



Unit 1



Unit 1: Units and Process Variables

Process Variables

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

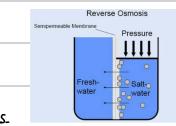
① Salt Water Desalination

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.

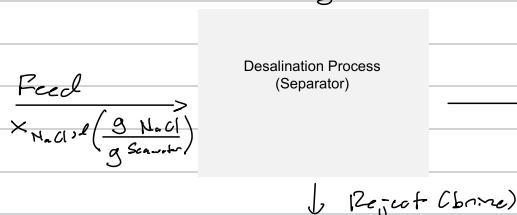
or measured

Tampa Bay Distillation



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

Process Flow Diagram for desalination



↓ Reject Brine)

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.

Relevant Process Variables

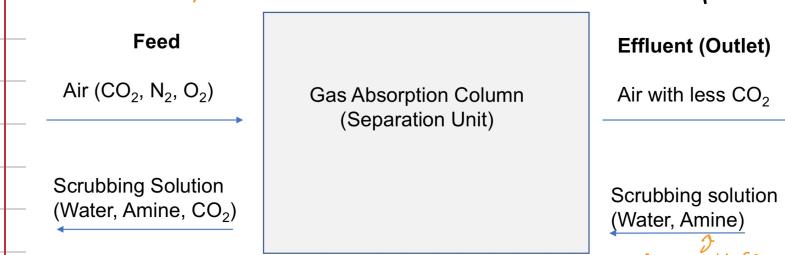
- mass fraction: $\frac{\text{mass of } i}{\text{mass of mixture}} = x_i \text{ or } y_i$ For systems reacting with products
- mol fraction: $\frac{\text{mol of } i}{\text{moles of mixture}} = \bar{x}_i \text{ or } \bar{y}_i$ for gases/vapors

• 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 CO_2 Capture

Chemical Engineers can design pollution control Systems (absorbers/membranes) to remove CO_2 from industrial waste
 Gas absorption columns: Use reactions to capture 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

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

Consider air is a mixture of CO_2 , N_2 , O_2 . By mass: 76.95% N_2 , 0.05% CO_2 , and 23% O_2 .

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

where y_i is molar masses 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 fractions for all species
- Assume a basis for gas calculations, 100 g air

Relevant Process Variables

- Air Pressure
 - Amine: CO_2 Reactions
 - ↳ Solution Concentrations
 - Fraction CO_2 Removed
 - Flowsheet (x_i, y_i, v_i, \dot{V}_i) $i = \text{species}$
 - ↳ Total Flowsheet (x_i, y_i, \dot{V}_i) gases
 - Composition of each stream (x_i vs. y_i)
 - Energy Flowsheets (H_i)
 - Temperature and Pressure
- Indirect Discussion
- Group Discussion

Unit 2



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

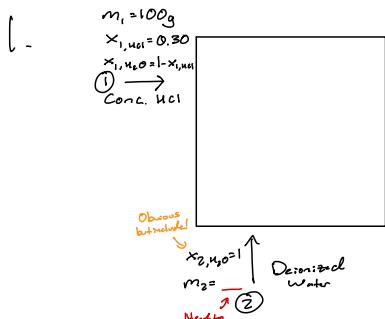
5. Write all material balances for all necessary subsystems

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 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 H_2O for m_2 using (i) result
- ↳ For ease, solve m_2 from mass balance

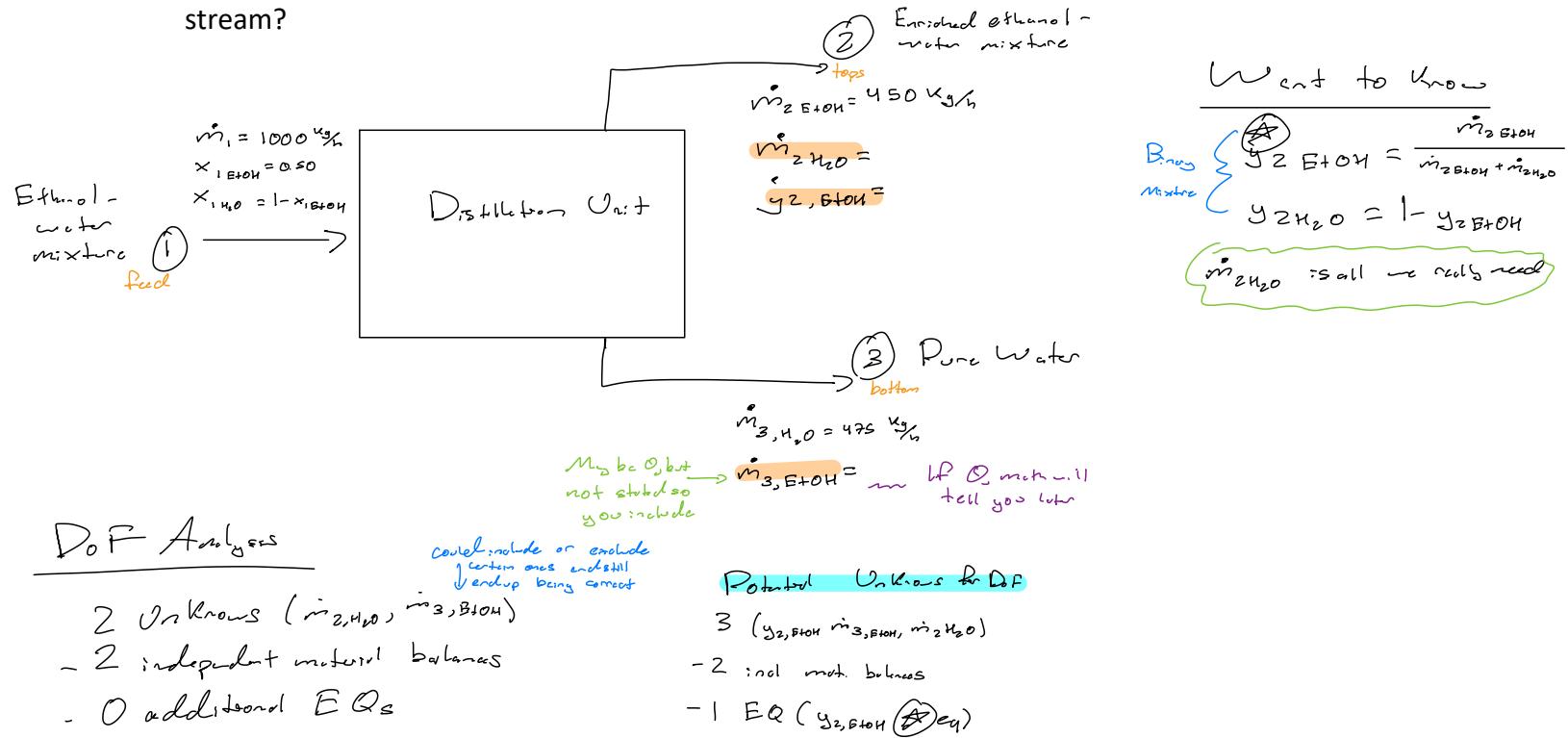
$$7. m_3 = \frac{m_1 x_{1,\text{HCl}}}{x_{1,\text{HCl}}}$$

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

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

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?



O DOF $y_{2, \text{EtOH}}$! It's Soluble!

Material Balances

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

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

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

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

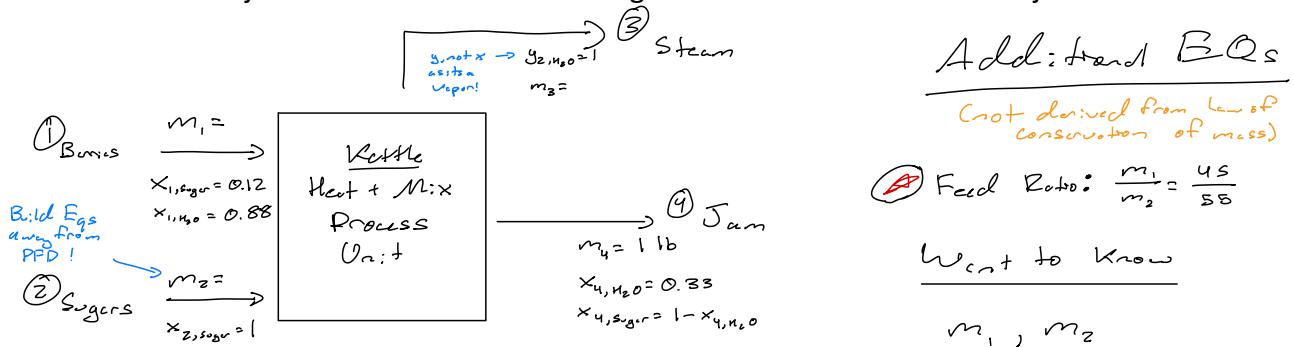
Total: $m_1 = m_{2, \text{EtOH}} + m_{2, \text{H}_2\text{O}} + m_{3, \text{EtOH}} + m_{3, \text{H}_2\text{O}}$

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 ~~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 (④)

① $\rightarrow Dof \leq 0 \checkmark$
Can solve!

Material Balances

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

$H_2O: m_1 x_{1,H_2O} = m_3 + m_4 x_{4,H_2O}$

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: $\frac{m_1}{m_2} = \frac{4S}{SS}$

To highlight everything you know

How to Solve

- Solve ④ for m_3
- Plug ④ into sugar balance to solve for m_2
- Plug m_2 into ④ to solve m_1

Solve \checkmark Not needed on HW unless specified

$$(i) m_3 = \frac{4S}{SS} m_2$$

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

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

$$m_2 = \frac{m_4 x_{4,sugar}}{\frac{4S}{SS} x_{1,sugar} + 1}$$

(iii) ...

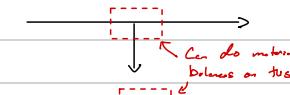
Don't need to do the algebra

Ron LOS

Multi-Unit Processes w/ Recycle and Bypass Streams

New Terminology

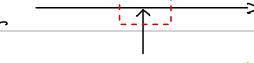
Splitting Point: Where 1 stream becomes 2 streams



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

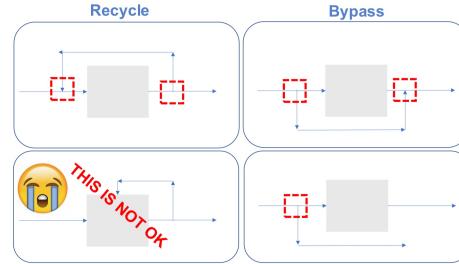
Recycle: Dilute a stream

Circulate a working fluid

Recover a catalyst

Reuse unreacted components

Bypass: Circumvent a unit operation
Overflow condition for safety

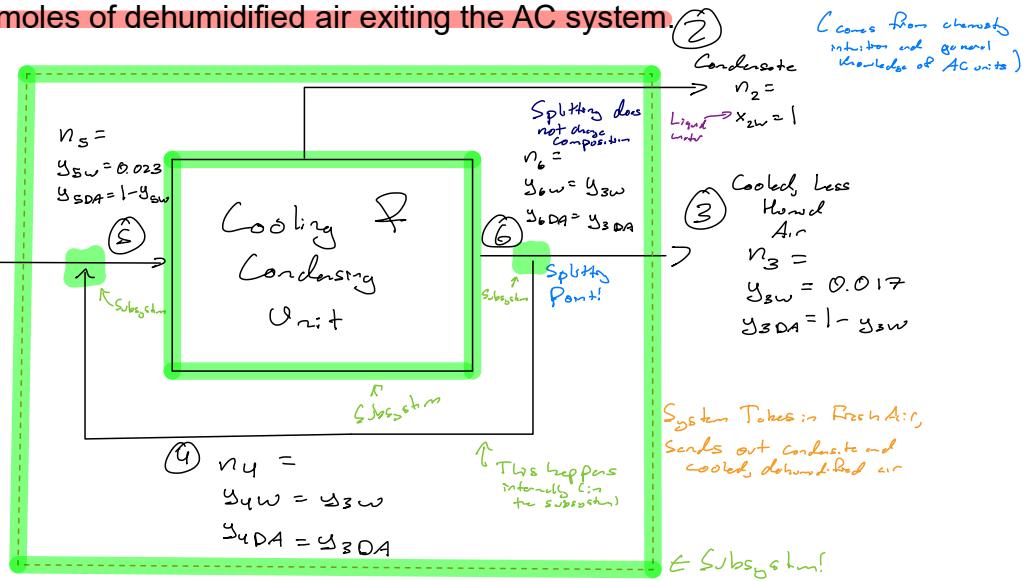


"The stream is
recycled into the
reactor" means stream
going into reactor!

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, mixing Point, cooling/condensing
Can and should Subdivide Mixing Point, cooling/condensing
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: $n_6 y_{6DA} = n_4 y_{4DA} + n_2 y_{2DA}$
 $\rightarrow n_6 = n_4 + n_2$

~ 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!

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 if

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

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

1 DoF if

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

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

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

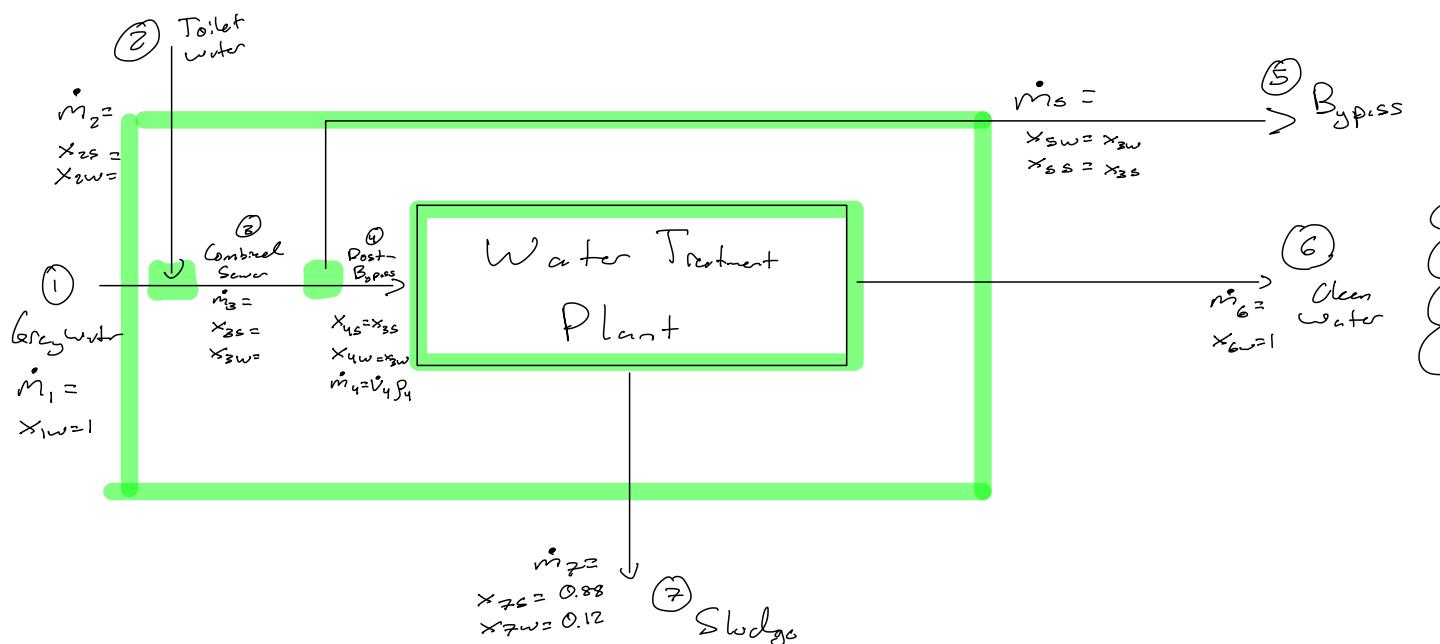
$$\text{Total: } n_6 = n_3 + n_4$$

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

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

$$\rho_4 = 10 \frac{\text{lbs}}{\text{gallon}}$$

* 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%

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

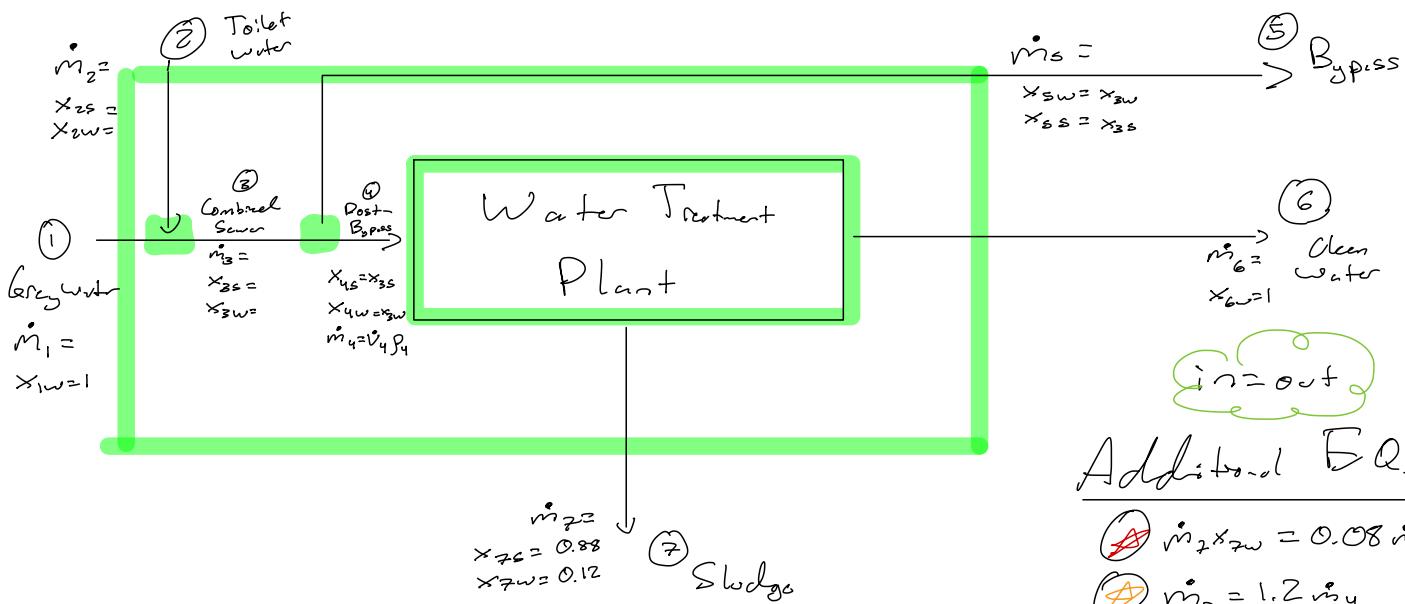
$$0.2 \dot{m}_4 = \dot{m}_5 \quad \text{This is also valid}$$

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

- You can
pinchout
just here
down
- 4 unknowns (m_5 , m_7 , x_{3w} , x_{2w})
 - 2 indep. material balances (b/c 2 species)
 - 2 add. transl. Eqs ($\cancel{m_2}$, $\cancel{m_3}$)
- 0 DoF Solvable

(Splitting Point)

- 4 unknowns (m_3 , x_{2s} , x_{3w} , m_6)
- 1 indep. material balance (Splitting point explained below)
- 2 additional Eqs ($\cancel{m_2}$, $\cancel{m_3}$)

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

Si: $m_3 x_{2s} = m_2 x_{2s} + m_5 x_{2s}$

H₂O: $m_3 x_{3w} = m_4 x_{3w} + m_5 x_{3w}$

Toatl: $m_3 = m_4 + m_5$

This one
already

Mixing Point

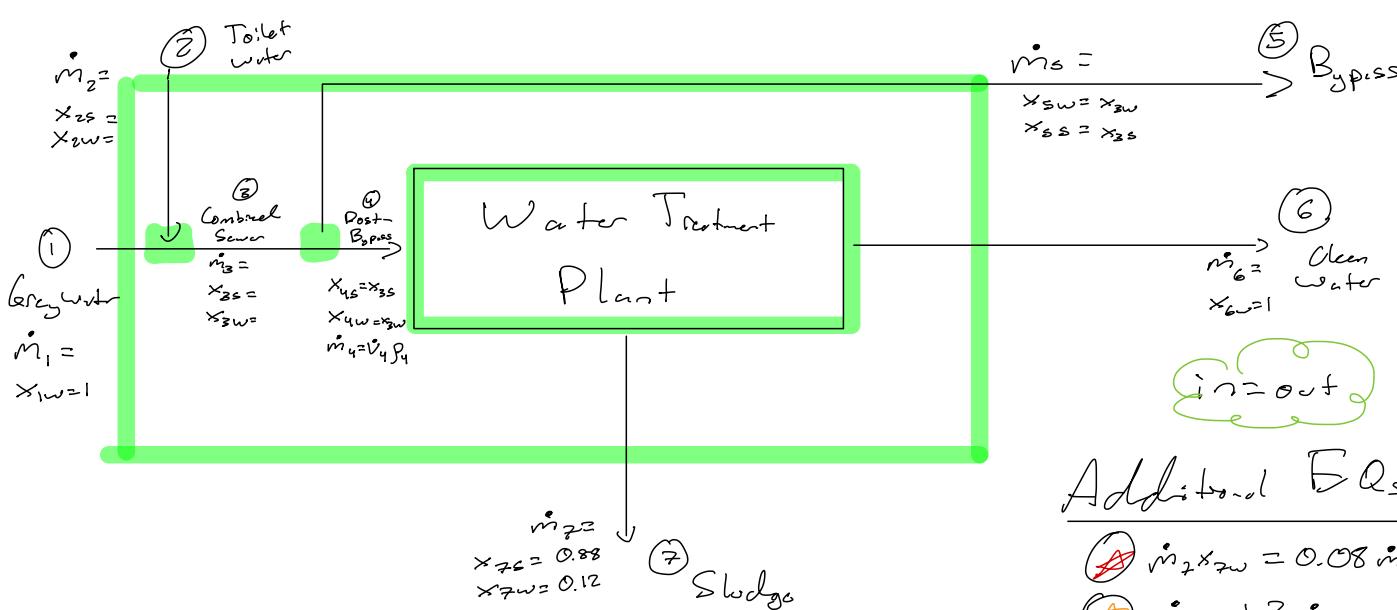
- 7 unknowns (m_1 , m_2 , m_3 , x_{2s} , x_{2w} , x_{3s} , x_{3w})
- 2 indep. balances (2 species) \leftarrow composition chose @ mixing pt.
- 2 additional Eqs ($\cancel{m_2}$, $\cancel{m_3}$)
- 3 DoF unsolvable \Rightarrow

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 ($\cancel{m_2}$, $\cancel{m_3}$)
- 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_3



Material Balances

Treatment

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

$$\text{in-out}$$

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

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

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

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

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

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?

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

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

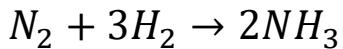
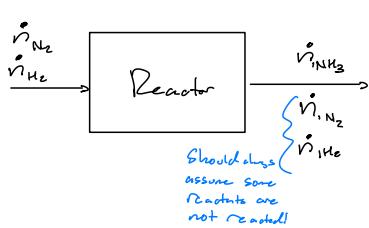
If prop side rxn occurred, what's the max mols that could be produced

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 "

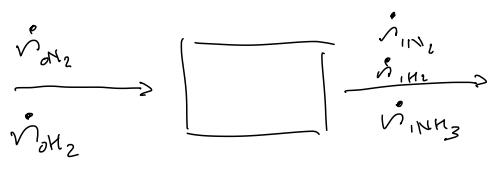
$\Rightarrow N_2$ is the limiting reactant

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

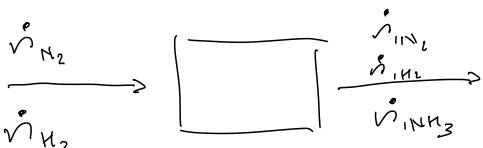


$$f_i = \frac{\dot{v}_{i, \text{reacted}}}{\dot{v}_{i, \text{fed}}}$$

$i = \text{species}$

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

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: described by "extents"

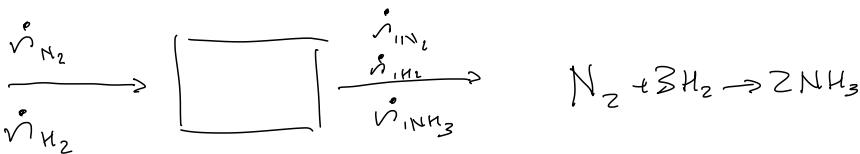
$$\text{Out} = \text{in} + \text{gen/consumption}$$

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

Extent of Reaction:

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

γ_{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 !!

$A \rightarrow 3B$

$\neq 3$

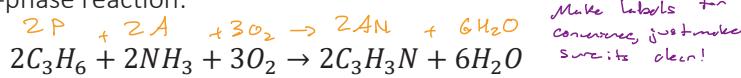
Moles are not conserved!

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

Unit 5: Material Balances on Reactive Systems

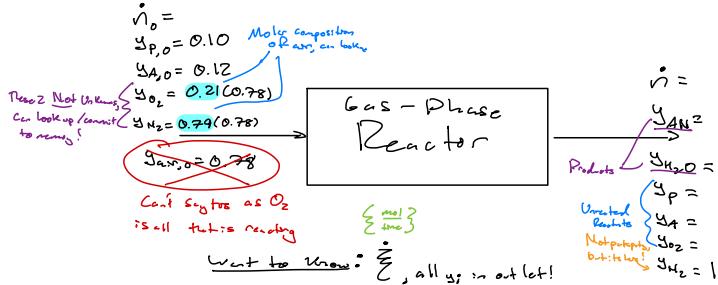
Example 1: Production of acrylonitrile

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!*

ΔX 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

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

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

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

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

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

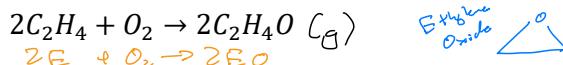
For reactive systems that include a recycle stream...

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:

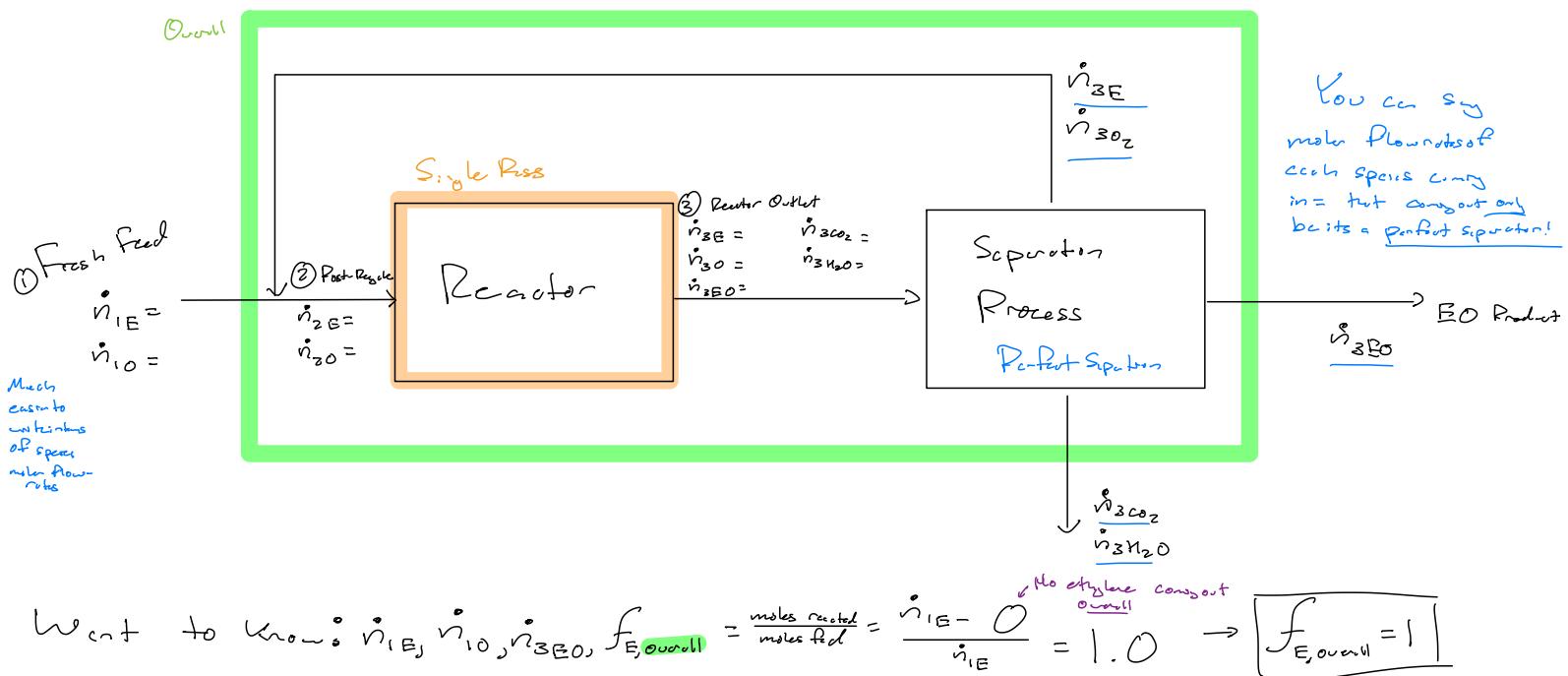


An undesired competing reaction is the combustion of ethylene:



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

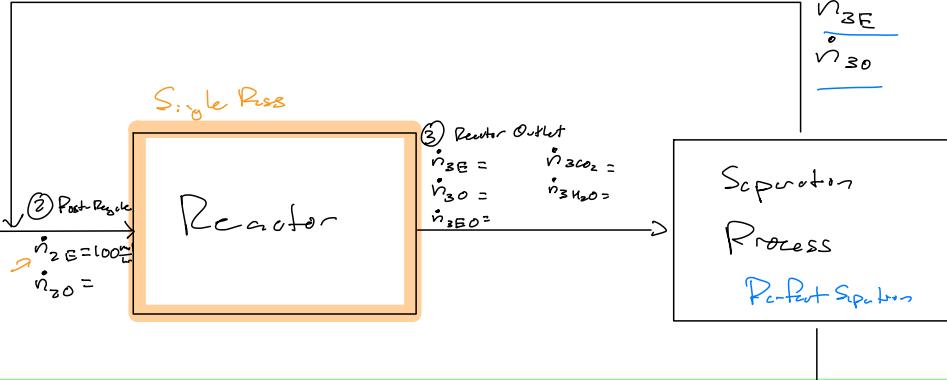
~~(1)~~ $\dot{n}_{2E} = 3\dot{n}_{2O}$ $\frac{\dot{n}_{2E}}{\dot{n}_{2O}} = 3$

$f_{E, \text{single}} = \frac{\dot{n}_{2E} - \dot{n}_{3E}}{\dot{n}_{2E}} = 0.20$ *Overall conversion*

~~(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}_{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 CO₂ Balance for \dot{n}_{3CO_2}
- Solve H₂O 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 ρ to ρ_s for an incompressible fluid

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

Good Sources
of values

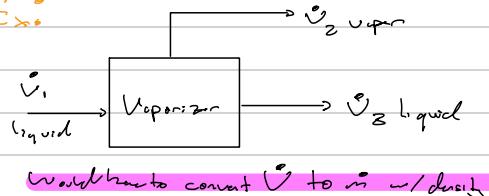
- Go to NIST chemical webbook
- Perry's chemical handbook
- Appendix B (in textbook)
- Wolfram Alpha

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_{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?

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

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

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

$V = \frac{RT}{P} \geq 20 \frac{L}{mol}$ 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

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*, 3rd edition. Chapter 5, pages 208-211

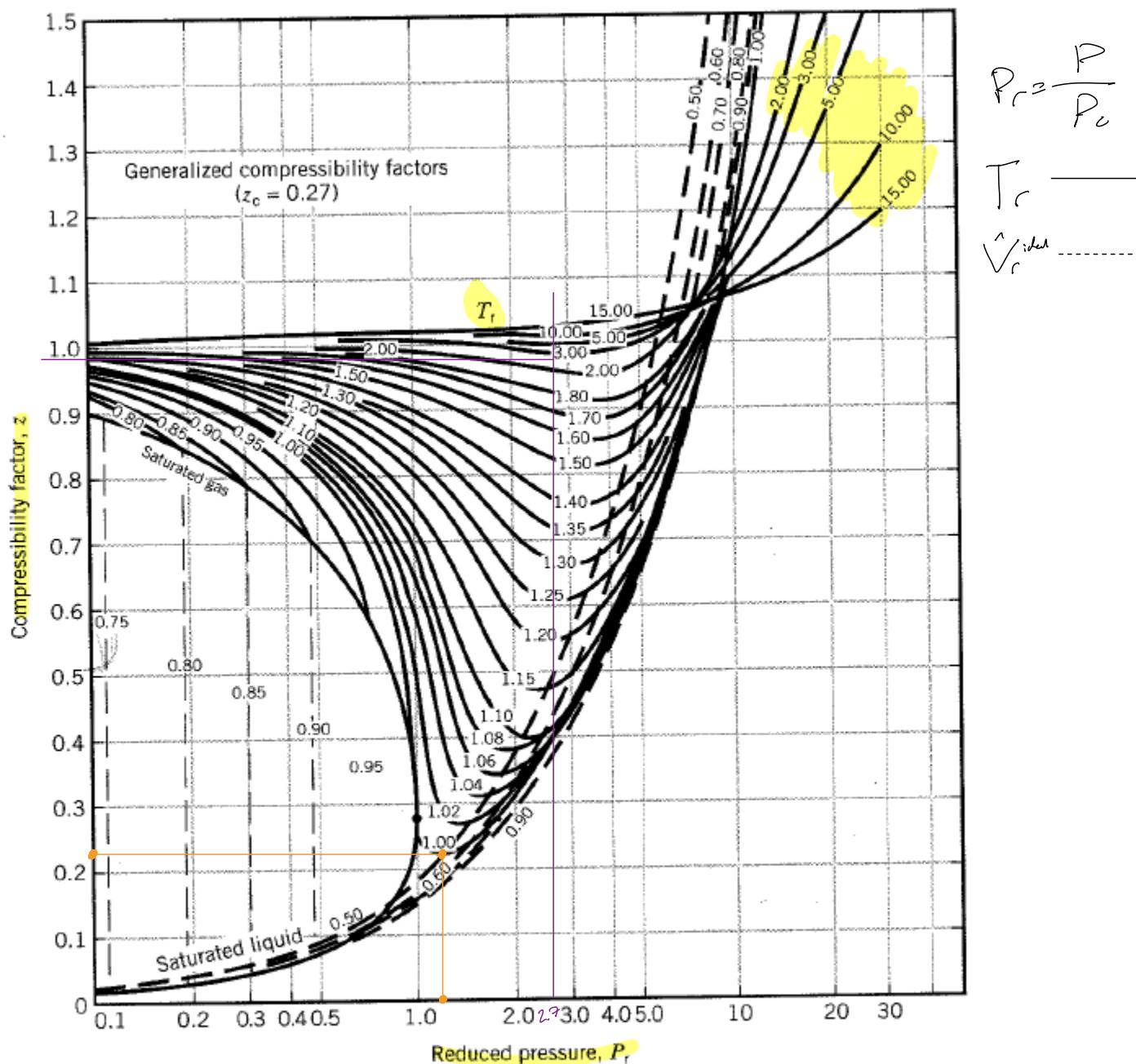


Figure 5.4-1 (Reprinted with permission from *Chemical Process Principles Charts*, 2nd Edition, by O. A. Hougen, K. M. Watson, and R. A. Ragatz, John Wiley & Sons, New York, 1960.)

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

T_r —
 $\sqrt{V_r}$ -----

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

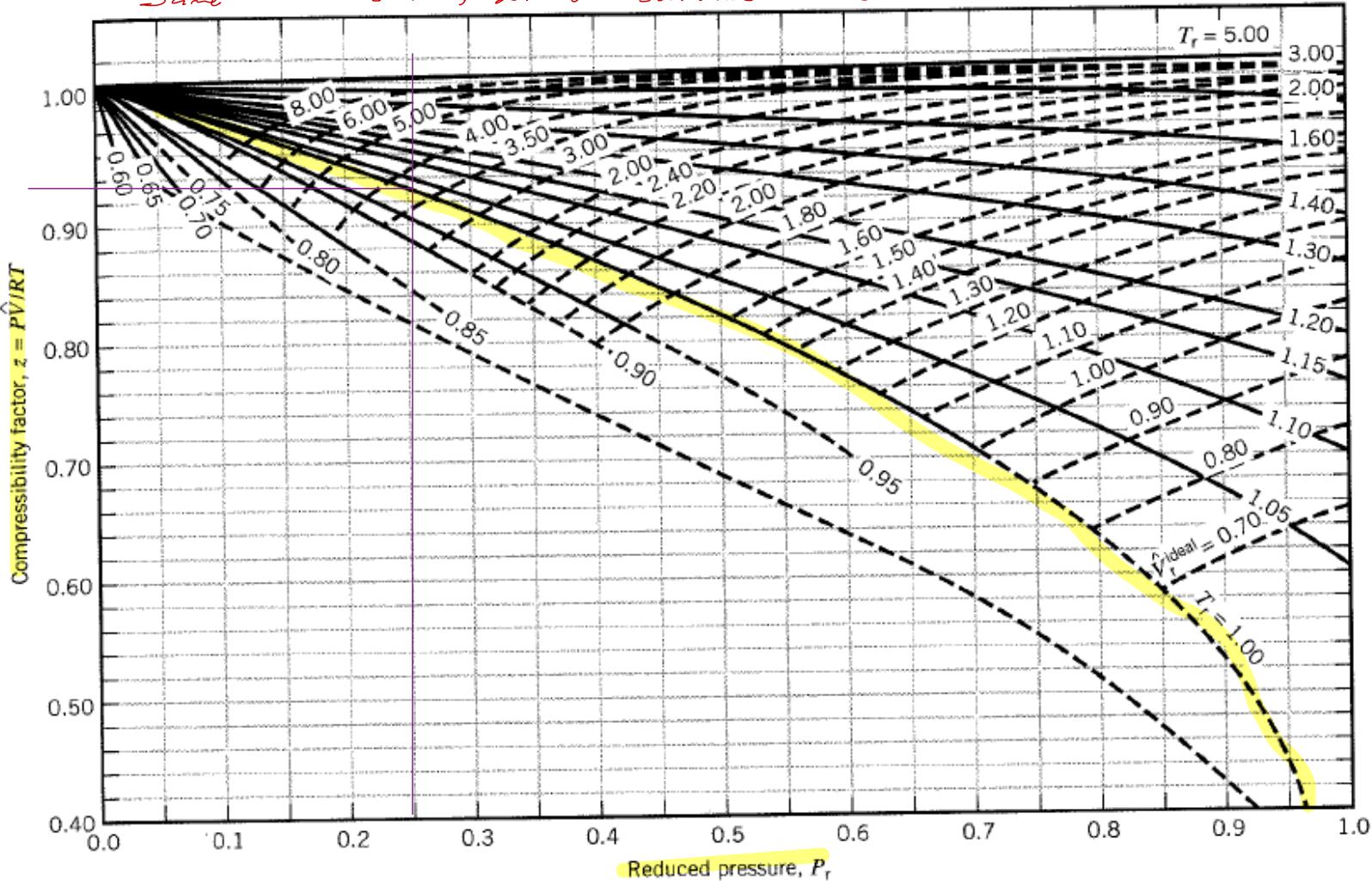


Figure 5.4-2 Generalized compressibility chart, low pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 175. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

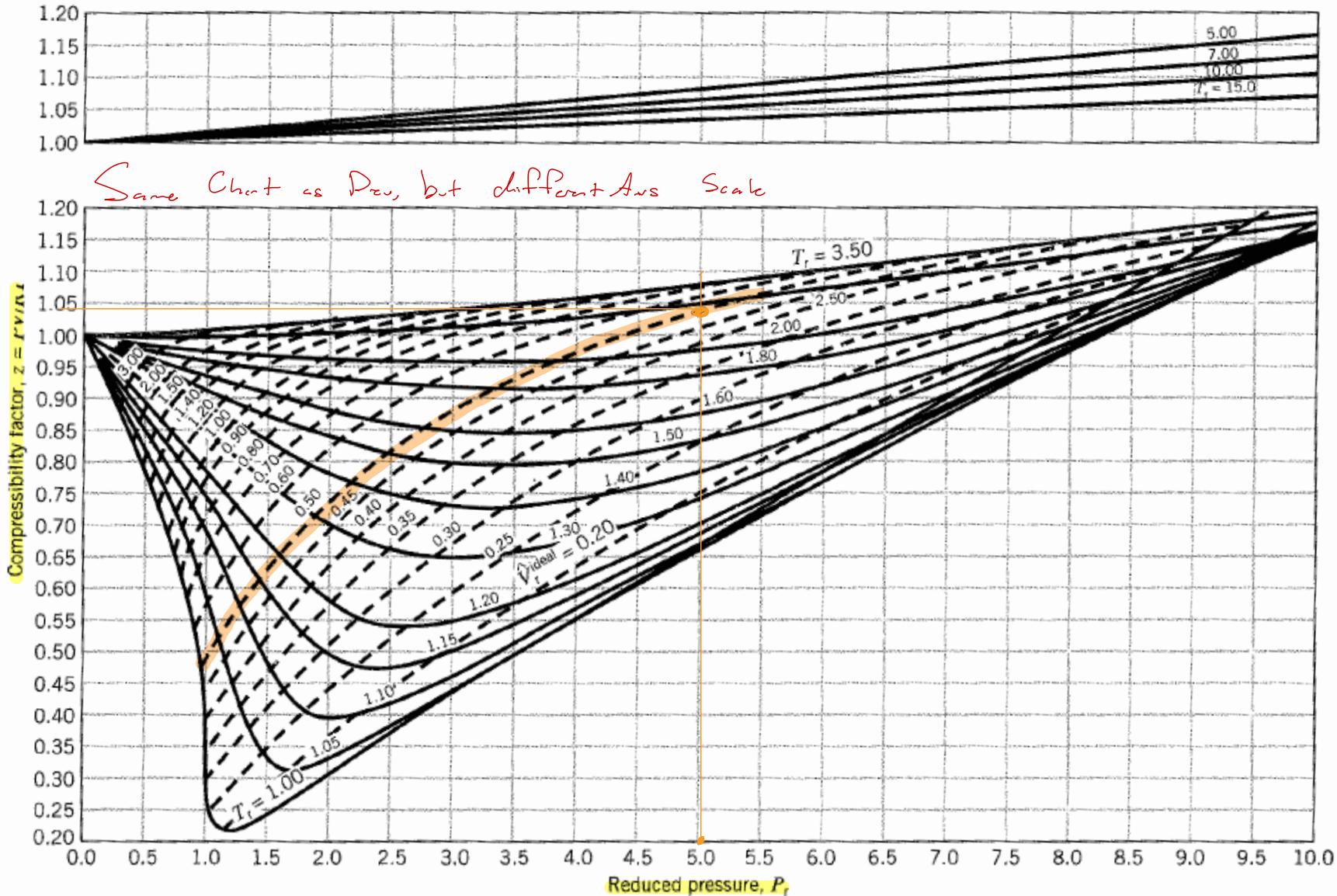


Figure 5.4-3 Generalized compressibility chart, medium pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 176. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

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*, 3rd edition. Chapter 5, pages 208-211

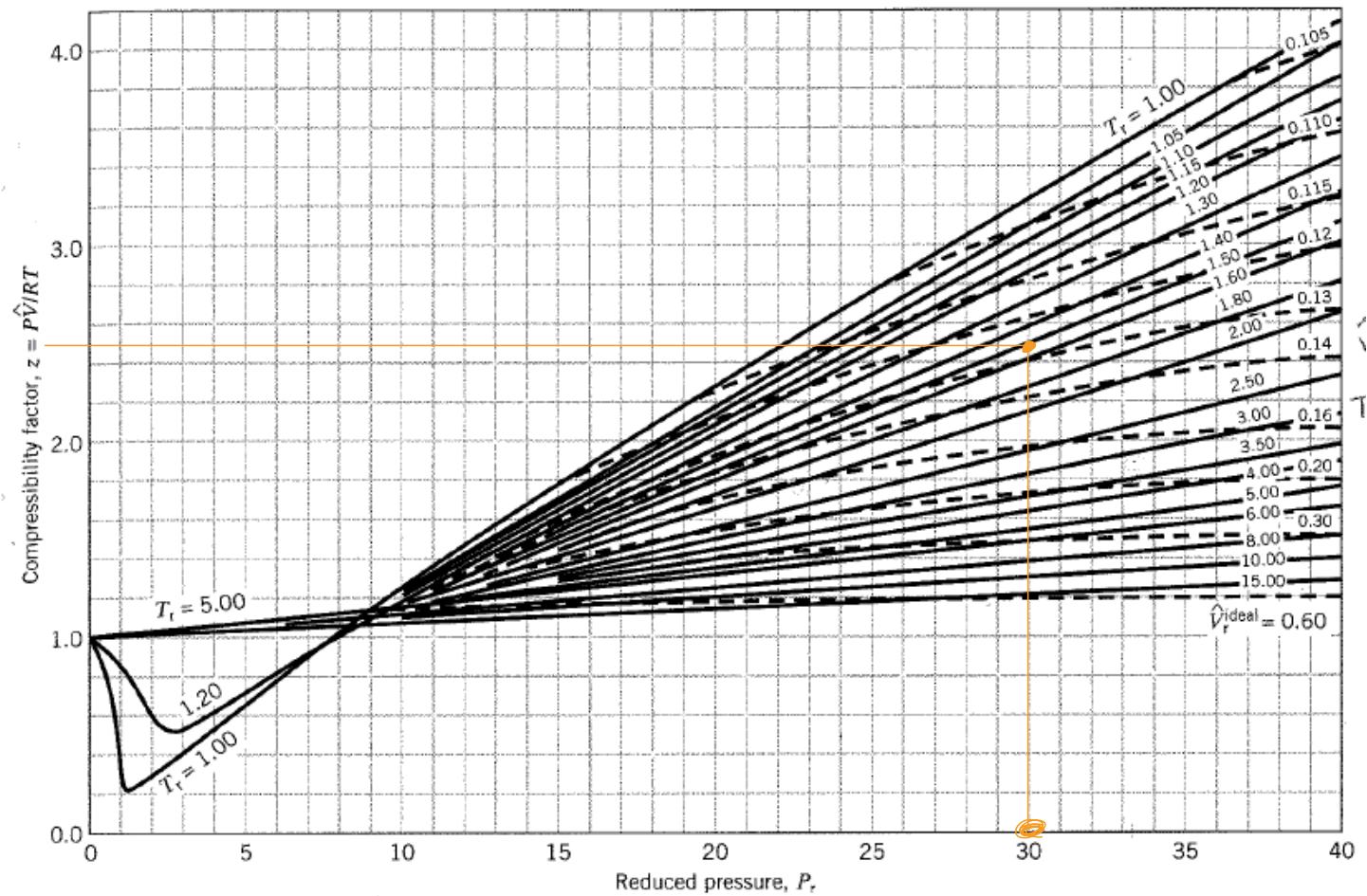
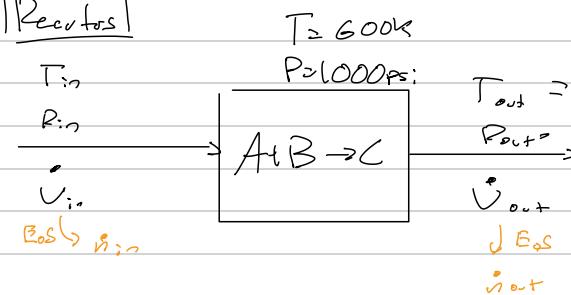


Figure 5.4-4 Generalized compressibility chart, high pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 177. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

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



$T_{in} + \Delta T$

$P_{in} = P_{out}$

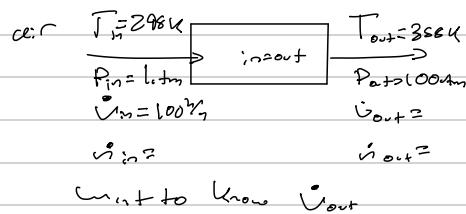
$V_{in} = V_{out}$

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

Fully isolated PFD with heat.

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

Compressor



Air Balances in and out

Apply V^2 law to determine

EoS for inlet & outlet

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

: If $V > 8 \frac{\text{L}}{\text{mol}}$ compressible $\Rightarrow C_v = C_p$
If $V > 20 \frac{\text{L}}{\text{mol}}$ others $\Rightarrow C_v = C_p$

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

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

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

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

$P_c = \sum y_i P_{ci}$

Calculate T_c' for air

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

$$= 0.79(126\text{K}) + 0.21(154\text{K})$$

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

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

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

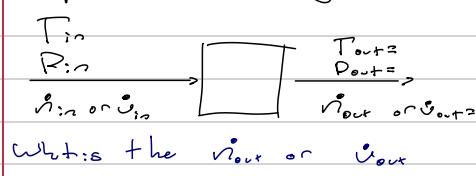
$$T_r = \frac{T_2}{T_c'} = \frac{358\text{K}}{132\text{K}} = 2.7$$

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

$Z = 0.95$ 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

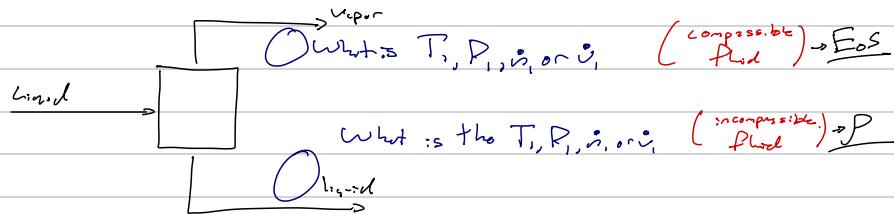
Additional Equations

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

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

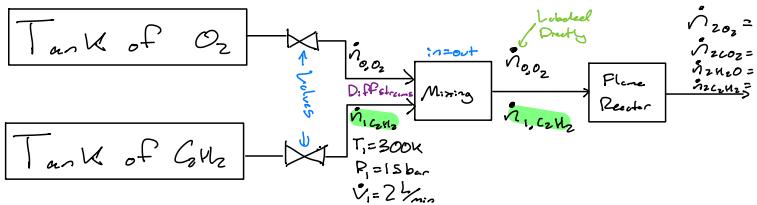
$$PV = zRT \quad V \leftarrow \text{constant} \quad \text{volume}$$

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 $\dot{m}_{C_2H_2}$ for usc:n reactor mxt. basis

1. C_2H_2 is a compressible or incompressible fluid

\hookrightarrow EoS can be used as it is compressible

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

\hookrightarrow Test: !

$$\text{EoS: } V = \frac{RT}{P} = \frac{(0.082 \frac{L_{atm}}{\text{mol} \cdot K})(300K)}{15\text{ atm}} = 1.6 \ll 20$$

1 atm $\approx 1\text{ bar}$

Can't use ideal g.s!!

3. Use $P_1 V_1 = z \dot{m}_{C_2H_2} RT_1$ we need to read z-value from generalized compressibility charts

$$T_r = \frac{T_1}{T_c} \quad P_r = \frac{P_1}{P_c} \Rightarrow T_r = \frac{300K}{309.5K} \approx 1 \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} z \approx 0.93$$

$$T_c = 309.5K \quad P_c = 61.6 \text{ atm} \quad P_r = \frac{15\text{ atm}}{61.6 \text{ atm}} = 0.25$$

Calculate $\dot{m}_{C_2H_2}$ using found $z = 0.93$

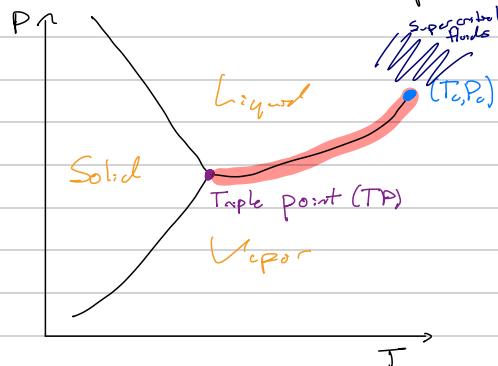
Unit 5



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

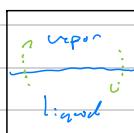
↳ steam tables (For given T , state, what is P ?)

↳ 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

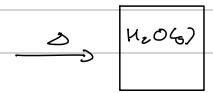
phase → 1 molecule of A must condense

What happens if we increase P ?

Conc A, increase fraction of A in the liquid phase

What happens if we decrease T ?

VLE



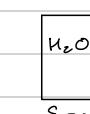
Saturated vapor

Supersaturated 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 $H_2O(g)$



Supersaturated

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

P_i^s = partial pressure of species i

Ideal Gases

$$P_i^s = y_i P_{\text{tot}}$$

Nonideal Gases

$$P_i^s = y_i P_{\text{tot}} \phi$$

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 supersaturated vapor: $P_i < P_{i,sat}$