



## **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

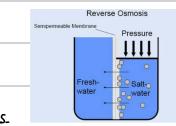
### ① Salt Water Desalination

Large scale thermal distillation may be energy and cost intensive

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

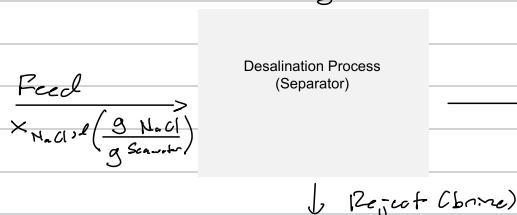
or measured

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.

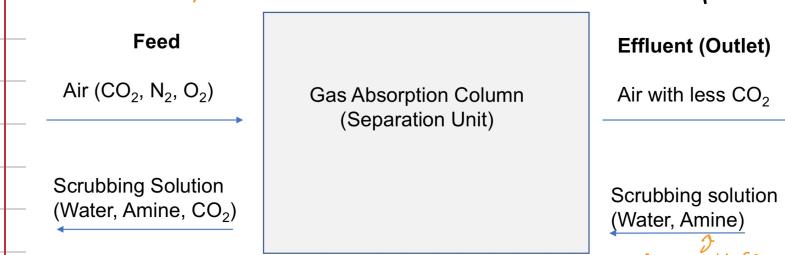
Process Variables  
For systems  
in right  
conditions  
mass fraction:  $x_i = \frac{\text{mass of } i}{\text{mass of mixture}}$   
mol fraction:  $y_i = \frac{\text{moles of } i}{\text{moles of mixture}}$

• Pressure, P

Mass flowrate,  $\dot{m}$  ( $\frac{\text{mass}}{\text{time}}$ )  
Volumetric flowrate,  $\dot{V}$  ( $\frac{\text{volume}}{\text{time}}$ )  
Molar flowrate,  $\dot{n}$  ( $\frac{\text{moles}}{\text{time}}$ )  
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  $n_i = 1 \text{ mol/min}$ .

Write an equation for  $V_i$ ,

$$PV = n_i RT \quad \text{and} \quad PV = \rho_i RT \quad \text{is also valid}$$

Be specific about stream which is ideal

$$\rightarrow V_i = \frac{n_i R T}{P_i}$$

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)

- 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

Material R  
use mostly

2. Perform a degree of freedom analysis on each subsystem

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

DOF

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

If  $\text{DOF} > 0$ , 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

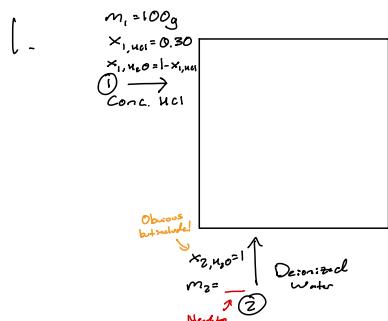
5. Write all material balances for all necessary subsystems

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:  $\rightarrow$  2 unknowns (masses)  $\rightarrow$  2 independent material balances  $\rightarrow$  2 equations

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  $\rightarrow$  2 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  
 (or have a better 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

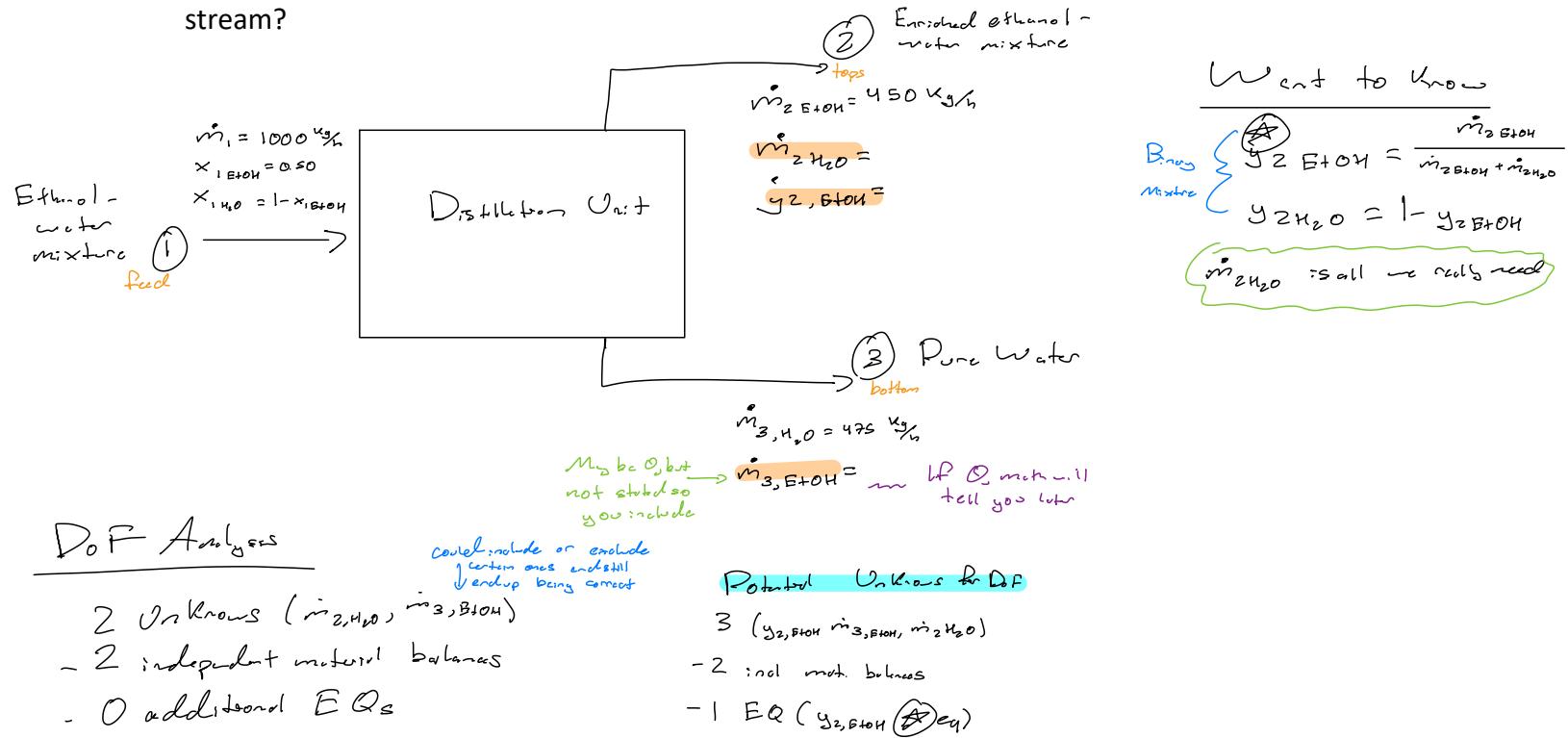
$$7. m_3 = \frac{m_1 x_{1,\text{HCl}}}{x_{1,\text{HCl}}}$$

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

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

Usually stop here or carry

**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?



DOF

Y<sub>2,EtOH</sub>! It's Soluble!

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Material Balances

$m_{in} + \text{generation} - \text{consumption} = m_{out}$

No physical separation/reaction occurs

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

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

$m_1 x_{1, \text{EtOH}} = m_{2, \text{EtOH}} + m_{3, \text{EtOH}}$

H<sub>2</sub>O:  $m_1 x_{1, \text{H}_2\text{O}} = m_{2, \text{H}_2\text{O}} + m_{3, \text{H}_2\text{O}}$

Total:  $m_1 = m_{2, \text{EtOH}} + m_{2, \text{H}_2\text{O}} + m_{3, \text{EtOH}} + m_{3, \text{H}_2\text{O}}$

Law of conservation of mass

It's steady-state!

So there is O accumulated

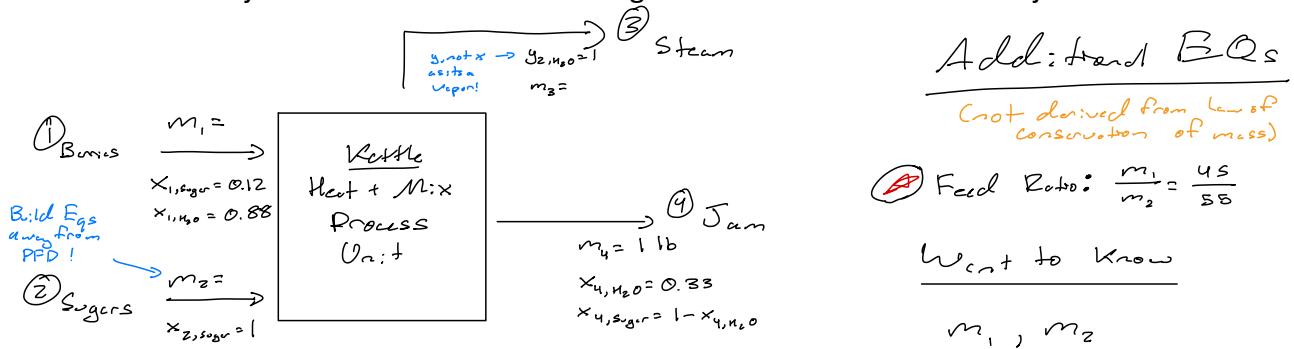
It's steady-state!

So there is O accumulated

### Plan of Attack

- Solve H<sub>2</sub>O for  $m_{2, \text{H}_2\text{O}}$
- Use  $m_{2, \text{H}_2\text{O}}$  in ~~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  
 $\Rightarrow m_i = \text{out}$

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

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) ...

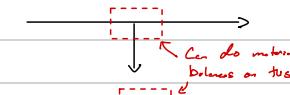
Don't need to do the algebra

Ron LOS

# Multi-Unit Processes w/ Recycle and Bypass Streams

## New Terminology

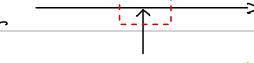
**Splitting Point:** Where 1 stream becomes 2 streams



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

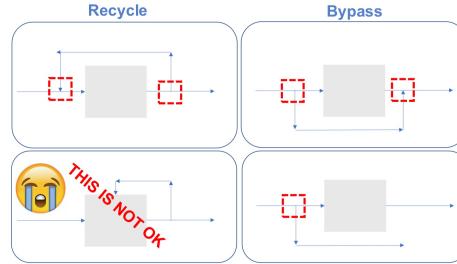
**Recycle:** Dilute a stream

Circulate a working fluid

Recover a catalyst

Reuse unreacted components

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

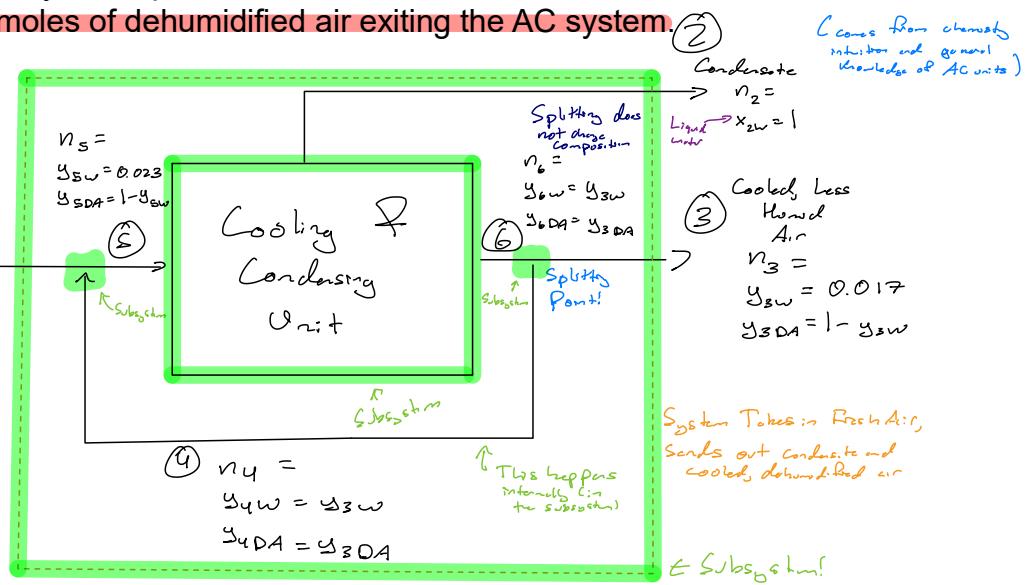


"The stream is  
recycled into the  
reactor" means stream  
going into reactor!

## 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:  $n_1, n_2, n_3$

DoF Analysis: ~~Can do 1 per subsystem present • Entire System, Splitting Point, mixing Point, cooling/condensing~~  
~~Can and should Subdivide Mixing Point, cool/condense~~  
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!

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

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

$\sim 1$  indep. material balances DA & W, but comp is fine so can only write 1 !!  
- 0 additional Eqs

2 DoF, cannot solve here!!

Mixing-DoF: 3 unknowns ( $n_1, n_4, n_5$ )

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

1 DoF !!

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

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

1 DoF !!

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

look at substreams with DofSI

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

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

(ii) Solve cool/condense  $\rightarrow$  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

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

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

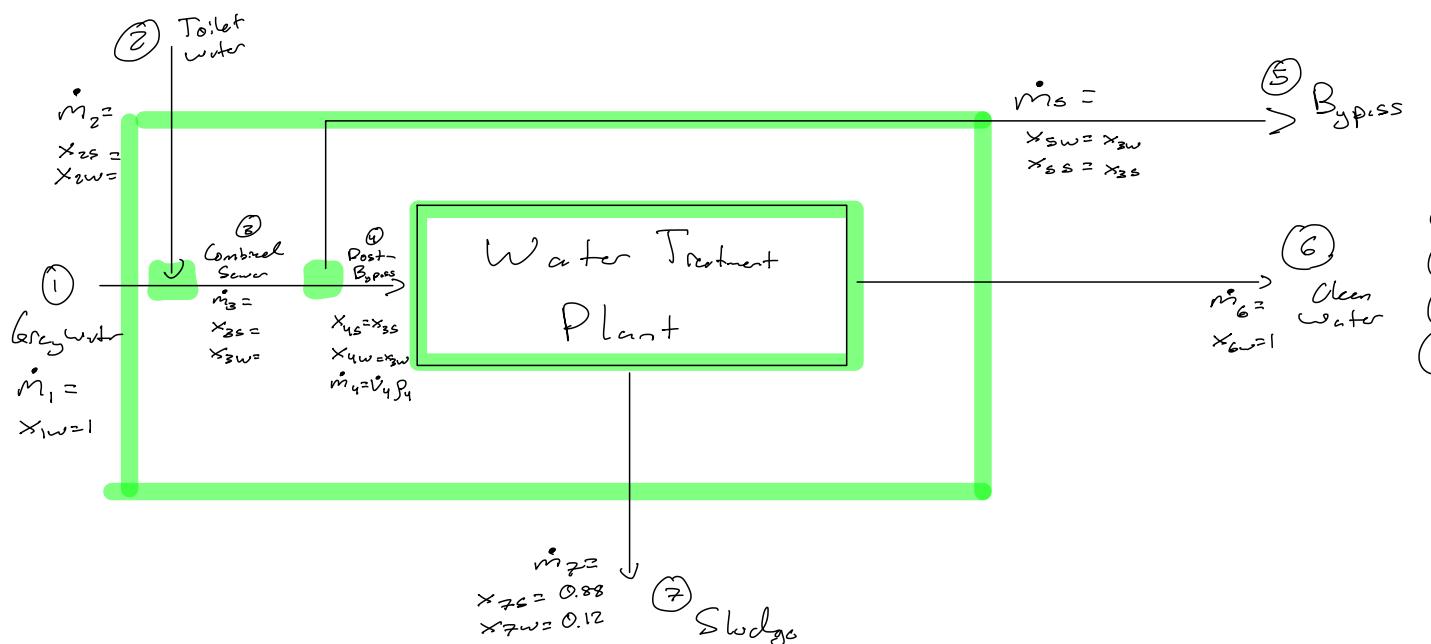
$$\text{Total: } n_6 = n_3 + n_4$$

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%

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

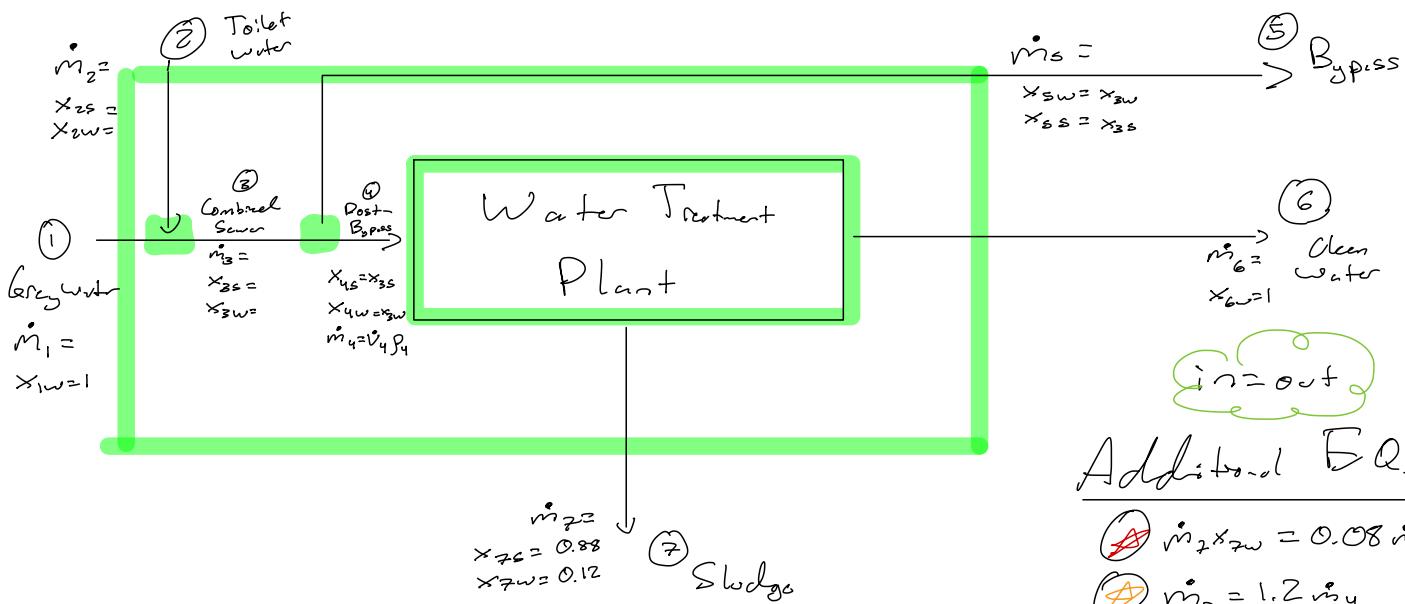
$$0.2 \dot{m}_4 = \dot{m}_5 \quad \text{This is also valid}$$

### Want to know

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

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

Wants to know  
way assumes  
 $\dot{m}_4 = \dot{m}_7$



DoF Analysis One per subsystem

### Water Treatment Plant

- 4 unknowns ( $m_5, m_7, x_{3S}, x_{3W}$ )
  - 2 indep. material balances (b/c 2 species)
  - 2 add. transl. Eqs (circled 1, circled 2)
- 0 DoF Solvable

### Splitting Point

- 4 unknowns ( $m_2, x_{2S}, x_{2W}, m_6$ )
- 1 indep. material balance (Splitting point explained below)
- 2 additional Eqs (circled 1, circled 2)

1 DoF  $\frac{1}{1}$

$$\text{S: } m_2 x_{2S} = m_3 x_{3S} + m_5 x_{5S}$$

$$\text{H}_2\text{O: } m_2 x_{2W} = m_3 x_{3W} + m_5 x_{5W}$$

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

These are already accounted for

### Mixing Point

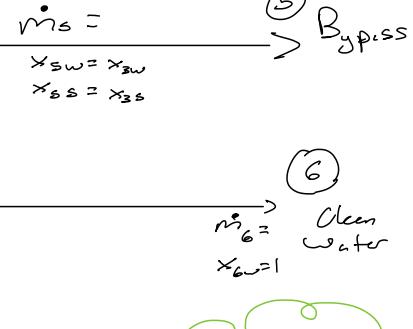
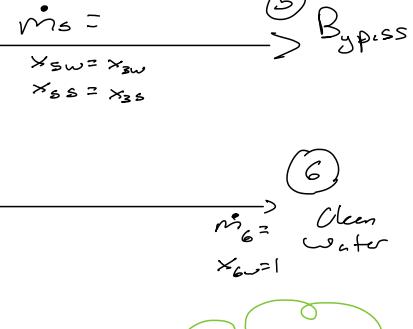
- 7 unknowns ( $m_1, m_2, m_3, x_{2S}, x_{2W}, x_{3S}, x_{3W}$ )
  - 2 indep. balances (2 species) ← composition chose @ mixing pt.
  - 2 additional Eqs (circled 1, circled 2)
- 3 DoF unsolvable

### Overall

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

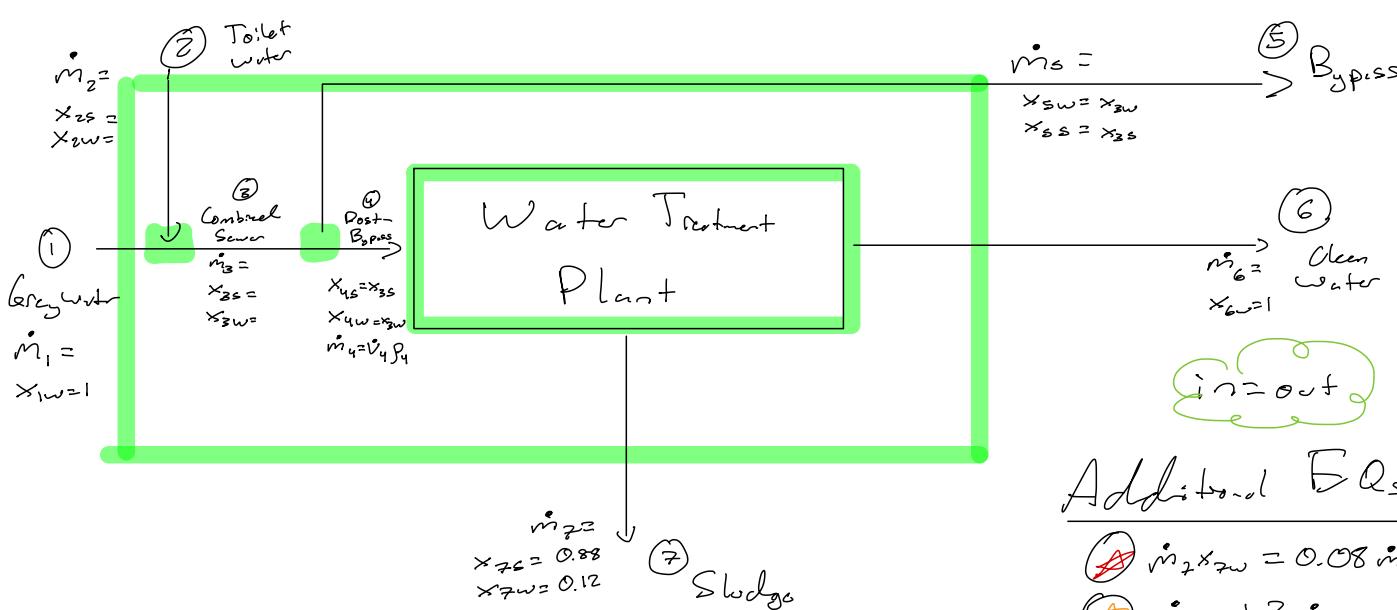
### Plant

- (i) Solo water Treatment Plant  
( $m_6, m_7, x_{3S}, x_{3W}$  will be known)
- (ii) Solo Splitting Point to get  $m_5$



### Additional Eqs

- ~~1~~  $m_2 x_{2W} = 0.08 m_4 x_{4W}$
  - ~~2~~  $m_3 = 1.2 m_4$
  - ~~3~~  $x_{3S} + x_{3W} = 1$  Build into PFD into same form
  - ~~4~~  $x_{2S} + x_{2W} = 1$
  - ~~5~~  $x_{5S} + x_{5W} = 1$
- Def. of mass flux



### Material Balances

Treatment

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

$$\text{in-out}$$

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

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

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

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

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

Splitting Point

See SS on Right

Additional Eqs

~~(1)  $\dot{m}_2 x_{2w} = 0.08 \dot{m}_4 x_{4w}$~~

~~(2)  $\dot{m}_3 = 1.2 \dot{m}_4$~~

Plan: treatment  $\rightarrow$  splitting

Mat Balance - Treatment

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

$$\text{norms} \quad x_{4w} + x_{4s} = 1$$

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

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

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

$$(y) \quad 0.08 \dot{m}_4 x_{4w} = \dot{m}_7 x_{7w}$$

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

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?

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

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

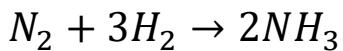
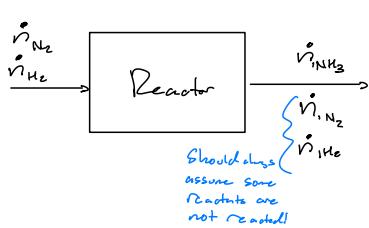
If prop side rxn occurred, what's the max mols that could be produced

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  $N_2$ "

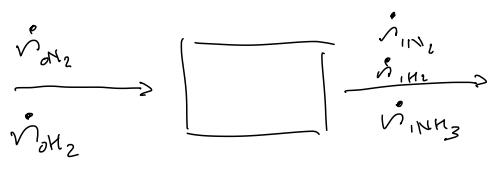
$\Rightarrow N_2$  is the limiting reactant

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

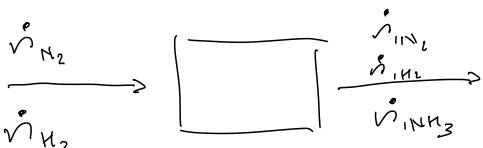


$$f_i = \frac{\dot{v}_{i, \text{reacted}}}{\dot{v}_{i, \text{fed}}}$$

$i = \text{species}$

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

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"

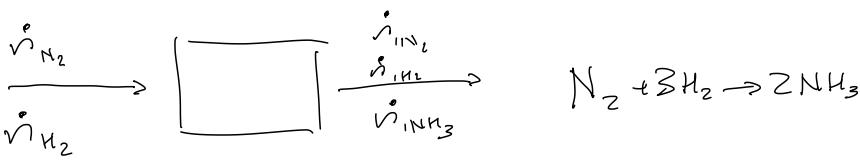
$$\text{Out} = \text{in} + \text{gen/consum}$$

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

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 !!

$A \rightarrow 3B$

$\neq 3$

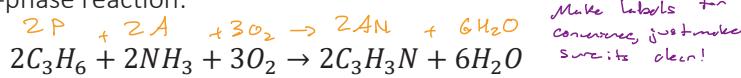
Moles are not conserved!

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

## Unit 5: Material Balances on Reactive Systems

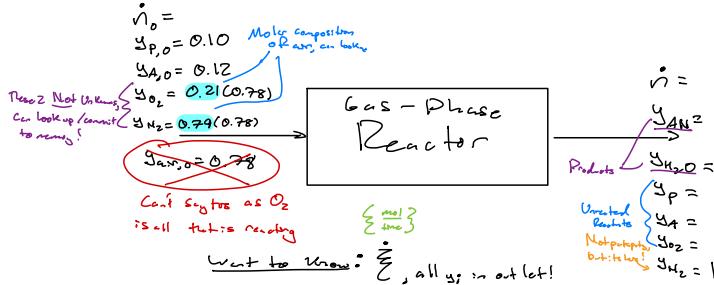
### Example 1: Production of acrylonitrile

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



DoF Analysis

Reactant: Assume  $n_0 = 100 \text{ mol}$   
 6 Unknowns ( $n_0, n_i$  is 5  $y_i$  from outlet stream)  
 - 6 Indep. Mat. Balances (bc 6 species:  $AN, H_2O, PA, O_2, N_2$ )  
 - 1 Additional EQ ( $f_p$ )  
 +1 Chemical Reaction ( $\frac{\dot{n}}{n}$ ) *Exhaust P Reaction is added to DoF!*

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

### Material Balances

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

*In-out-gain-loss = accumulation*

$$G_{\text{in}} \rightarrow n_i = n_{i,0} + \dot{n}_i \frac{\dot{n}}{n}$$

$$P: n_{y_P} = n_0 y_{P,0} + (-2) \frac{\dot{n}}{n}$$

$$A: n_{y_A} = n_0 y_{A,0} + (-2) \frac{\dot{n}}{n}$$

$$N_2: n_{y_{N_2}} = n_0 y_{N_2,0} + 0 \frac{\dot{n}}{n}$$

*No Reactive species (inert)*

$$O_2: n_{y_{O_2}} = 0 + 6 \frac{\dot{n}}{n}$$

*Not used up*

$$AN: n_{y_{AN}} = 0 + 2 \frac{\dot{n}}{n}$$

$$O_2: n_{y_{O_2}} = n_0 y_{O_2,0} + (-3) \frac{\dot{n}}{n}$$

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

Addl. Const. EQs

$$f_p = \frac{\text{mol Pranted excess from molar balance}}{\text{mol P fed}} = \frac{n_0 P_{0,0} - n_{y_P}}{n_0 P_{0,0}} = 0.30$$

Addl. Const. EQs

$$f_p = \frac{\text{mol Pranted excess from molar balance}}{\text{mol P fed}} = \frac{n_0 P_{0,0} - n_{y_P}}{n_0 P_{0,0}} = 0.30$$

Alternate Approach

$$\begin{aligned} n_{AN} &= \\ n_{H_2O} &= \\ n_P &= \\ n_A &= \\ n_{O_2} &= \\ n_{N_2} &= \end{aligned}$$

*Only molar fractions, assume a basis  $y$*

How to Solve

(i) Solve  $f_p$  for  $n_{y_P}$  *→ Plug into P balance → solve  $\frac{\dot{n}}{n}$*

(ii) Solve A balance for  $n_{y_A} \left( \frac{\text{moles A}}{n} \right)$

(iii) Solve  $N_2$  balance for  $n_{y_{N_2}}$

(iv) Solve  $H_2O$  balance for  $n_{y_{H_2O}}$

(v) Solve AN for  $n_{y_{AN}}$

(vi) Solve  $O_2$  for  $n_{y_{O_2}}$

(vii) Calculate  $n_{y_P}$  from  $f_p$

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

$$y_i = \frac{u_i n}{\sum u_i n} = \frac{\text{moles of } i}{\text{total moles}}$$

*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

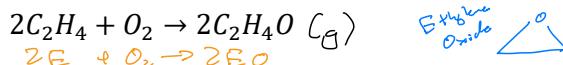
For reactive systems that include a recycle stream...

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:

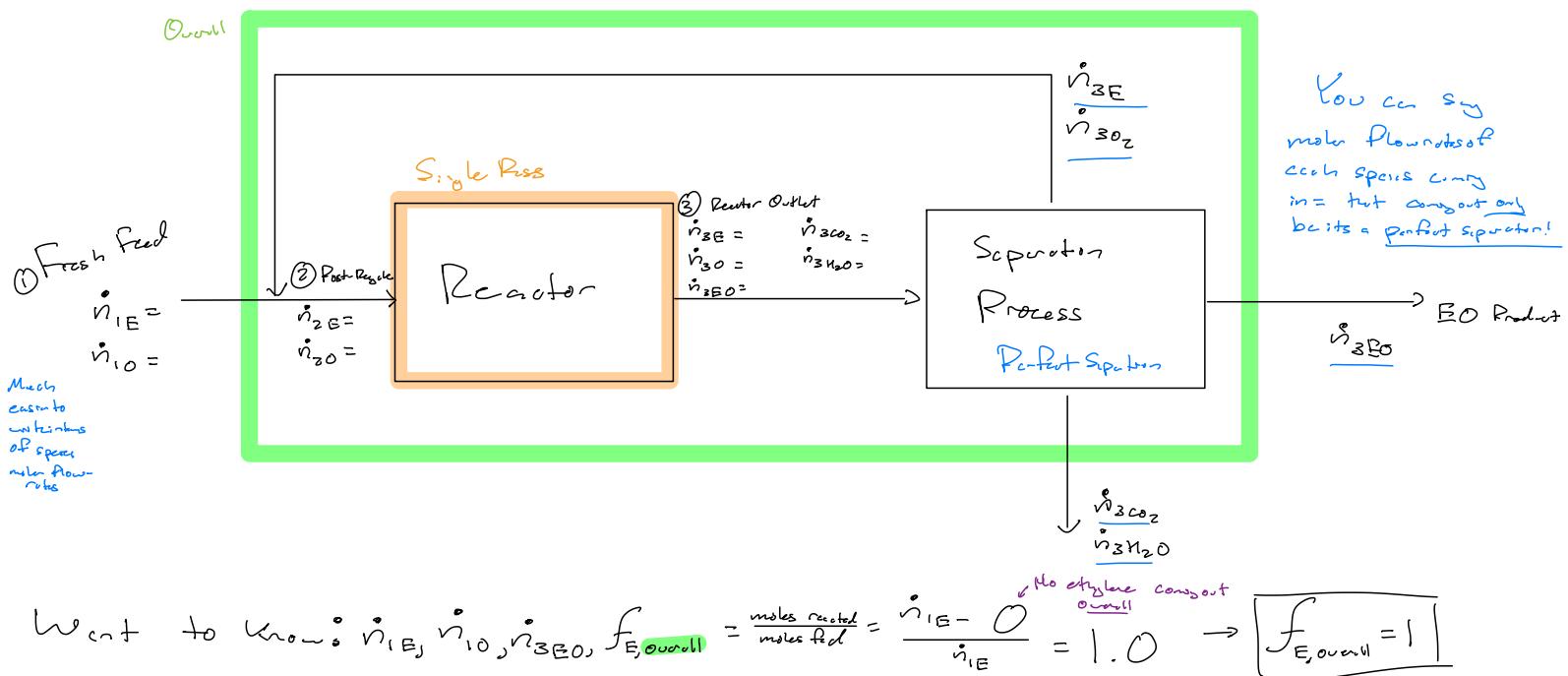


An undesired competing reaction is the combustion of ethylene:



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

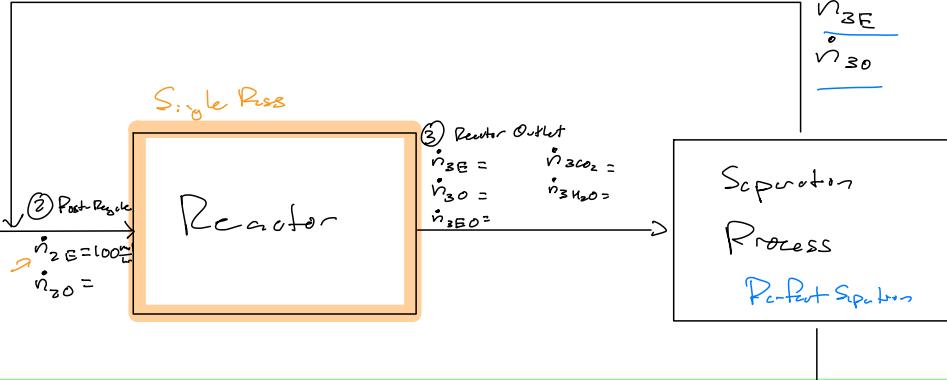
~~(1)~~  $\dot{n}_{2E} = 3\dot{n}_{2O}$   $\frac{\dot{n}_{2E}}{\dot{n}_{2O}} = 3$

$f_{E, \text{single}} = \frac{\dot{n}_{2E} - \dot{n}_{3E}}{\dot{n}_{2E}} = 0.20$  D.P. reactor term

~~(2)~~  $\frac{\dot{n}_{2E} - \dot{n}_{3E}}{\dot{n}_{3EO}} = \frac{100}{40}$  100 moles E reacted 40 moles EO produc

We only contend with reactions if the reaction is taking place in the subsystem

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**

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# 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

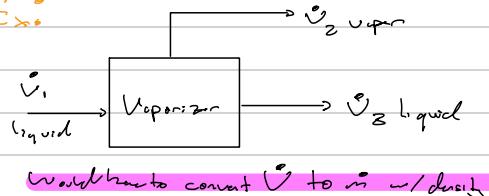
- Go to NIST chemical webbook
- Perry's chemical handbook
- Appendix B (in textbook)
- Wolfram Alpha

Bad Sources  
of values

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

When would we use these properties?

Ex:



Volume is not a conserved quantity  
we cannot write Mass Balances w/ it 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. ( $T$ ,  $P$  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?

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

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

$V = \frac{RT}{P} > 5 \frac{L}{mol}$  for diatomic gases ← contrast air ( $N_2/O_2$ ) as diatomic

$V = \frac{RT}{P} > 20 \frac{L}{mol}$  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 ECHB 225  
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 chart

## 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)
- char of corresponding states: certain phys. properties of a gas strongly depend on the proximity of the gas to its critical state

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

critical state temp

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

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