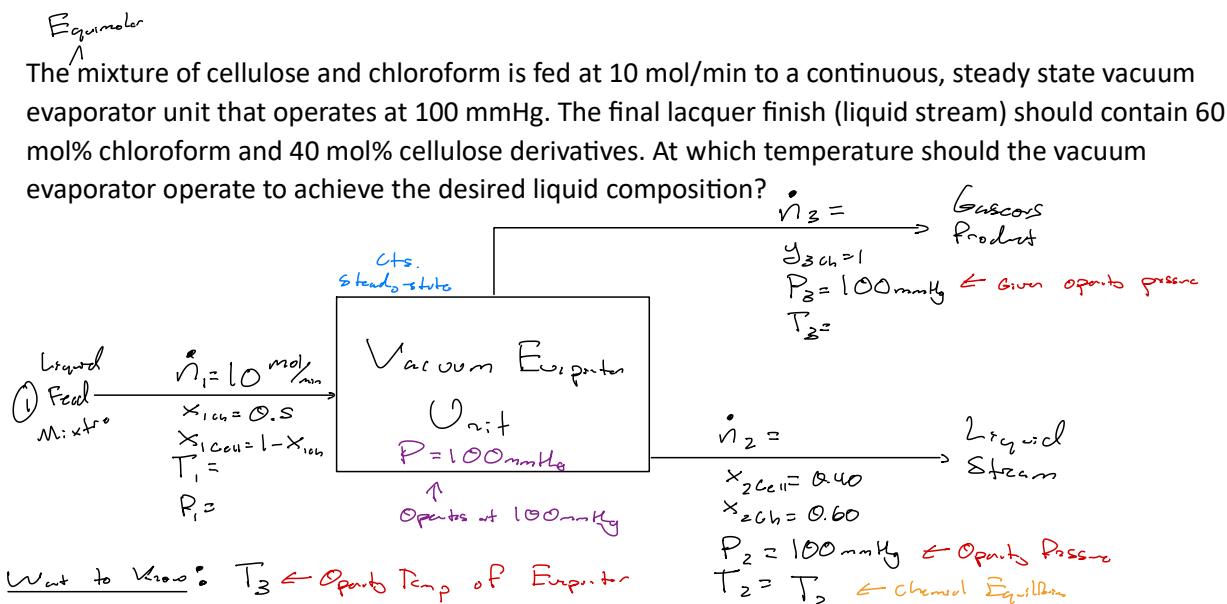
- (i) Vapour-liquid equilibrium (equal  $T, P, n$ )
- (ii) Upper phase that behaves ideally  $C_{i,\text{upper}}^{n,L,T}$   
Activity coeff  $\gamma = 1$
- (iii) Liquid phase behaves ideally  
 $C_{i,\text{lower}}^{n,L,T}$  constant in homogeneous

Chemical Potential

You can also set up systems with conditions equivalent to those it was based in

### Example 1: Concentrating lacquer finishes by evaporating chloroform

Chloroform is a commonly used solvent for floor polishes and lacquer wood finishes. Lacquer finishes contain cellulose derivatives dissolved in chloroform. During manufacturing, the cellulose derivatives are dissolved in an excess of chloroform then the mixture is fed to an evaporator to concentrate the solution. Here, the chloroform is the only volatile species.



### Additional EQs:

① Ideal Gas Law:  $PV = nRT$

Raoult's Law:  $y_i P = x_i P_i^{\text{sat}}$

- no chloroform
- Assume solutions & liquid streams
- VLE

Chloroform Only

②  $y_{3,CH} P_3 = x_{2,CH} P_2^{\text{sat}}$  ← 2nd 3 in VLB, look at process!

③ Antoine Eq:  $\log_{10} P_2^{\text{sat}} = A - \frac{B}{T_2 + C}$

$$\begin{cases} A = \\ B = \\ C = \end{cases}$$

### Material Balances

$$\text{Chl: } \dot{n}_1 x_{1,CH} = \dot{n}_3 + \dot{n}_2 x_{2,CH}$$

$$\text{Cell: } \dot{n}_1 x_{1,Cou} = \dot{n}_2 x_{2,Cou}$$

$$\text{Total: } \dot{n}_1 = \dot{n}_2 + \dot{n}_3$$

For non-reactive systems moles are conserved

How to Solve ( $n_i$  unknowns)

- Solve Cell for  $\dot{n}_2$
- Solve Total for  $\dot{n}_3$

### DOF Analysis (Solving for all $n_i$ & $T$ )

4 Unknowns ( $\dot{n}_2, \dot{n}_3, T_3, P_2^{\text{sat}}$ )

+ 0 General Relations

- 2 Liquid Mat Balances (2 species CH & Cou)

- 2 Additional EQs (O, O)

DOF R

### How to Solve Continued (Operating Temperature $T_2$ )

$$④ y_{3,CH} P_3 = x_{2,CH} P_2^{\text{sat}}$$

$$⑤ \log_{10} P_2^{\text{sat}} = A - \frac{B}{T_2 + C}$$

⑥ Solve ④ for  $P_2^{\text{sat}}$  (Raoult's Law)

⑦ Use ⑥ to calculate  $T_2$  (Antoine Eqn.)

↳ Get  $A, B, C$  from Table

$$\begin{cases} A = 6.96328 \\ B = 1163.03 \\ C = 227.40 \end{cases}$$

Use Bottom Constants on Table B.4 as range is large

$$P^* = P_i^{S_t}$$

$T$  = Process Temperature

$A, B, C$  = constants specific to each species

Table B.4 Antoine Equation Constants<sup>a</sup>

$$\log_{10} p^* = A - \frac{B}{T + C} \quad p^* \text{ in mm Hg, } T \text{ in } ^\circ\text{C}$$

Example: The vapor pressure of acetaldehyde at 25°C is determined as follows:

$$\log_{10} p_{\text{C}_2\text{H}_4\text{O}}^*(25^\circ\text{C}) = 8.00552 - \frac{1600.017}{25 + 291.809} = 2.9551$$

$$\Rightarrow p_{\text{C}_2\text{H}_4\text{O}}^*(25^\circ\text{C}) = 10^{2.9551} = 902 \text{ mm Hg}$$

Write entire value  
From table from A, B,  
& C.

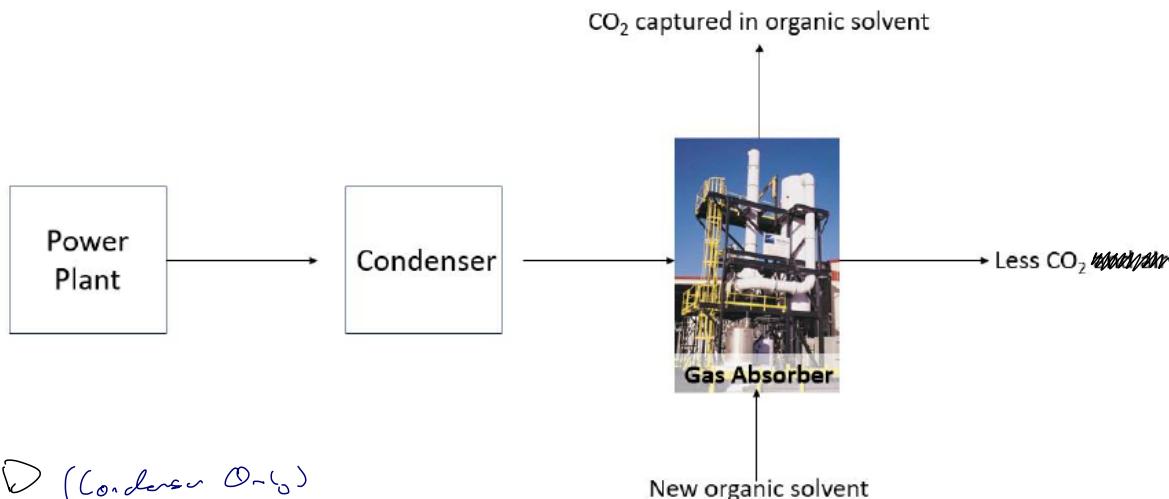
Can also find  
values on NIST  
Chemical Webbook

Compound	Formula	Range (°C)	A	B	C
Acetaldehyde	C <sub>2</sub> H <sub>4</sub> O	-0.2 to 34.4	8.00552	1600.017	291.809
Acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	29.8 to 126.5	7.38782	1533.313	222.309
Acetic acid*	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	0 to 36	7.18807	1416.7	225
Acetic anhydride	C <sub>4</sub> H <sub>6</sub> O <sub>3</sub>	62.8 to 139.4	7.14948	1444.718	199.817
Acetone	C <sub>3</sub> H <sub>6</sub> O	-12.9 to 55.3	7.11714	1210.595	229.664
Acrylic acid	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	20.0 to 70.0	5.65204	648.629	154.683
Ammonia*	NH <sub>3</sub>	-83 to 60	7.55466	1002.711	247.885
Aniline	C <sub>6</sub> H <sub>7</sub> N	102.6 to 185.2	7.32010	1731.515	206.049
Benzene	C <sub>6</sub> H <sub>6</sub>	14.5 to 80.9	6.89272	1203.531	219.888
n-Butane	n-C <sub>4</sub> H <sub>10</sub>	-78.0 to -0.3	6.82485	943.453	239.711
i-Butane	i-C <sub>4</sub> H <sub>10</sub>	-85.1 to -11.6	6.78866	899.617	241.942
1-Butanol	C <sub>4</sub> H <sub>10</sub> O	89.2 to 125.7	7.36366	1305.198	173.427
2-Butanol	C <sub>4</sub> H <sub>10</sub> O	72.4 to 107.1	7.20131	1157.000	168.279
1-Butene	C <sub>4</sub> H <sub>8</sub>	-77.5 to -3.7	6.53101	810.261	228.066
Butyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	20.0 to 150.0	8.71019	2433.014	255.189
Carbon disulfide	CS <sub>2</sub>	3.6 to 79.9	6.94279	1169.110	241.593
Carbon tetrachloride	CCl <sub>4</sub>	14.1 to 76.0	6.87926	1212.021	226.409
Chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	62.0 to 131.7	6.97808	1431.053	217.550
Chlorobenzene*	C <sub>6</sub> H <sub>5</sub> Cl	0 to 42	7.10690	1500.0	224.0
Chlorobenzene*	C <sub>6</sub> H <sub>5</sub> Cl	42 to 230	6.94504	1413.12	216.0
Chloroform	CHCl <sub>3</sub>	-10.4 to 60.3	6.95465	1170.966	226.232
Chloroform*	CHCl <sub>3</sub>	-30 to 150	6.90328	1163.03	227.4
Cyclohexane	C <sub>6</sub> H <sub>12</sub>	19.9 to 81.6	6.84941	1206.001	223.148
Cyclohexanol	C <sub>6</sub> H <sub>12</sub> O	93.7 to 160.7	6.25530	912.866	109.126
n-Decane	n-C <sub>10</sub> H <sub>22</sub>	94.5 to 175.1	6.95707	1503.568	194.738
1-Decene	C <sub>10</sub> H <sub>20</sub>	86.8 to 171.6	6.95433	1497.527	197.056
1,1-Dichloroethane	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	-38.8 to 17.6	6.97702	1174.022	229.060
1,2-Dichloroethane	C <sub>2</sub> H <sub>4</sub> Cl	-30.8 to 99.4	7.02530	1271.254	222.927
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	-40.0 to 40	7.40916	1325.938	252.616
Diethyl ether	C <sub>4</sub> H <sub>10</sub> O	-60.8 to 19.9	6.92032	1064.066	228.799
Diethyl ketone	C <sub>5</sub> H <sub>10</sub> O	56.5 to 111.3	7.02529	1310.281	214.192
Diethylene glycol	C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>	130.0 to 243.0	7.63666	1939.359	162.714
Dimethyl ether	C <sub>2</sub> H <sub>6</sub> O	-78.2 to -24.9	6.97603	889.264	241.957
Dimethylamine	C <sub>2</sub> H <sub>7</sub> N	-71.8 to 6.9	7.08212	960.242	221.667
N,N-Dimethylformamide	C <sub>3</sub> H <sub>7</sub> NO	30.0 to 90.0	6.92796	1400.869	196.434
1,4-Dioxane	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	20.0 to 105.0	7.43155	1554.679	240.337
Ethanol	C <sub>2</sub> H <sub>6</sub> O	19.6 to 93.4	8.11220	1592.864	226.184
Ethanolamine	C <sub>2</sub> H <sub>7</sub> NO	65.4 to 170.9	7.45680	1577.670	173.368
Ethyl acetate	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	15.6 to 75.8	7.10179	1244.951	217.881
Ethyl acetate*	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	-20 to 150	7.09808	1238.710	217.0
Ethyl chloride	C <sub>2</sub> H <sub>5</sub> Cl	-55.9 to 12.5	6.98647	1030.007	238.612
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	56.5 to 137.1	6.95650	1423.543	213.091

<sup>a</sup>Adapted from T. Boublík, V. Fried, and E. Hala, *The Vapour Pressures of Pure Substances*, Elsevier, Amsterdam, 1973. If marked with an asterisk (\*), constants are from Lange's *Handbook of Chemistry*, 9th Edition, Handbook Publishers, Inc., Sandusky, OH, 1956.

(continued)

Flue gas containing CO<sub>2</sub> and water vapor exits a power plant at 100 mol/h, 150°C and 5 atm. The vapor phase mole fraction of the CO<sub>2</sub> is 0.15 (375 times the amount existing in the atmosphere). Gas absorption can be used to capture the waste CO<sub>2</sub> as shown in the absorber unit below. The flue gas must undergo a pretreatment step in a condenser to remove the water vapor present. Design a condenser operating at equilibrium at 60°C and 1 atm. What is the final composition of the vapor phase leaving the condenser? What percent of water is condensed?



PFD (Condenser O<sub>2</sub>)

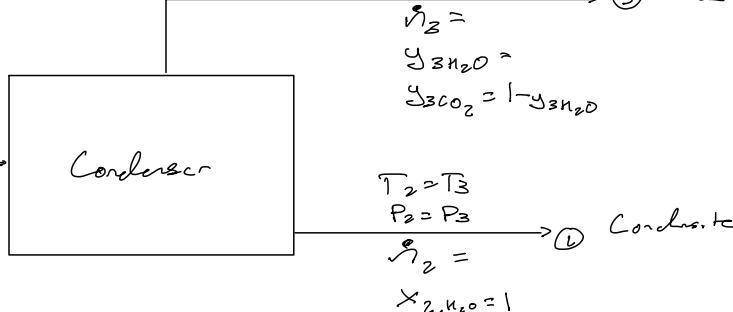
$$\text{Flue Gas} \quad \textcircled{1} \quad i_1 = 100 \text{ mol/hr}$$

$$y_{1, \text{CO}_2} = 0.15$$

$$y_{1, \text{H}_2\text{O}} = 1 - y_{1, \text{CO}_2}$$

$$T_1 = 150^\circ\text{C}$$

$$P_1 = 5 \text{ atm}$$



D.o.F Analysis

- 3 Knowns ( $i_1, i_2, i_3, y_{3, \text{H}_2\text{O}}$ ) u:f counts  
 $P_{\text{H}_2\text{O}}^{\text{sat}}$
- 2 Independent Mat. Balances (2 species)
- + 0 Overall Pans
- 1 Additional Eq ( $\frac{\text{Rate}_{\text{H}_2\text{O}}}{\text{Rate}_{\text{CO}_2}} = k$ ) forwards  
symmetric

D.o.F

Material Balances

$$\text{CO}_2: \dot{m}_{1, \text{CO}_2} = i_3 y_{3, \text{CO}_2} \quad \text{in-out + gen - cons = acc}$$

$$\text{H}_2\text{O}: \dot{m}_{1, \text{H}_2\text{O}} = \dot{m}_{2, \text{H}_2\text{O}} + i_2 y_{2, \text{H}_2\text{O}}$$

$$\text{Total: } \dot{m}_1 = \dot{m}_2 + \dot{m}_3$$

$$\textcircled{1} \text{ Raoult's Law: } y_{3, \text{H}_2\text{O}} P_3 = P_{\text{H}_2\text{O}}^{\text{sat}}$$

$$\textcircled{2} \text{ Antoine Eq: } \log_{10} P_{\text{H}_2\text{O}}^{\text{sat}} = A - \frac{B}{T_3 + C}$$

$$\text{Want to know: } y_{3, \text{CO}_2} = ?$$

$$y_{3, \text{H}_2\text{O}} = ?$$

$$\% \text{ condensate} = \frac{i_2}{i_1 y_{1, \text{H}_2\text{O}}} = ?$$

Additional Equations

$$\textcircled{3} \text{ Raoult's Law: } y_{3, \text{H}_2\text{O}} P_3 = x_{2, \text{H}_2\text{O}} P_{\text{H}_2\text{O}}^{\text{sat}}$$

$$y_{3, \text{H}_2\text{O}} P_3 = P_{\text{H}_2\text{O}}^{\text{sat}}$$

$$\textcircled{4} \text{ Antoine Eq: } \log_{10} P_{\text{H}_2\text{O}}^{\text{sat}} = A - \frac{B}{T_2 + C}$$

How to Solve

- (i) Use  $\textcircled{3}$  to calculate  $P_{\text{H}_2\text{O}}$  at  $T_2$  using  $T_3$ , and ABC from Table B.4

$$\begin{cases} A = \\ B = \\ C = \end{cases}$$

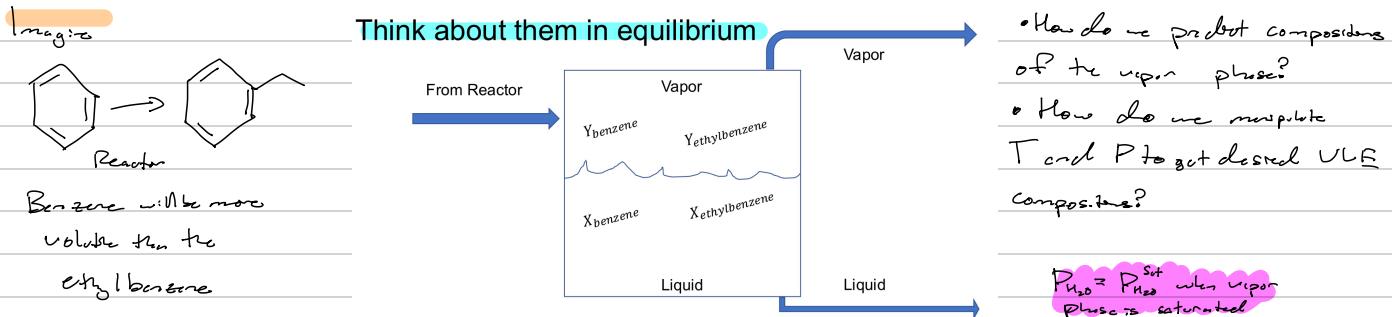
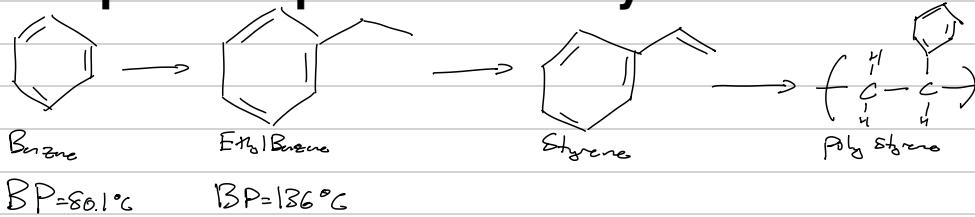
- (ii) Calculate  $y_{3, \text{H}_2\text{O}}$  from Raoult's Law  $\textcircled{3}$

- (iii) Use CO<sub>2</sub> Balance to calculate  $i_2$

- (iv) Use total balance to find  $i_3$

$$(v) \text{ Calculate \% Condensate} = \frac{i_2}{i_1 y_{1, \text{H}_2\text{O}}} \times 100$$

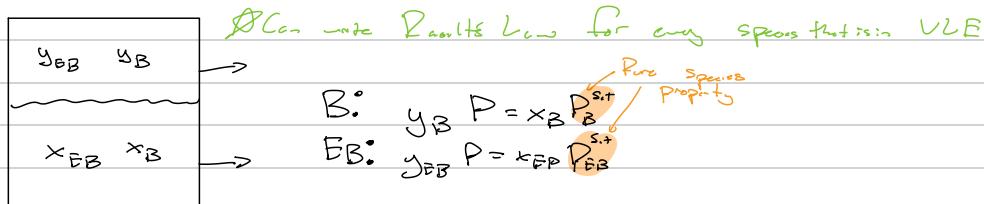
# Multiple Component VLE Systems



## Vocab / Jargon / Notes

- For single species VLE systems, we usually talk about the boiling temperature ( $T_{\text{boil}}$ ).
  - $\hookrightarrow$  Table B.1,  $T_{\text{boil},i} = \text{_____} @ P = 1 \text{ atm}$  This is the normal boiling point
  - Boiling occurs when  $P_{\text{H}_2\text{O}} = P_{\text{total}}$
  - Vapor pressure is  $\text{atm}$
- Evaporation is a surface phenomenon
- Bubble point is the temperature at which the first bubble forms when heating a liquid
  - $\hookrightarrow$  Denoted  $T_{\text{bub}}$  & what we see as the boil point for a pure species
- Dewpoint is the temperature at which the first droplet forms when isobarically cool a vapor ( $T_{\text{dew}}$ )
- For a single species system:  $T_{\text{bub}} = T_{\text{dew}} = T_{\text{boil}}$
- Raoult's Law:  $y_i P = x_i P_i^{\text{sat}}$ 
  - $y_i = \text{vap. phase mol frac}$ ,  $x_i = \text{liquid phase mol frac}$
  - $P = \text{system pressure}$ ,  $P_i^{\text{sat}} = \text{sat. pres. of spec. } i @ T$

## Distributions



(i) Consider a mixture of ideal gases:

$$\sum P_i = P = \sum y_i P \quad \text{globally}$$

$$P = y_{\text{A}} P + y_{\text{B}} P \quad \text{for our system}$$

(ii) Rewrite B:  $y_B = \frac{x_B P_{\text{B}}^{\text{sat}}}{P}$ ,  $E.B.: y_{\text{B}} = \frac{x_{\text{B}} P_{\text{B}}^{\text{sat}}}{P}$

(iii) Plug (ii) eqs into (i)

$$P = x_{\text{B}} P_{\text{B}}^{\text{sat}} + x_{\text{B}} P_{\text{B}}^{\text{sat}}$$

↑                        ↑  
depends on system T; can still be calculated with Raoult's eqn

Know T, P  $\rightarrow$  can calculate  $x_{\text{B}}$  &  $x_{\text{B}}$

This temperature is  $T_{\text{bub}}$

Bubble Point equation for a binary mixture

### Dew Point Calculations & Condensate

$$(i) Raoult's Law: y_i P = x_i P_i^{\text{sat}}$$

$$B: x_B P = y_B P_B^{\text{sat}}$$

$$BB: y_{BB} = x_{BB} P_{BB}^{\text{sat}}$$

$$\sum x_i > 1$$

(ii) Raoult's Raoult's

$$BB: x_{BB} = \frac{y_{BB} P}{P_{BB}^{\text{sat}}}, \quad B: x_B = \frac{y_B P}{P_B^{\text{sat}}}$$

(iii) Combine with  $\sum x_i > 1$

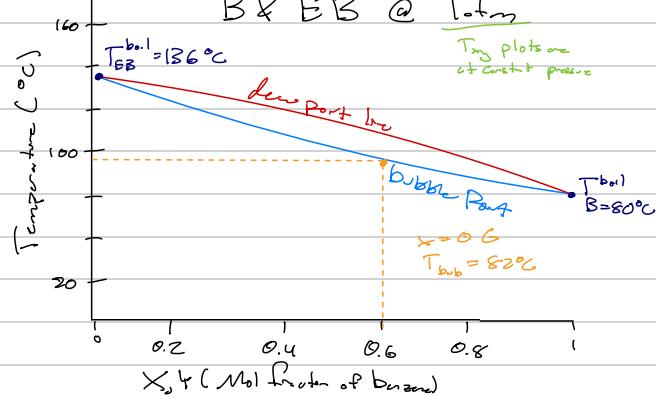
$$1 = \frac{y_{BB} P}{P_{BB}^{\text{sat}}} + \frac{y_B P}{P_B^{\text{sat}}}$$

Dew point equations  
for binary mixture

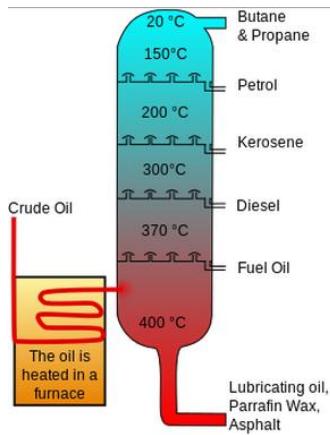
### Txy Diagrams

B & EB @ Latm

Txy plots are  
at constant pressure



### Example 1: Crude Oil Production



Crude oil production relies on a fractional distillation process that leads to many by-products. The top product stream of the fractional distillation column is a gaseous butane/propane mixture. This product stream can be further separated using a partial condenser to manufacture butane and propane.

The temperature of the butane/propane mixture exiting in the tops stream is at a temperature of 20C (298K) and a flowrate of 1 million moles per hour. The saturated vapor enters the condenser which operates at 240K. The vapor phase mol fraction of propane in the stream exiting the condenser is 0.82 and the vapor phase flowrate is 300,000 moles per hour. The liquid mixture exiting the condenser has a composition of  $X_B=0.57$  and  $x_P=0.43$ .

Q: What is the pressure of the condenser? ~~What is the composition of the tops stream?~~

Relevant Information:

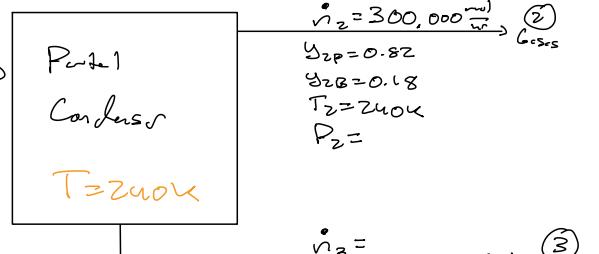
$$\log_{10}(P^{sat}) = A - \frac{B}{T + C}$$

$P^{sat}$  = vapor pressure (bar), T = temperature (K)

Antoine Constants			
	A	B	C
Propane	4.53678	1149.36	24.906
Butane	4.35576	1175.581	-2.071

# PFD

① "Top" Gas flow  
 $\dot{N}_1 = 1 \text{ million molcs/hr}$   
 $y_{1B} =$   
 $y_{1P} = 1 - y_{2B}$   
 $T_1 = 298 \text{ K}$

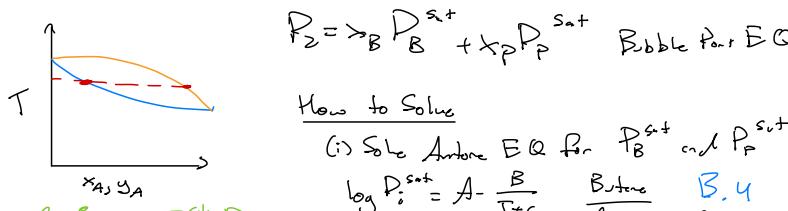


do not write  $P_2$  for Partial Condenser  
 this would be trivial pressure!

Want to know:  $P_{\text{condenser}} = P_2 = P_3$

## Partial Condenser

- no chemical rxns
  - VLE
  - multiple condensate species
- } Can use bubble point and dewpt Eqs



How to Solve

(i) Solve Antoine Eq for  $P_B^{\text{sat}}$  and  $P_P^{\text{sat}}$

$$\log P_i^{\text{sat}} = A - \frac{B}{T+C}$$

$$\text{Butane } B=4.4$$

$$\text{Propane } A=4.63678$$

$$B=1149.36$$

$$C=-2.021$$

$$C=24.906$$

$$P_B^{\text{sat}} = 0.3 \text{ bar}$$

$$P_P^{\text{sat}} = 1.6$$

(ii) Use bubble point equation to solve for  $P_2$

$$P_2 = (0.57)(0.3 \text{ bar}) + (0.43)(1.6 \text{ bar})$$

$$\boxed{P_2 = 0.9 \text{ bar}}$$

Antoine Constants			
	A	B	C
Propane	4.53678	1149.36	24.906
Butane	4.35576	1175.581	-2.071

$$\dot{N}_2 = 300,000 \text{ molcs/hr} \quad (2)$$

$$y_{2P} = 0.82$$

$$y_{2B} = 0.18$$

$$T_2 = 240\text{K}$$

$$P_2 =$$

$$\dot{N}_3 = \quad (3)$$

$$x_{3P} = 0.43$$

$$x_{2B} = 0.57$$

$$T_3 = 240\text{K}$$

$$P_3 = P_2$$

$$\text{Bubble point: } P^{\text{tot}} = x_i P_i^{\text{sat}} + x_j P_j^{\text{sat}} \quad \text{From Antoine}$$

$$\text{Dew point: } 1 = \frac{y_i P_i^{\text{sat}}}{P_i^{\text{sat}}} + \frac{y_j P_j^{\text{sat}}}{P_j^{\text{sat}}}$$

With VLE, you have  
 $T_{\text{dew}} > T_{\text{bubble}} > T_{\text{condenser}}$

If you are given  $x_i, y_i, P$  → calculate  $T$

$$P^{\text{tot}} = x_i P_i^{\text{sat}} + x_j P_j^{\text{sat}}$$

$$P^{\text{tot}} = x_i \cdot 10^A \left[ A - \frac{B}{T+C} \right] + x_j \cdot 10^A \left[ A - \frac{B}{T+C} \right]$$

How? L. Guess a temperature →  $T^{\text{guess}}$

2. Use  $T^{\text{guess}}, x_i, y_i$  to calculate  $P^{\text{tot}}$

3. Force  $P^{\text{tot}}(\text{calculated from } T^{\text{guess}}) = P$  by  $T^{\text{guess}}$

## **Unit 6**

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# Energy Balances of Non-Reactive Systems

## Recall: Open Systems

- Mass crosses boundary
- Continuous / Semi-Batch

## Closed Systems

- Mass does not cross system boundaries
- Batch Processes

## Types of Energy

(i) **Kinetic Energy**: due to motion  $E_k = \frac{1}{2} m u^2$

(ii) **Potential Energy**: due to change in position ( $\Delta E_p = m g z$ )

(iii) **Internal Energy**: due to [temperature, molecular translation/vibration] "all other energy" ( $U_{closed}$ )

Note: Small Thermodynamics Book with 10 pages posted to canvas for potential help with derivations

$$\begin{aligned} E_k &= \frac{1}{2} m u^2 \\ E_p &= m g z \\ U & \end{aligned}$$

dot just means energy/time

## Energy Exchange

(i) **Heat**: Energy that flows in or out of a system due to change in temperature ( $\Delta T$ )

$$Q \quad \begin{array}{l} \text{when heat is added to the system} \\ \text{when heat is removed from the system} \end{array}$$

(ii) **Work**: Energy that flows in or out of a system due to other driving forces ( $\Delta P, \Delta G, \Delta \text{Voltage}$ )

$$W \quad \begin{array}{l} \text{when work is being done by system on surroundings} \\ \text{when work is done by surroundings on system} \end{array}$$

Note distinction from ECHB228

## First Law of Thermodynamics

(i) **Closed Systems**:  $\Delta U + \Delta E_k + \Delta E_p = Q - W$

(ii) **Open Systems**:  $\Delta U + \Delta E_k + \Delta E_p = Q - W$

$$\begin{aligned} \Rightarrow W &= W_{\text{shaft}} + W_{\text{flow}} \\ &\begin{array}{l} \text{Friction force involved here} \\ \text{Fluid has to push fluid in front of it out of the way} \\ \text{Fluid pushing on each other} \end{array} \\ W_{\text{flow}} &= \Delta(PV) \end{aligned}$$

$$\therefore \Delta U + \Delta E_k + \Delta E_p = Q - W_{\text{shaft}} - \Delta(PV) \xrightarrow{\text{into}} \Delta U + \Delta(PV) + \Delta E_k + \Delta E_p = Q - W_{\text{shaft}}$$

Using Enthalpy ( $H$ ):  $\Delta H + \Delta E_k + \Delta E_p = Q - W_{\text{shaft}}$  1st Law for open systems which we will use mostly this class as we like etc. steady state

### Units

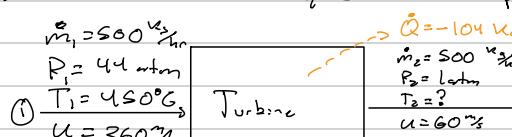
$\cdot H$  for a closed system  $\left\{ \begin{array}{l} \text{if } \frac{H_2 - H_1}{m_2 - m_1} = \text{if } \bar{H} \text{ or if } \hat{H} \\ \text{if } \frac{H_2 - H_1}{m_2 - m_1} \text{ or } \hat{H} \end{array} \right.$

**Remark:** Specific properties we say property that is on a process or per mol basis

$$\Delta H = \hat{H}_{\text{final}} - \hat{H}_{\text{initial}} \quad \& \quad \Delta \bar{H} = \bar{H}_{\text{final}} - \bar{H}_{\text{initial}}$$

Always keep track of your units

## Basic ECHB228-examples



$$\therefore u_2 = 70 \text{ kJ/kg}$$

Want to know:  $T_2 \quad \{ \text{ }^\circ\text{C} \}$

New governing equation will be 1st Law of Thermodynamics

$$\begin{aligned} \text{(i) 1st Law: } \Delta H + \Delta E_k + \Delta E_p &= Q - W \\ \text{using } P \text{ classes, } \text{ negligible position change, } \text{ large change in } u, \text{ both given} & \end{aligned}$$

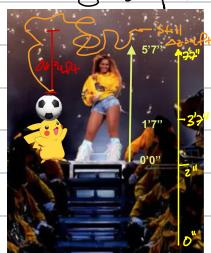
(ii) Want 1st L. using process variables from the PFD

$$\begin{cases} \Delta E_k = \frac{1}{2} m (u_2^2 - u_1^2) \\ \Delta H = \frac{u_2 - u_1}{\text{kg/hr}} = m (\bar{H}_2 - \bar{H}_1) \end{cases}$$

Most of time  $\Delta H$  for phase change channel reactions will be much greater than  $\Delta E_k$  or  $\Delta E_p$

## State Properties

- Only depend on the state of current system, not process path



$$\Delta E_p = m_g \Delta z$$

$$\text{Path 1)} \Delta z = 4 \text{ ft}$$

$$\text{Path 2)} \Delta z = 4 \text{ ft}$$

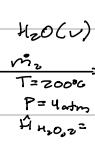
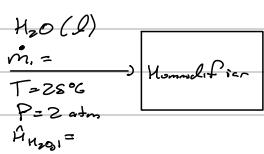
$$\text{Path 3)} \Delta z = 7' 7'' - 3' 7'' = 4 \text{ ft!}$$

Reference state is arbitrary

Reference states must be consistent within a single  $\Delta z$  calc!

## Enthalpy

Example: Homoclinic River / Steam Generator



$$\Delta T$$

$$\Delta P$$

$$\Delta \text{phase}$$

$\hat{H}$  is defined by 3 types:

(i) Temperature

(ii) Pressure

(iii) Phase

Process Path: species  $(T, P, \text{phase}) \rightarrow$  species  $(T, P, \text{phase})$

$$\Delta \hat{H}_{\text{process}} = \hat{H}_{\text{final}, H_2O} - \hat{H}_{\text{initial}, H_2O} = \hat{H}_2 - \hat{H}_1$$

For two scenarios

Could read directly from the steam tables, ref point = triple point of water

$$\hat{H}_2(200^\circ C, 4 \text{ atm}, g) = \hat{H}_{\text{steamtable}} - \hat{H}_{\text{ref state}}$$

$$\hat{H}_1(28^\circ C, 2 \text{ atm}, l) = \hat{H}_{\text{steamtable}} - \hat{H}_{\text{ref state}}$$

$$\rightarrow \Delta \hat{H}_{\text{process}} = [\hat{H}_{\text{final}} - \hat{H}_{\text{ref}}] - [\hat{H}_{\text{initial}} - \hat{H}_{\text{ref}}] \quad \hat{H}_{\text{ref}} \text{ cancels out anyway}$$

Important: Reference states need to cancel out in our  $\Delta \hat{H}$  calc!

(i) Cannot mix & match reference states for a given species OR we cannot use values from tables that use different reference states

(ii) The actual state does not matter  $(T, P, \text{phase})$

(iii) Can choose any  $T, P, \text{phase}$  that we want to make the calculations simple

Hypothetical Process Paths: Write a "hypothetical" (not real) process for each species that changes one state variable at a time  $(T, P, \text{phase})$  so we can calculate  $\hat{H}$  associated with each hypothetical step



$E + OH(T_{\text{final}}, 1 \text{ atm}, l)$

$2. \Delta \text{phase} @ \text{const } T \& P$

$E + OH(T_{\text{final}}, 1 \text{ atm}, v)$

$3. \Delta T @ \text{const phase } P$

$E + OH(200^\circ C, 1 \text{ atm}, v)$

$4. \Delta P @ \text{const } T \& l$

$E + OH(200^\circ C, 2 \text{ atm}, v)$

From your  $P$  know a known property, choose one state property at a time to get to final conditions from the initial.

Want to know

$$\Delta \hat{H}_{\text{process}} = \hat{H}_{\text{out, } E + OH} - \hat{H}_{\text{in, } E + OH}$$

$$= [\hat{H}_{\text{out, } E + OH} - \hat{H}_{\text{ref}}] - [\hat{H}_{\text{in, } E + OH} - \hat{H}_{\text{ref}}]$$

$\rightarrow$  Assume inlet conditions as ref state

$$\Rightarrow E + OH(28^\circ C, 1 \text{ atm}, l), \hat{H}_{\text{in, } E + OH} - \hat{H}_{\text{ref}} = 0$$

$$\Delta \hat{H}_{\text{process}} = \hat{H}_{\text{out, } E + OH} - \sum \hat{H}_{\text{in, } \text{species phase}} = \hat{H}_1 + \hat{H}_2 + \hat{H}_3 + \hat{H}_4$$

$\Delta T$  at constant phase and  $P$  (isobaric heating or cooling)

$$(i) \text{For ideal gas: } \Delta U = \int_{T_1}^{T_2} C_V(T) dT$$

$C_V$  is a function of  $T$

$$\Delta H = \int_{T_1}^{T_2} C_P(T) dT$$

$C_P$  can be found in appendix B

$$(ii) \text{For solid/liquid: } \Delta U = \int_{T_1}^{T_2} C_V(T) dT$$

$$\Delta H = \int_{T_1}^{T_2} C_P(T) dT$$

### Heat Capacities

$C_P$  &  $C_V$  describe how much energy is required to raise 1 mol or 1 kg of a substance by 1°C or 1K.

$$\sum \frac{kJ}{mol \cdot K} \text{ or } \sum \frac{kJ}{kg \cdot K}$$

$\Delta$  phase at constant  $T$  and  $P$

lookup  $H$  or  $U$  in Table B.1 for the normal phase change

$$\Delta H_{\text{vap}}^{\circ}$$

Heat of vaporization for the pure species at  $T_{\text{boil}}$  (Latm)

$$\rightarrow \Delta H_{\text{vap}}^{\circ} = -\Delta H_{\text{condensation}}^{\circ}$$

$$C_V = \text{const volume heat capacity}$$

$$C_P = \text{const pressure heat capacity}$$

$$\text{For ideal gases: } C_P = C_V + R$$

$$\text{For liquids/solids: } C_P \approx C_V$$

$\Delta P$  at constant  $T$  and phase (isothermal expansion or compression)

$$(i) \text{For ideal gas: } \Delta G = \Delta H = 0$$

$$(ii) \text{Solids/Liquids: } \Delta G = 0$$

$$\Delta H = \Delta G + \Delta(PV)$$

$P$  is constant

$$\therefore \Delta H = \Delta V P = \gamma \Delta P$$

$\gamma$  is constant for solids and incompressible fluids

### General Procedure for Solving Energy Balances

1. Draw and fully label at PFD
2. Determine if the material balance is solvable (units 1 & 2 steps here)
3. Write the energy balance for this system – start with the 1<sup>st</sup> law of thermodynamics, cancel terms, justify why  $\Delta E_p + \Delta E_k + \Delta H = Q - W$  no moving parts You should always write two and then cancel terms!  
This course will focus on  $\Delta H$  and  $Q$  mostly  
in this course usually  $\Delta E_p \approx 0$  usually  $\Delta E_k \approx 0$
4. Identify a reference state for each species most of the time reference states = ref conditions  
↳ some species ( $T, P_{phase}$ )
5. Draw the theoretical path for each species starting from the reference state
6. Write  $\Delta\hat{H}$  equations for each theoretical step
7. Look up all tabulated values for  $\Delta\hat{H}$ ,  $C_p(T)$ , MW, density – cite where they came from
8. Explain how you would solve both the material balances and the energy balance

Example—Energy balance on a distillation column with two species

In a continuous steady-state process, an equimolar mixture of benzene/toluene is fed to a vacuum distillation column at 1 mol/min. The column operates at equilibrium conditions at 50°C and 34.8 mmHg. The feed to the column is at atmospheric pressure and -10°C. Additional information regarding the stream compositions is given on the diagram. What is the required heating rate of the column (kJ/min)?

$$\dot{H} \left( \frac{\text{kJ}}{\text{min}} \right) = \dot{n} \left( \frac{\text{mol}}{\text{min}} \right) \dot{h} \left( \frac{\text{kJ}}{\text{mol}} \right)$$

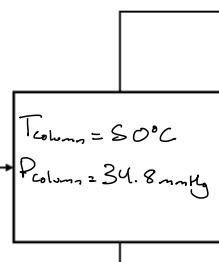
1. Draw and fully label a PFD

Temperature & pressure matter for VLE and energy balances!

DOF Analysis  
not required  
post-column

Liquid

$$\begin{aligned}\dot{n}_1 &= 1 \frac{\text{mol}}{\text{min}} \\ x_{1B} &= 0.5 \\ x_{1T} &= 0.5 \\ P_1 &= 760 \text{ mmHg} \\ T_1 &= -10^\circ\text{C}\end{aligned}$$



$$\begin{aligned}\dot{n}_2 &= \\ y_{2B} &= 0.68 \\ y_{2T} &= 0.32 \\ T_2 &= T_{\text{column}} \\ P_2 &\approx P_{\text{column}}\end{aligned}$$

Pay attention  
to phases & temp  
and pressures

Want to know  
 $\dot{Q} \approx \frac{\text{kJ}}{\text{min}}$

$\dot{n}_3 =$

$$\begin{aligned}x_{3B} &= 0.4 & T_3 &= T_2 \\ x_{3T} &= 0.6 & P_3 &\approx P_2\end{aligned}$$

0 DOF

2. DOF Analysis

- 2 unknowns ( $\dot{n}_2, \dot{n}_3$ )
- + 0 chemical reactions
- 2 ind. mat. balances (B & T species)

0 DOF

4. Choose a reflux state (per specie)

Choose  $T$  (l, -10°C, 760 mmHg)  $A_1 = 0$

usually the most common

B (l, -10°C, 760 mmHg)  $A_{1B} = 0$

$$\Rightarrow \dot{Q} = [ \dot{n}_2 y_{2B} \hat{h}_{2B} + \dot{n}_2 y_{2T} \hat{h}_{2T} ] + [ \dot{n}_3 x_{3B} \hat{h}_{3B} + \dot{n}_3 x_{3T} \hat{h}_{3T} ]$$

Stream 1 is given as the reflux state  
lets  $A_{1T}, A_{1B} = 0$

Material Balances

$$B: \dot{n}_1 x_{1B} = \dot{n}_2 y_{2B} + \dot{n}_3 x_{3B}$$

$$T: \dot{n}_1 x_{1T} = \dot{n}_2 y_{2T} + \dot{n}_3 x_{3T}$$

$$\text{Total: } \dot{n}_1 = \dot{n}_2 + \dot{n}_3$$

3. Write First Law

$$\Delta E_p + \Delta E_k + \Delta H = \dot{Q} - \dot{W}$$

no  $\Delta B$  or  $\Delta U$   
no moving parts

$$\Rightarrow \dot{Q} = \Delta H$$

$$\dot{Q} = \Delta H \left( \frac{\text{kJ}}{\text{min}} \right) = \dot{H}_{\text{exit}} - \dot{H}_{\text{initial}}$$

$$= \sum \dot{n}_i \hat{h}_i - \sum \dot{n}_i \hat{A}_i \quad i = \text{species}$$

$$= \sum \dot{n}_i \hat{h}_i - \sum \dot{n}_i \hat{A}_i \quad \text{Final} \quad \text{Initial}$$

$$= \sum \dot{n}_i x_i \hat{h}_i - \sum \dot{n}_i x_i \hat{h}_i \quad \text{Final outlet} \quad \text{Initial inlet}$$

$$\Rightarrow \dot{Q} = [ \dot{n}_2 y_{2B} \hat{h}_{2B} + \dot{n}_2 y_{2T} \hat{h}_{2T} ] + [ \dot{n}_3 x_{3B} \hat{h}_{3B} + \dot{n}_3 x_{3T} \hat{h}_{3T} ] - [ \dot{n}_1 x_{1B} \hat{h}_{1B} + \dot{n}_1 x_{1T} \hat{h}_{1T} ]$$

$\hat{h}_{1B}, \hat{h}_{2B}$  will be more useful

$$\begin{aligned}&\text{Stream 2} \\ &[ \dot{n}_2 y_{2B} \hat{h}_{2B} + \dot{n}_2 y_{2T} \hat{h}_{2T} ] \\ &\text{Stream 3} \\ &[ \dot{n}_3 x_{3B} \hat{h}_{3B} + \dot{n}_3 x_{3T} \hat{h}_{3T} ]\end{aligned}$$

$\dot{n}_3 x_i$  or  $x_{iB}$ , just  
within 1 b-line

S. To calculate  $\hat{H}_{2T}$  [Stream 2:  $T(V, 50^\circ C, 34.8 \text{ mmHg})$ ]

$T(l, -10^\circ C, 760 \text{ mmHg}) * \text{ref slnt } \hat{H}_{1T20}$

$\hat{H}_a T(l, T_{boil,T} = 110.6^\circ C, 760 \text{ mmHg}) * T_{boil,T} \text{ from table B1}$

$\hat{H}_b T(v, T_{boil,T} = 110.6^\circ C, 760 \text{ mmHg}) \Delta P \text{ const } T \& P$

$\hat{H}_c T(v, 50^\circ C, 760 \text{ mmHg})$

$\hat{H}_d T(v, 50^\circ C, 34.8 \text{ mmHg})$

On table B2 Write the equations for each thermal step

$$C = \text{solid}$$

$$l = \text{liquid}$$

$$g = \text{gas}$$

$$\text{Form 1 uses 2nd specific double substitution factor}$$

$$\hat{H}_a = \int_{-10^\circ C}^{110.6^\circ C} C_{P,T\text{liquid}}(T) dT \Delta T, \text{const } P \& \text{phase}$$

$$\hat{H}_b = \hat{H}_{vap} = 34.8 \frac{\text{kJ}}{\text{mol}}$$

$$\hat{H}_c = \int_{110.6^\circ C}^{50^\circ C} C_{P,T\text{vapor}}(T) dT \Delta T, \text{const } P \& \text{phase}$$

$$\hat{H}_d = 0 \quad \Delta P, \text{constant } T \& \text{phase}$$

$\Delta P, C_p$  expressions

$$\partial C_p = a + bT + cT^2 + dT^3$$

$$\partial C_p = a + bT + cT^{-2}$$

$$\text{where } C_{P,T\text{liquid}} = \frac{148.8}{10^3} + \frac{32.4}{10^5 T}$$

$$C_{P,T\text{vapor}} = \frac{44.18}{10^3} + \frac{38.00}{10^5 T} - \frac{27.86}{10^8 T^2} + \frac{80.33}{10^{12} T^3}$$

On a quiz or test we would just show integration up to step 2 plugging tem in. But below is not necessary unless specified.

$$\Rightarrow \hat{H}_{2T} = \hat{H}_a + \hat{H}_b + \hat{H}_c + \hat{H}_d$$

To calculate  $\hat{H}_{3B}$  [Stream 3:  $B(l, 50^\circ C, 34.8 \text{ mmHg})$ ]

$B(l, -10^\circ C, 760 \text{ mmHg})$

$$\hat{H}_e = \int_{-10^\circ C}^{50^\circ C} C_{P,B\text{liquid}}(T) dT \Delta T, \text{const } P \& \text{phase}$$

$\hat{H}_f B(l, 50^\circ C, 760 \text{ mmHg})$

$$\hat{H}_g = \hat{V}_{B,l} \Delta P = \hat{V}_{B,l} (34.8 \text{ mmHg} - 760 \text{ mmHg}) \rightarrow \left\{ \begin{array}{l} L \cdot \text{mmHg} \\ \text{moles} \end{array} \right\} \text{ needs to get to } \frac{\text{kg}}{\text{mol}}$$

$$\text{where } C_{P,B,l} = \frac{126.5}{10^3} + \frac{23.4}{10^5 T} \quad \text{Table B2 Form 1}$$

$$\hat{H}_{3B} = \hat{H}_e + \hat{H}_f$$

To calculate  $\hat{H}_{1T}$  and  $\hat{H}_{1B}$

$B(l, -10^\circ C, 760 \text{ mmHg}) \quad \hat{H}_{1B} = 0 \quad \text{already @ process}$

$T(l, -10^\circ C, 760 \text{ mmHg}) \quad \hat{H}_{1T} = 0 \quad \text{be this is our reference state}$

To calculate  $\hat{H}_{2B}$  [Stream 2:  $B(v, 50^\circ C, 34.8 \text{ mmHg})$ ]

$B(l, -10^\circ C, 760 \text{ mmHg})$

$\Delta T, \text{const phase } P \rightarrow \text{Table B1}$

$\hat{H}_g B(l, T_{boil,B} = 80.0^\circ C, 760 \text{ mmHg})$

$\Delta P, \text{const } T \& \text{phase}$

$\hat{H}_b B(v, T_{boil,B} = 80.0^\circ C, 760 \text{ mmHg})$

$\Delta T, \text{const phase } P$

$\hat{H}_i B(v, 50^\circ C, 760 \text{ mmHg})$

$\Delta P, \text{const } T \& \text{phase}$

$\hat{H}_o B(v, 50^\circ C, 34.8 \text{ mmHg})$

$$\begin{aligned} \text{Table B2} \\ a > 10^3 & \quad b > 10^5 & c > 10^8 & \quad d > 10^{12} \\ l & 148.8 & 32.4 & \\ d & 44.18 & 38.00 & -27.86 & 80.33 \end{aligned} \quad \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} \text{Form 1}$$

$$\text{Form Variables} \quad \text{Table B2 Form 1}$$

$$\partial C_p = a + bT + cT^2 + dT^3$$

$$\partial C_p = a + bT + cT^{-2}$$

$$\text{where } C_{P,T\text{liquid}} = \frac{148.8}{10^3} + \frac{32.4}{10^5 T}$$

$$C_{P,T\text{vapor}} = \frac{44.18}{10^3} + \frac{38.00}{10^5 T} - \frac{27.86}{10^8 T^2} + \frac{80.33}{10^{12} T^3}$$

1 L = 0.03 kg