



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

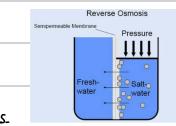
① Salt Water Desalination

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.

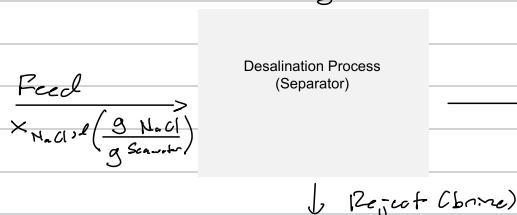
or measured

Tampa Bay Distillation



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

Process Flow Diagram for desalination



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

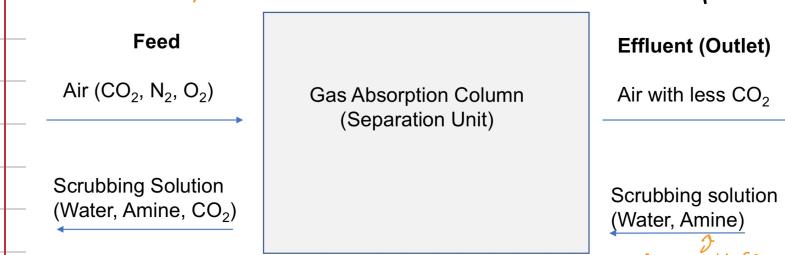
- mass fraction: $\frac{\text{mass of } i}{\text{mass of mixture}} = x_i \text{ or } y_i$ For systems reacting with products
- mol fraction: $\frac{\text{mol of } i}{\text{moles of mixture}} = \bar{x}_i \text{ or } \bar{y}_i$ for gases/vapors

• Pressure, P

- Mass Flowrate, \dot{m} ($\frac{\text{mass}}{\text{time}}$)
- Volumetric Flowrate, \dot{V} ($\frac{\text{volume}}{\text{time}}$)
- Molar Flowrate, \dot{n} ($\frac{\text{mol/s}}{\text{time}}$)
- 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 when 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 fractions 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
 - Flows (m_i, n_i, v_i) i = species
 - ↳ Total Flows (n, v) gases
 - Composition of each stream (x_i vs. y_i)
 - Energy Flows (H)
 - 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)

- 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

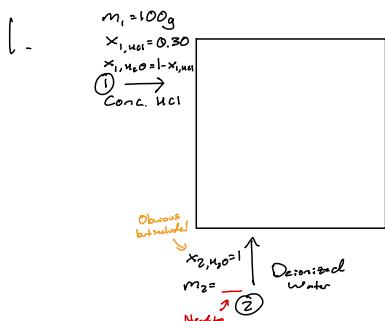
5. Write all material balances for all necessary subsystems

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

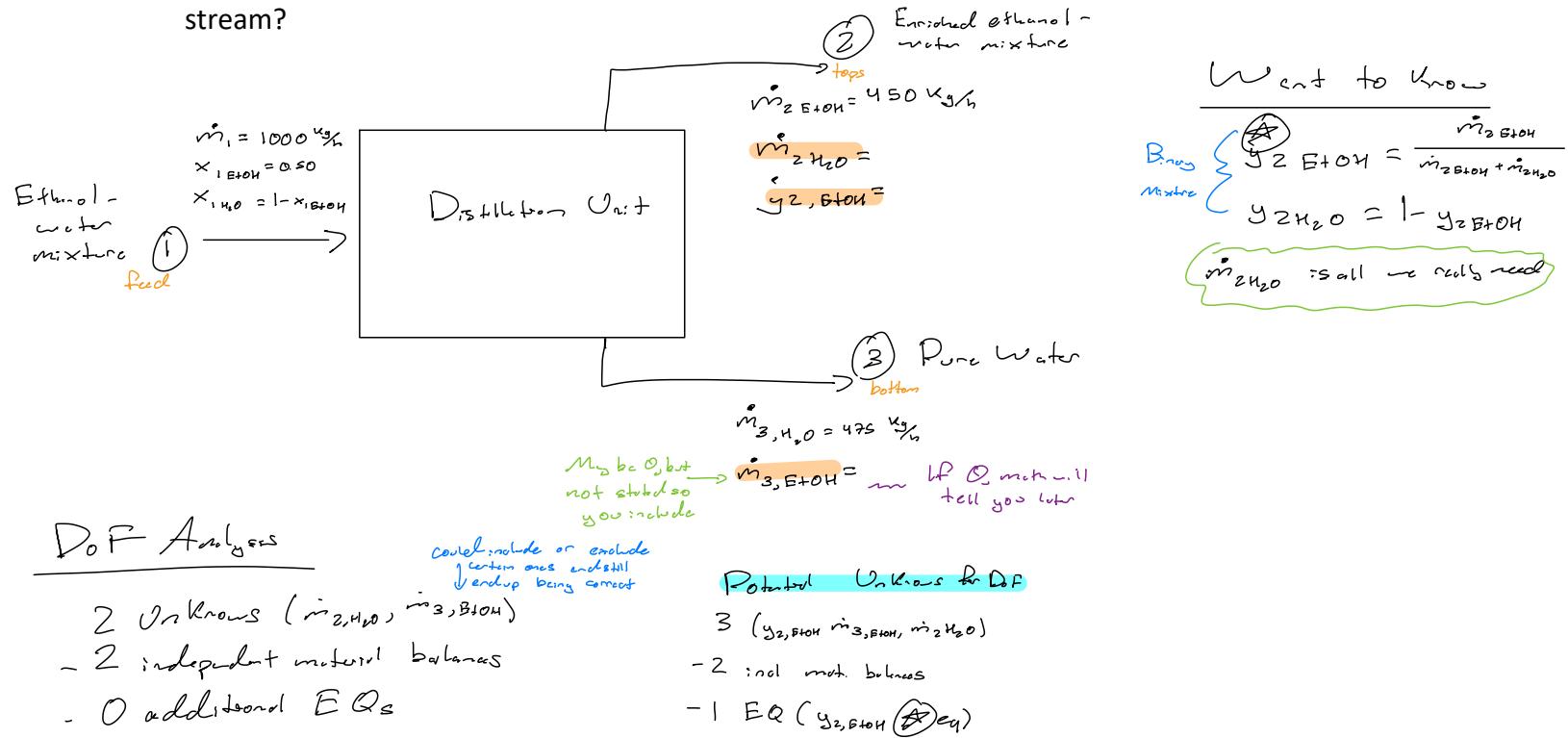
$$7. m_3 = \frac{m_1 x_{1,\text{HCl}}}{x_{1,\text{HCl}}}$$

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

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

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?



D.o.F

Y_{2,EtOH}! It's Soluble!

Material Balances

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

No physical separation/reaction occurs

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

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

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

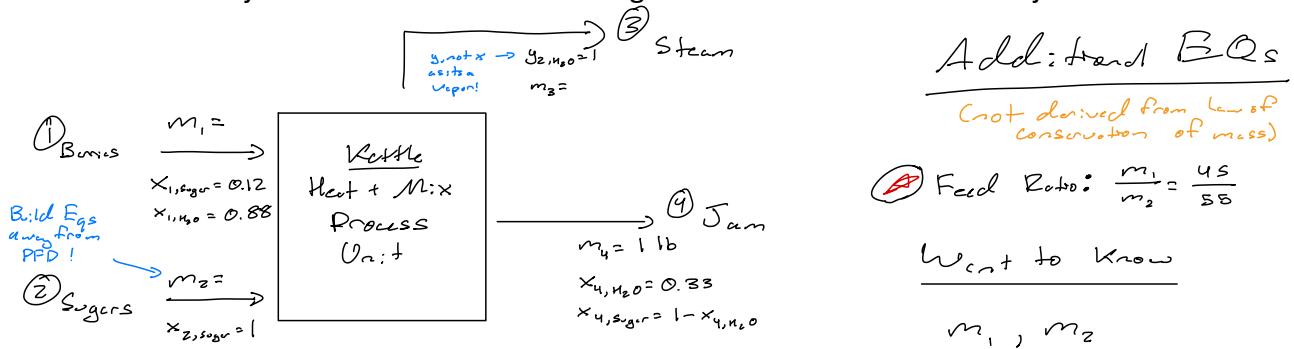
Total: $m_1 = m_{2, \text{EtOH}} + m_{2, \text{H}_2\text{O}} + m_{3, \text{EtOH}} + m_{3, \text{H}_2\text{O}}$

It's steady-state!
So there is 0 accumulation

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 ($\cancel{m_4}$)

$\cancel{m_4} \rightarrow DOF \leq 0 \checkmark$
Can solve!

Material Balances

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

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

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: $\frac{m_1}{m_2} = \frac{4S}{SS} \cancel{\frac{m_4}{m_3}}$

To highlight everything you know

How to Solve

- Solve $\cancel{m_4}$ for m_3
- Plug $\cancel{m_4}$ into sugar balance to solve for m_2
- Plug m_2 into $\cancel{m_4}$ to solve m_1

Solve $\cancel{m_4}$ Not needed on HW unless specified

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

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

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

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

(iii) ...

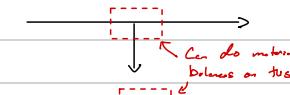
Don't need to do the algebra

Ron LOS

Multi-Unit Processes w/ Recycle and Bypass Streams

New Terminology

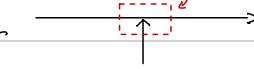
Splitting Point: Where 1 stream becomes 2 streams



Note

is a subsystem

Mixing Point: Where 2 or more streams become 1 Stream



for all pictures
and PFD here

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



Recycle vs. Bypass

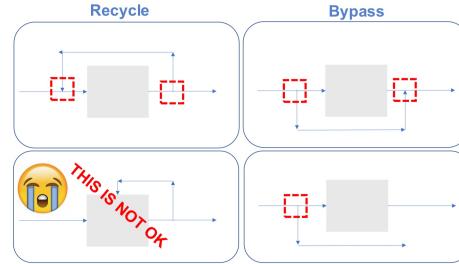
Recycle: Dilute a stream

Circulate a working fluid

Recover a catalyst

Reuse unreacted components

Bypass: Circumvent a unit operation
Overflow condition for safety

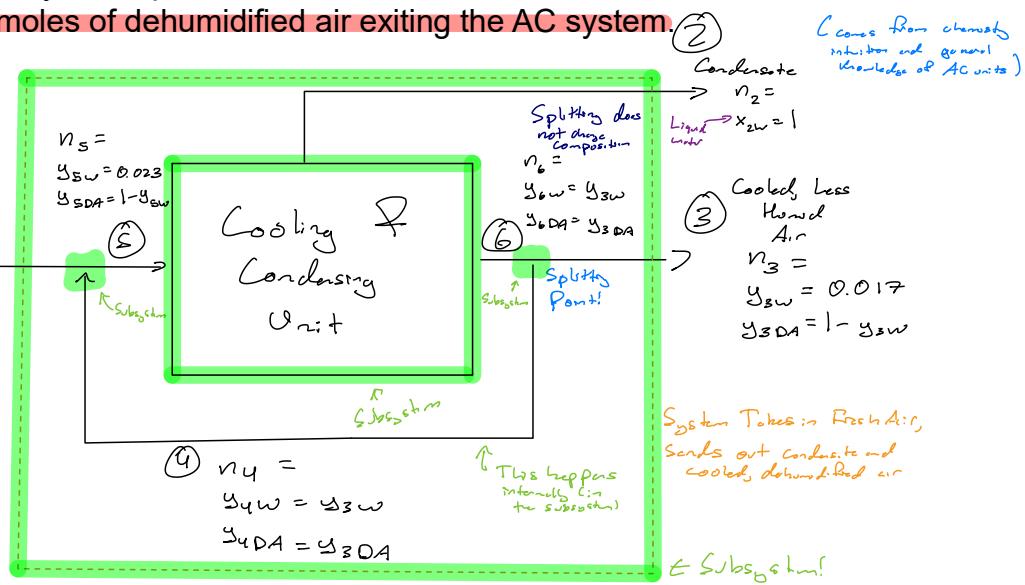


"The stream is
recycled into the
reactor" means stream
going into reactor!

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: $n_6 y_{sw} = n_4 y_{sw} + n_2 y_{sw}$
DA: $n_6 y_{da} = n_4 y_{da} + n_2 y_{da}$
 $\rightarrow n_6 = n_4 + n_2$

~ 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 substitutions with DofSI

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

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

(ii) Solve cooling/condens → 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

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

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

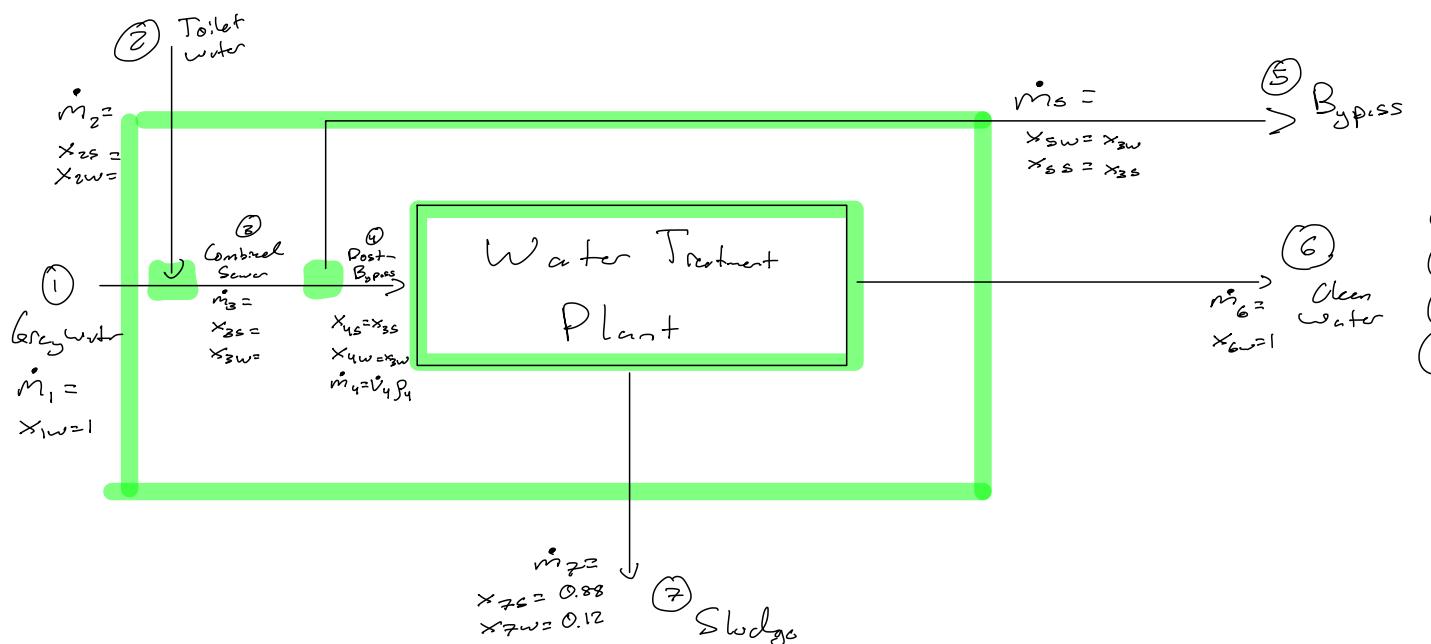
$$\text{Total: } n_6 = n_3 + n_4$$

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%

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

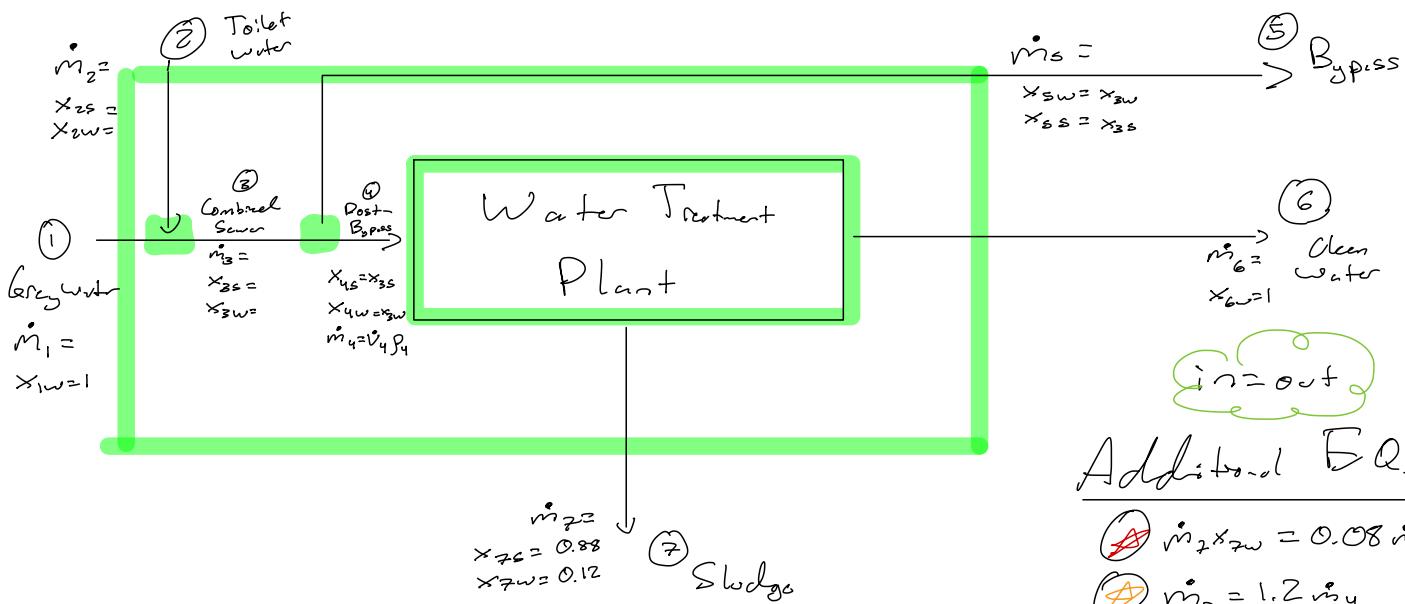
$$0.2 \dot{m}_4 = \dot{m}_5 \quad \text{This is also valid}$$

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

- 4 unknowns (m_6, m_7, x_{3w}, x_{5s})
 - 2 indep. material balances (b/c 2 species)
 - 2 add. transl. Eqs (~~(1)~~, ~~(2)~~)
- 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 (~~(1)~~, ~~(2)~~)

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

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

$$H_2O: m_3 x_{3w} = m_4 x_{3w} + m_5 x_{3w}$$

$$Total: m_3 = m_4 + m_5$$

This is already

Mixing Point

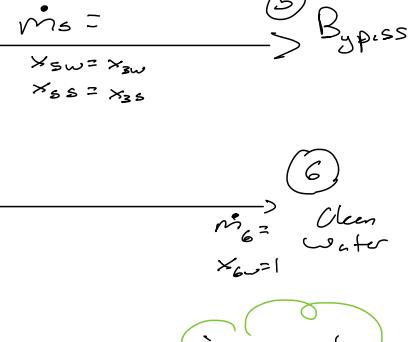
- 7 unknowns ($m_1, m_2, m_3, x_{2s}, x_{3w}, x_{5s}, x_{5w}$)
 - 2 indep. balances (2 species) \leftarrow composition chose @ mixing pt.
 - 2 additional Eqs (~~(1)~~, ~~(2)~~)
- 3 DoF unsolvable

Overall

- 9 unknowns ($m_1, m_2, m_3, m_4, m_5, m_6, x_{2s}, x_{3w}, x_{5s}, x_{5w}$)
 - 2 indep. balances (2 species)
 - 2 additional Eqs (~~(1)~~, ~~(2)~~)
- 5 DoF Unsolvable!

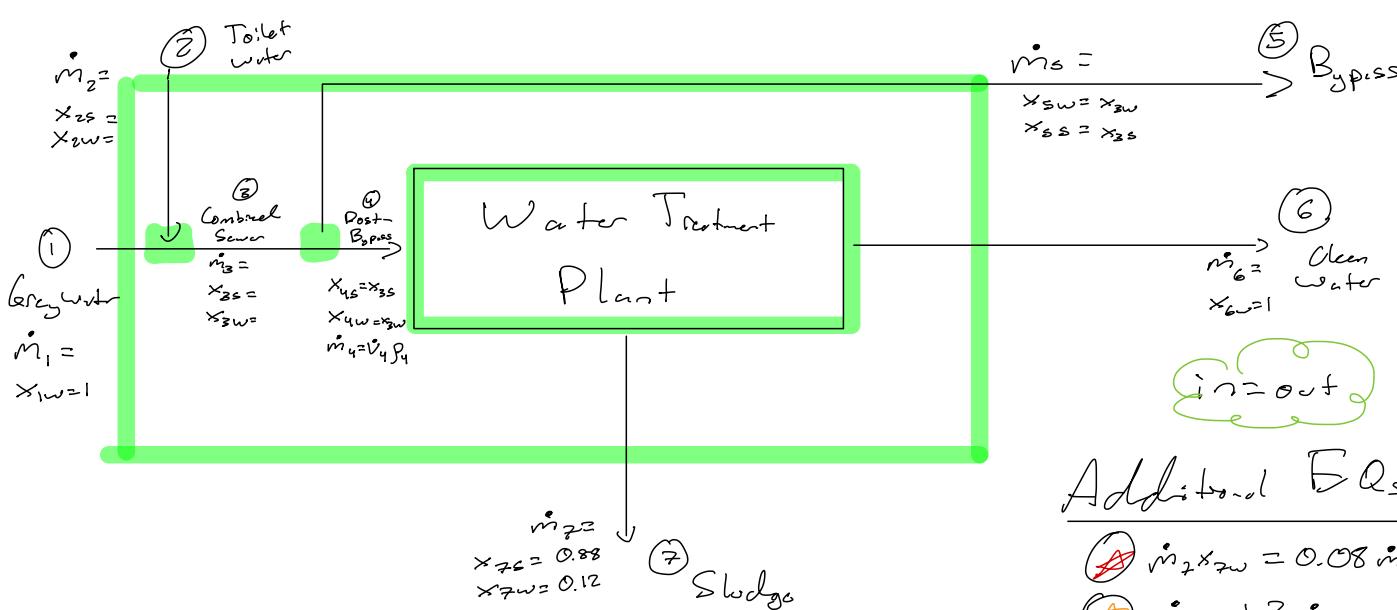
Plant

- (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)~~ $x_{3s} + x_{2w} = 1$ \leftarrow Breakdown into PEP into same time
 - ~~(4)~~ $x_{2s} + x_{2w} = 1$
 - ~~(5)~~ $x_{5w} + x_{5s} = 1$
- DoF of mass flows



Material Balances

Treatment

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

in-out

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

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

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

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

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

Splitting Point

See SS on Right

Additional Eqs

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

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

Plan: treatment \rightarrow splitting

Mat Balance - Treatment

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

norms

$$x_{4w} + x_{4s} = 1$$

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

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

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

$$0.08 \dot{m}_4 x_{4w} = \dot{m}_7 x_{7w}$$

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

How to Solve

$$1. \text{ calculate } \dot{m}_4 = \dot{v}_4 \rho$$

$$2. \text{ solve (1) for } \dot{m}_7 \text{ and plug into } S - \text{solve } x_{4s}$$

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

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

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

Splitting point

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

$$6. \text{ calculate } \dot{m}_5 \text{ from } \cancel{\dot{m}_2}$$

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

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

Solution Steps

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

$$(2) \text{ Solve (1) for } \dot{m}_7 \text{ and plug into } S \text{ balance to solve for } x_{4s}$$

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

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

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

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?

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

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

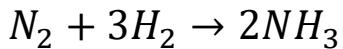
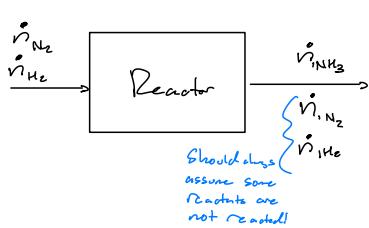
If prop side rxn occurred, what's the max mols that could be produced

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 "

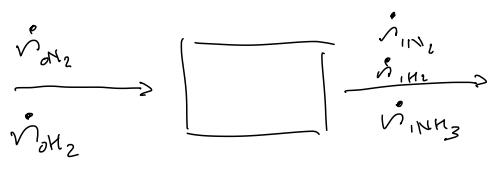
$\Rightarrow N_2$ is the limiting reactant

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

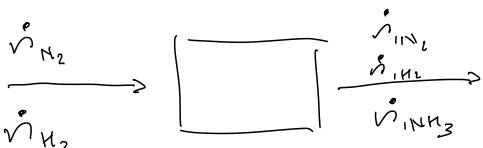


$$f_i = \frac{\dot{v}_{i, \text{reacted}}}{\dot{v}_{i, \text{fed}}}$$

$i = \text{species}$

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

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"

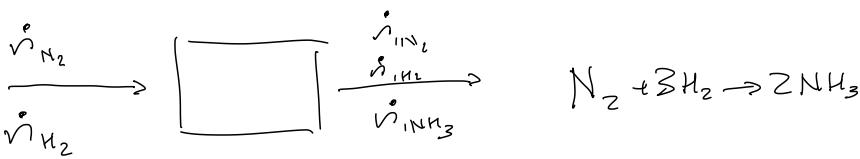
$$\text{Out} = \text{in} + \text{gen/consum}$$

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

Extent of Reaction:

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

γ_{ij} = stoich. coef. 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 !!

$A \rightarrow 3B$

$\neq 3$

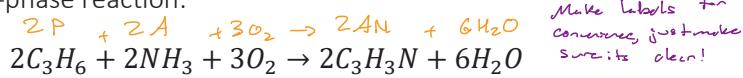
Moles are not conserved!

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

Unit 5: Material Balances on Reactive Systems

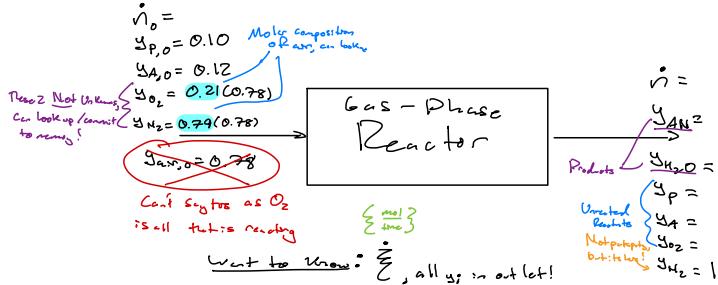
Example 1: Production of acrylonitrile

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 10 mol% propylene (C_3H_6), 12 mol% ammonia (NH_3) and 78 mol% 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

$$f_p = \frac{\text{mol P reacted}}{\text{mol P fed}} = \frac{n_{p,0} - n_{p,f}}{n_{p,0}} = 0.30$$

Alternate Approach

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

DoF Analysis

Reactn: Assume $n_0 = 100 \text{ mol}$
 6 \neq Unknowns (n_{O_2} 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 ($\frac{2}{3}$) \leftarrow Extent of Reaction is added to DoF!

ΔX DoF \Rightarrow Assume Basis to bring DoF to 0.

Material Balances

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

in-out-gain-loss = accumulation

$$G: \dot{n}_P = \dot{n}_{P,0} + \dot{n}_P - \dot{n}_P$$

$$P: \dot{n}_{H_2O} = \dot{n}_{H_2O,0} + (-2) \frac{2}{3}$$

$$A: \dot{n}_{NH_3} = \dot{n}_{NH_3,0} + (-2) \frac{2}{3}$$

$$N_2: \dot{n}_{N_2} = \dot{n}_{N_2,0} + 0 \frac{2}{3}$$

No Reactive Species (Inert)
Results in: in = out

$$O_2: \dot{n}_{O_2} = 0 + 6 \frac{2}{3}$$

Not Inert $\frac{2}{3}$

$$AN: \dot{n}_{AN} = 0 + 2 \frac{2}{3}$$

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

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

How to Solve

(i) Solve f_p for n_{H_2O} \rightarrow Plug into P balance \rightarrow solve $\frac{2}{3}$

(ii) Solve A balance for n_{AN} ($\frac{\text{moles } A}{6}$)

(iii) Solve N_2 balance for n_{N_2}

(iv) Solve H_2O balance for n_{H_2O}

(v) Solve AN for n_{AN}

(vi) Solve O_2 for n_{O_2}

(vii) Calculate n_{H_2O} from f_p

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

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

Given generic definition in terms of what you solved for

Addl. Reactn Eqs

$$f_p = \frac{\text{mol P reacted}}{\text{mol P fed}} = \frac{n_{p,0} - n_{p,f}}{n_{p,0}} = 0.30$$

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

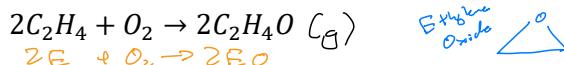
For reactive systems that include a recycle stream...

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:

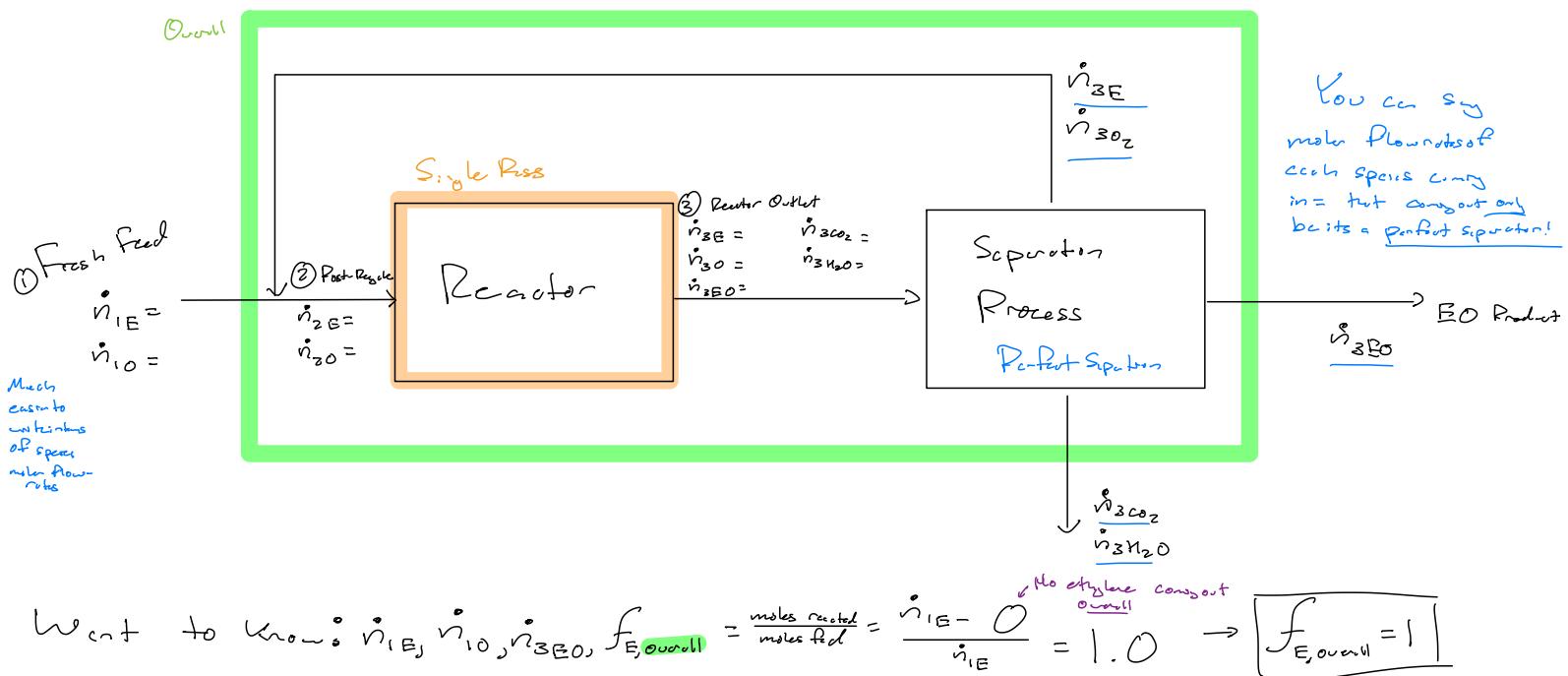


An undesired competing reaction is the combustion of ethylene:



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

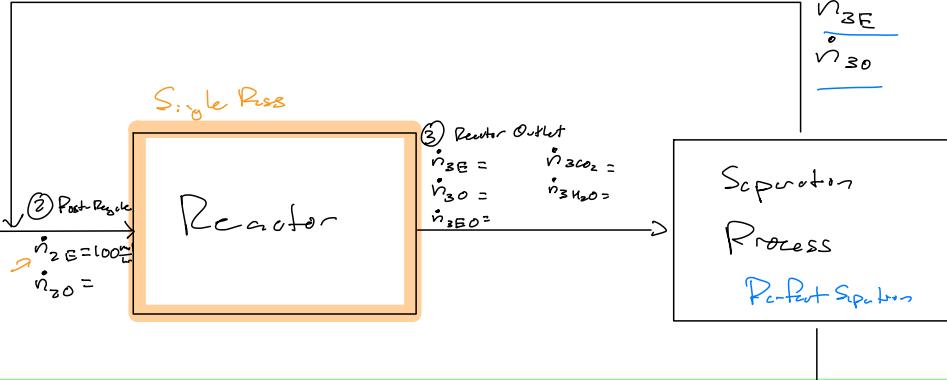
$$\cancel{\textcircled{1}} \quad \dot{n}_{2E} = 3\dot{n}_{2O} \quad \cancel{\textcircled{2}} \quad \frac{\dot{n}_{2E}}{\dot{n}_{2O}} = 3$$

$$f_{E, \text{single}} = \frac{\dot{n}_{2E} - \dot{n}_{3E}}{\dot{n}_{2E}} = 0.20 \quad \text{Due to overall conversion}$$

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

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

Assume as basis: $\dot{n}_{2E} = 100 \frac{\text{mol E}}{\text{hr}}$

67 Unknowns ($\dot{n}_{1E}, \dot{n}_{1O}, \dot{n}_{2E}, \dot{n}_{3E}, \dot{n}_{3O}, \dot{n}_{3EO}, \dot{n}_{3CO_2}, \dot{n}_{3H_2O}$)

- 5 Indep Mat Balances (5 species)

- 3 Additional Eqs ($\textcircled{1}$, $f_{E,\text{overall}}$, $\textcircled{2}$)

+ 2 Indep. Cheml Reacs ($\dot{\Sigma}_1, \dot{\Sigma}_2$)

0 DOF \Downarrow

Mixing

No rxns take place
in mixing part

5 Unknowns ($\dot{n}_{1E}, \dot{n}_{1O}, \dot{n}_{2E}, \dot{n}_{3E}, \dot{n}_{3O}$)

- 2 Indep Mat Balances (2 species E & O)

- 2 Additional Eqs ($\textcircled{3}$, $f_{E,\text{mix}}$) \leftarrow But useful as
0 Cheml Reacs (mixing part)

1 DOF \Downarrow Constitute $\textcircled{3}$ as + mols EO

Overall

Extent of reaction is tied to
Reactant conversion

5 Unknowns ($\dot{n}_{1E}, \dot{n}_{1O}, \dot{n}_{2E}, \dot{n}_{3E}, \dot{n}_{3O}$)

- 5 Indep Material Balances (5 species crossing the boundary)

- 0 Additional Eqs (None or relevant \Downarrow)

+ 2 Chemical Reactions ($\dot{\Sigma}_1, \text{overall}, \dot{\Sigma}_2, \text{overall}$) \leftarrow $\dot{\Sigma}_1, \dot{\Sigma}_2$ \neq $\dot{\Sigma}_{\text{overall}}$

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 = $\dot{n}_i + (\text{gen/consum})$
 $\Rightarrow \dot{n}_i = \dot{n}_{in} + \sum \dot{n}_j \dot{\Sigma}_j$

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

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

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

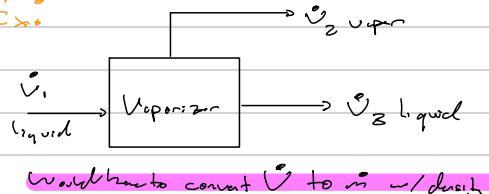
- Go to NIST chemical webbook
- Perry's chemical handbook
- Appendix B (in textbook)
- Wolfram Alpha

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/ 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_{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, see 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

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

T_c critical state temp

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

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

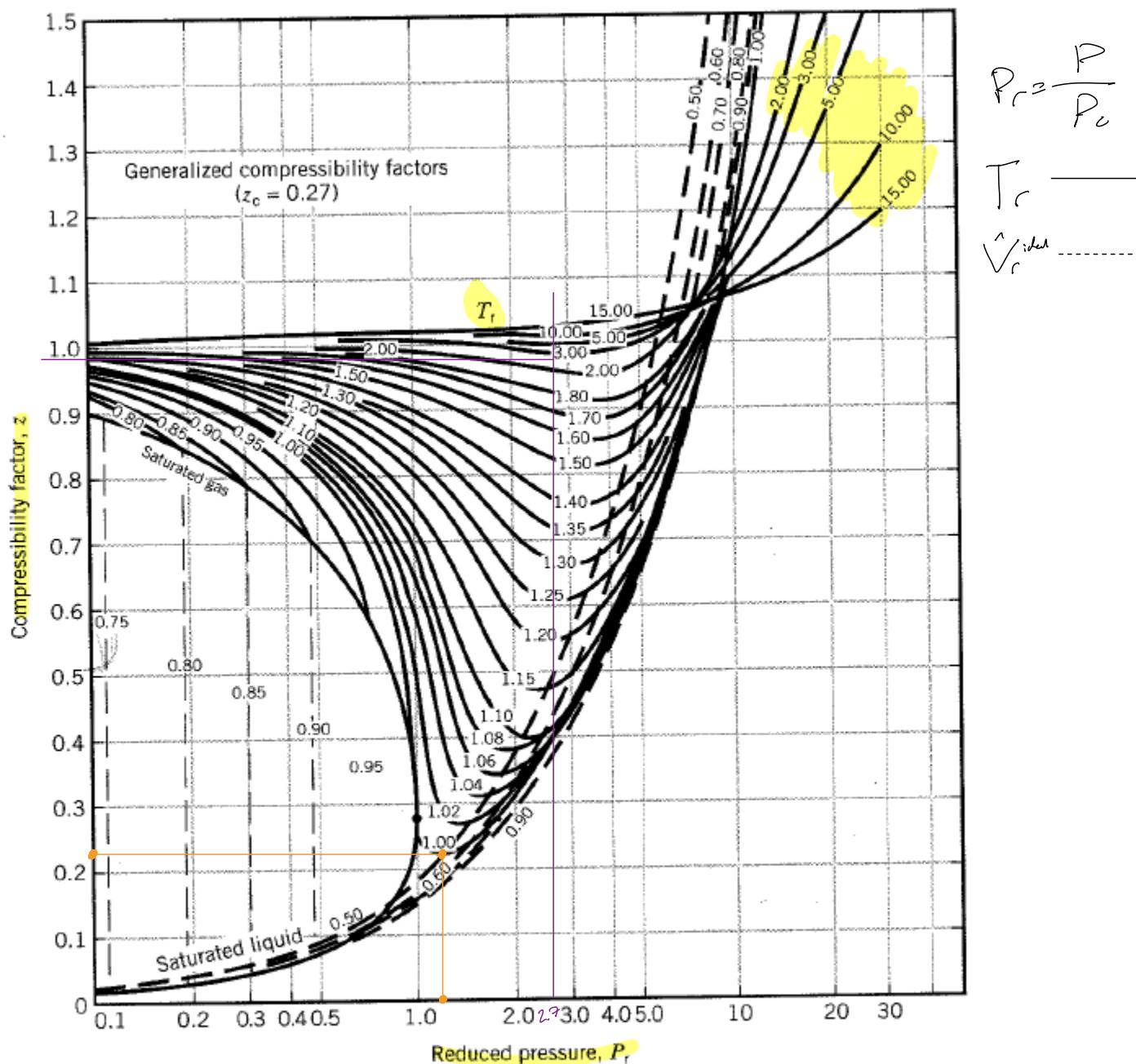


Figure 5.4-1 (Reprinted with permission from *Chemical Process Principles Charts*, 2nd Edition, by O. A. Hougen, K. M. Watson, and R. A. Ragatz, John Wiley & Sons, New York, 1960.)

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

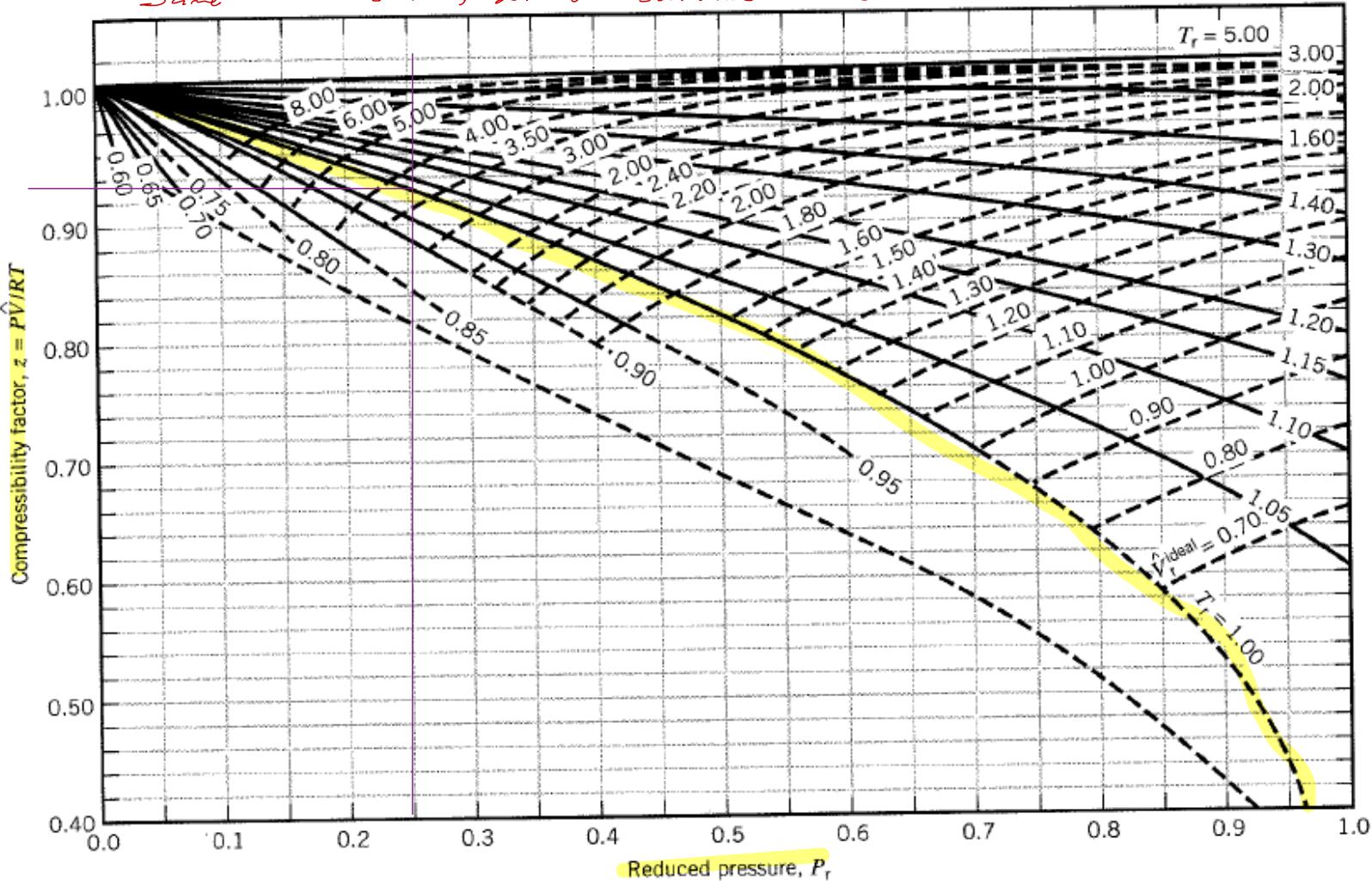


Figure 5.4-2 Generalized compressibility chart, low pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 175. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

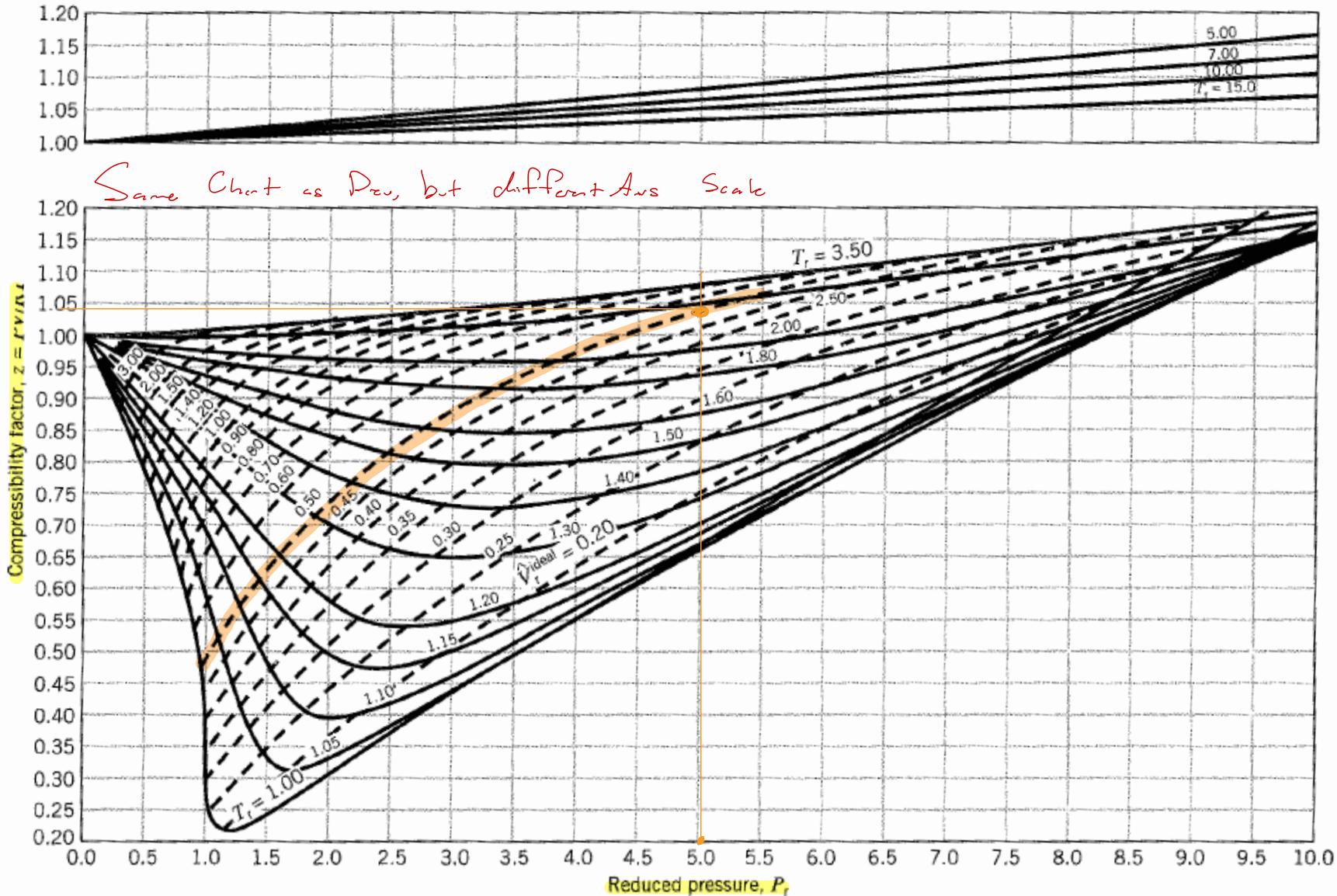


Figure 5.4-3 Generalized compressibility chart, medium pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 176. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

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

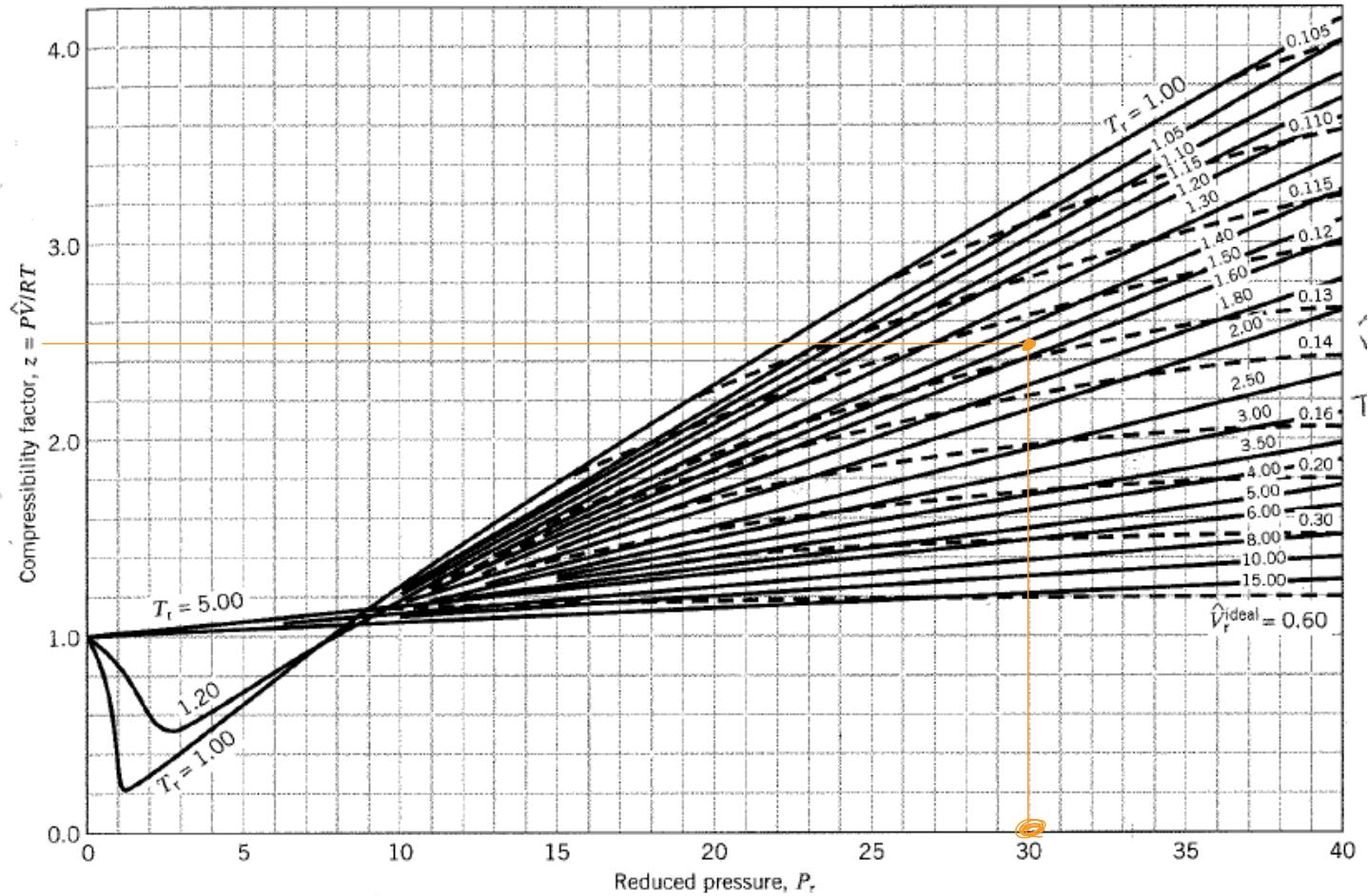
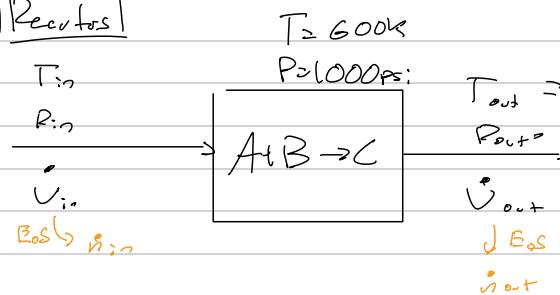


Figure 5.4-4 Generalized compressibility chart, high pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 177. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

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



$T_{in} + \Delta T$

$P_{in} = P_{out}$

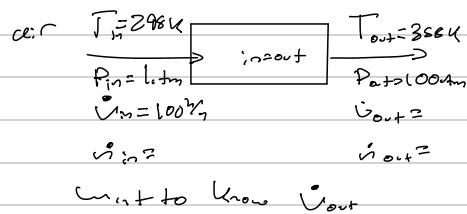
$V_{in} = V_{out}$

J_{EoS}
 Q_{in}

Fully isolated PFD with ΔT

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

Compressor



Mol Balances: $n_{in} = n_{out}$

Apply ∇ test to determine

EoS for inlet & outlet

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

: If $\nabla > 8 \frac{\text{L}}{\text{mol}}$ compressible \Rightarrow (ideal)

: If $\nabla > 20 \frac{\text{L}}{\text{mol}}$ others \Rightarrow (ideal)

$$\nabla = \frac{(10.08 \frac{\text{L}}{\text{atm}})(358\text{K})}{100 \text{ atm}}$$

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

Not ideal!

How to Solve

(i) Use ideal G.s to calculate n_i , $P_i V_i = n_i RT_i$

(ii) Use total Balance to calculate n_2 as $n_1 = n_2$ 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

$$T_c = \sum y_i T_{ci}$$

$$P_c = \sum y_i P_{ci}$$

Kay's rule for
mixtures (ideal)

Calculate T_c' for air

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

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

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

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

Table B.1

Calculate P_r' for air

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

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

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

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

Molar Balance

Only written in either mass or moles!!

Calculate Reduced Properties, T_r and P_r

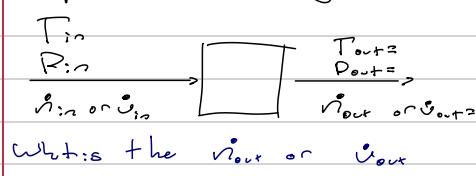
$$T_r = \frac{T_2}{T_c'} = \frac{358\text{K}}{132\text{K}} = 2.7$$

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

$Z = 0.95$ 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

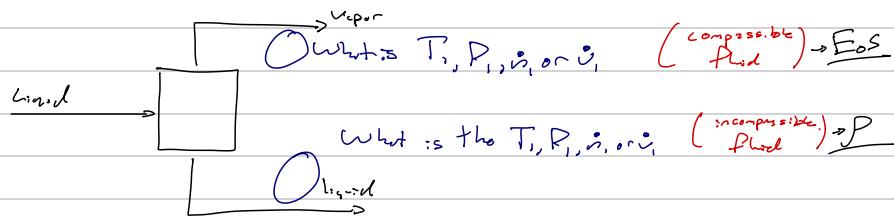
Additional Equations

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

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

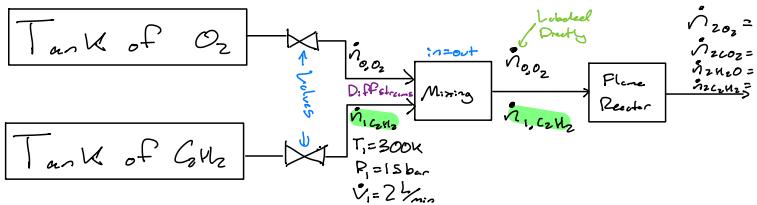
$$P \bar{V} = zRT \quad V \leftarrow \text{constant} \quad \text{volume}$$

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: !

$$\text{EoS: } V = \frac{RT}{P} = \frac{(0.082 \frac{\text{L}_{\text{atm}}}{\text{mol}\cdot\text{K}})(300\text{K})}{1\text{ atm}} = 1.6 < 2.0$$

1 atm ≈ 1 bar

Can't 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 charts

$$T_r = \frac{T_1}{T_c} \quad P_r = \frac{P_1}{P_c} \Rightarrow \left. \begin{array}{l} T_r = \frac{300\text{K}}{309.5\text{K}} \approx 1 \\ P_r = \frac{1\text{ atm}}{61.6\text{ atm}} = 0.25 \end{array} \right\} z \approx 0.93$$

$T_c = 309.5\text{K}$

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

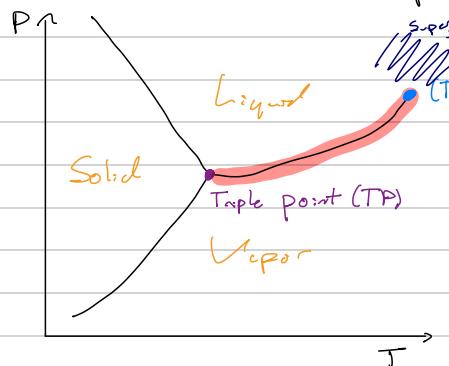
Unit 5



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

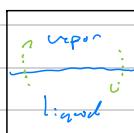
↳ steam tables (For given T , state, what is P ?)

↳ 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



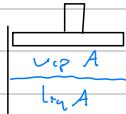
Rate of condensation = Rate of evaporation

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

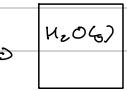
phase → 1 molecule of A must condense

What happens if we increase P ?

Concen A, increase fraction of A in the liquid phase

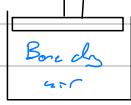
What happens if we decrease T ?

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

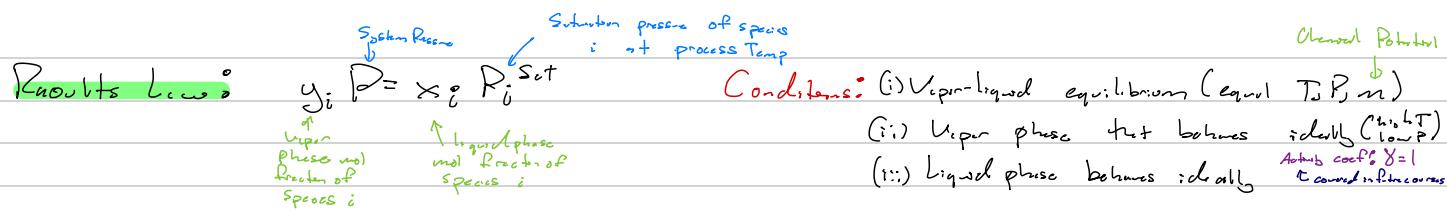
$$P_i = y_i P_{tot}$$

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

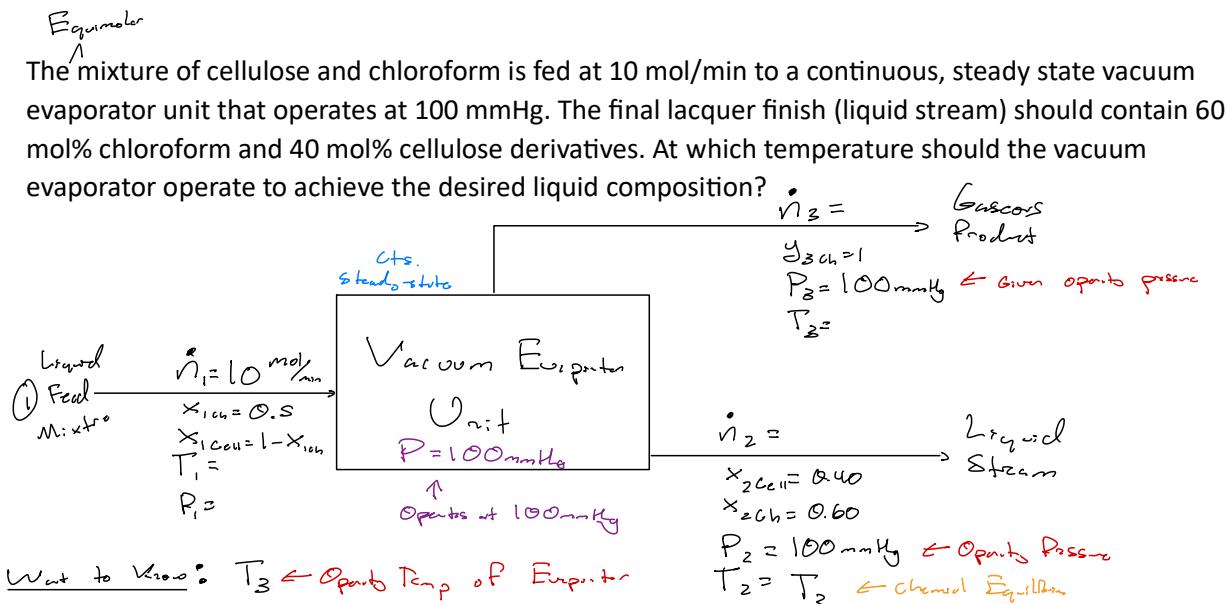
Bubble Point Temperature (T_{bp}): temperature at which first bubble forms when vaporizing a saturated liquid



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

$$\begin{aligned} \text{Chl: } n_1 x_{1,CH} &= n_3 x_{3,CH} \\ \text{Cell: } n_1 x_{1,Cou} &= n_2 x_{2,Cou} \\ \text{Total: } n_1 &= n_2 + n_3 \end{aligned}$$

For non-reactive systems moles are conserved

How to Solve (n_i unknowns)

- Solve Cell for n_2
- Solve Total for n_3

DOF Analysis (Solving for all n_i & T)

4 Unknowns ($n_2, n_3, T_3, P_2^{\text{sat}}$)

+ 0 General Relations

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

- 2 Additional EQs (O, O)

DOF R

How to Solve (Operating Temperature T_2)

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

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

(iii) Solve ④ for P_2^{sat} (Raoult's Law)

(iv) Use ⑤ to calculate T_2 (Antoine Eqn.)

↳ Get A, B, C from Table

Most likely

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

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^a

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

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.

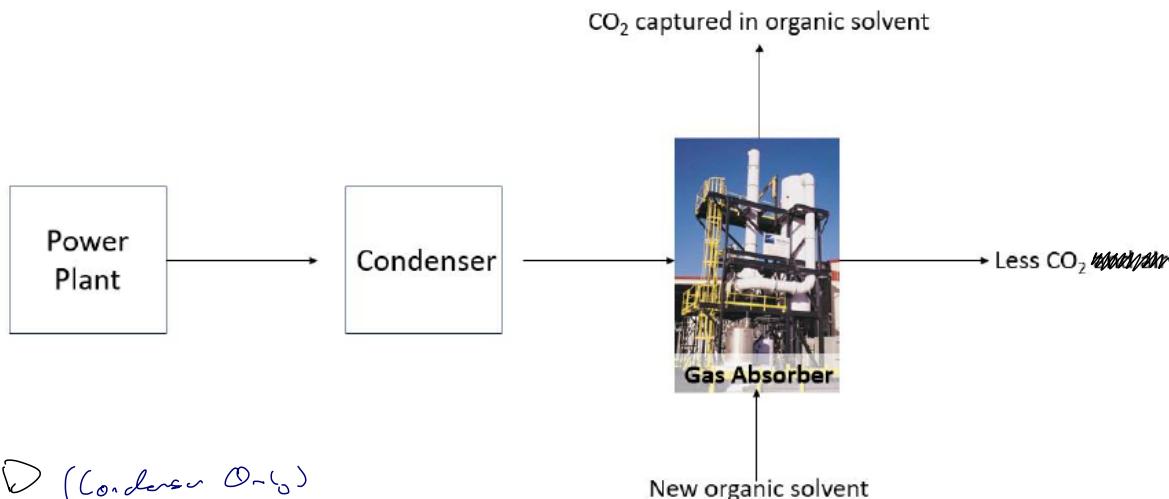
Can also find
values on NIST
Chemical Webbook

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

^aAdapted 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 CO₂ and water vapor exits a power plant at 100 mol/h, 150°C and 5 atm. The vapor phase mole fraction of the CO₂ is 0.15 (375 times the amount existing in the atmosphere). Gas absorption can be used to capture the waste CO₂ 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 O₂)

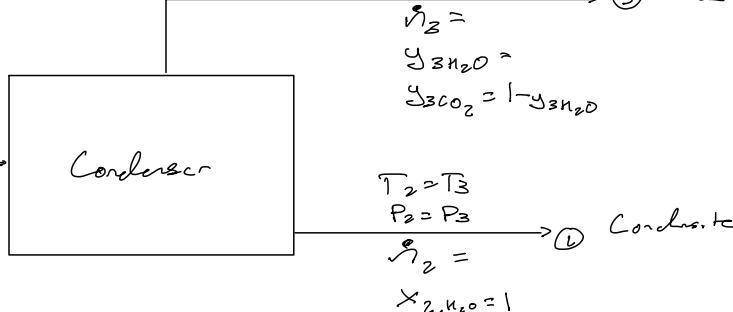
$$\text{Flue Gas} \quad \textcircled{1} \quad i_1 = 100 \text{ mol/hr}$$

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

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

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

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



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 ($\frac{\text{Rate}_{\text{H}_2\text{O}}}{\text{Rate}_{\text{CO}_2}} = 1$) for cond

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

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

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

$$\textcircled{4} \text{ Antoine Eq: } \log_{10} P_{\text{H}_2\text{O}}^{\text{sat}} = A - \frac{B}{T_3 + C}$$

How to Solve

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

$$EA = ?$$

$$B = ?$$

$$C = ?$$

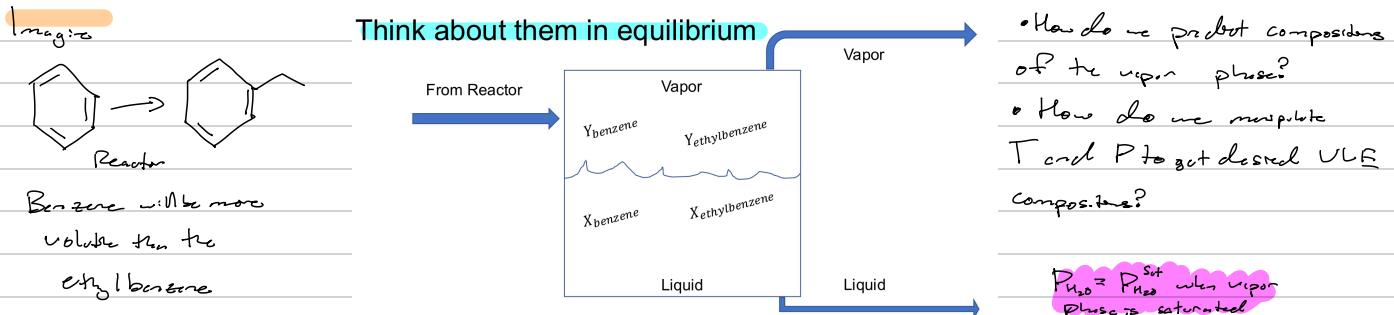
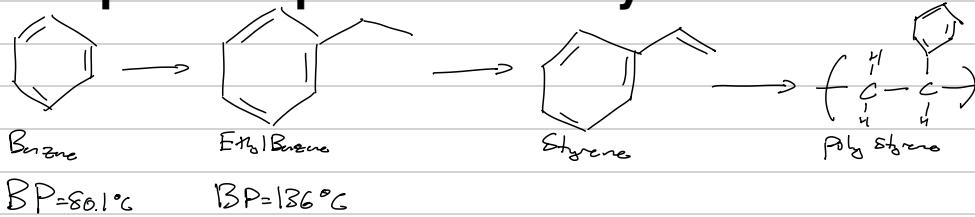
- (ii) Calculate $y_{3, \text{H}_2\text{O}}$ from Raoult's Law $\textcircled{3}$

- (iii) Use CO₂ Balance to calculate i_2

- (iv) Use total balance to find i_3

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

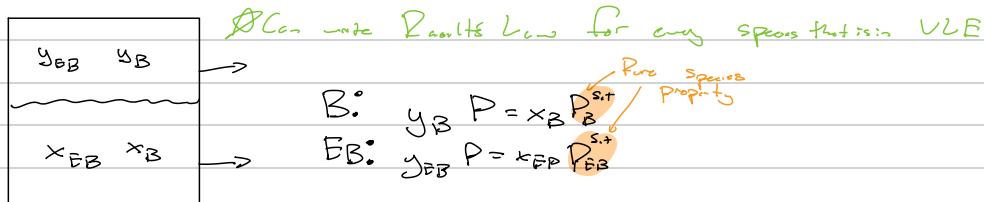
Multiple Component VLE Systems



Vocab / Jargon / Notes

- For single species VLE systems, we usually talk about the boiling temperature (T_{boil}).
 - \hookrightarrow Table B.1, $T_{\text{boil},i} = \text{_____} @ P = 1 \text{ atm}$ This is the normal boiling point
 - Boiling occurs when $P_{\text{vap}} = P_{\text{atm}}$
 - Vapor pressure is atm
- Evaporation is a surface phenomenon
- Bubble point is the temperature at which the first bubble forms when heating a liquid
 - \hookrightarrow Denoted T_{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_{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:

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

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

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

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

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

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

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

This temperature is T_{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 $\sum x_i > 1$

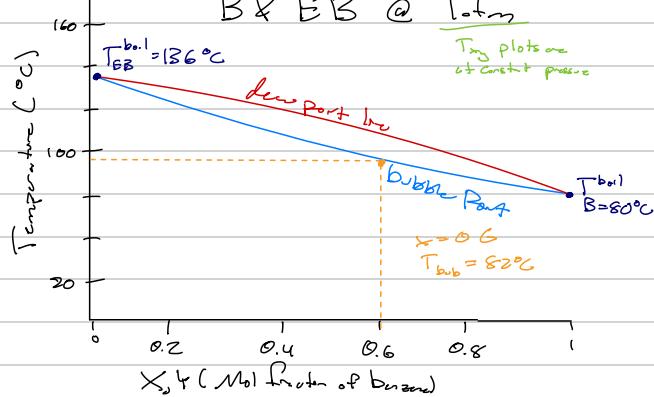
$$1 = \frac{y_{BB} P}{P_{BB}^{\text{sat}}} + \frac{y_B P}{P_B^{\text{sat}}}$$

Dew point equations
for binary mixture

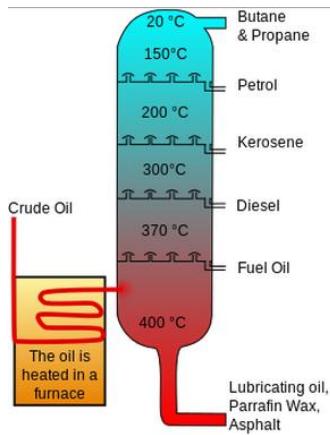
Txy Diagrams

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:

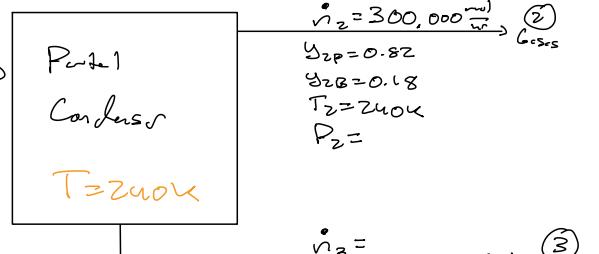
$$\log_{10}(P^{sat}) = A - \frac{B}{T + C}$$

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: $P_{\text{condenser}} = P_2 = P_3$

Antoine Constants

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

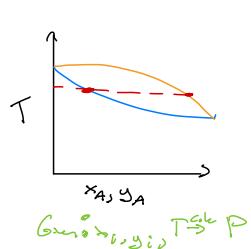
$$\dot{N}_2 = 300,000 \text{ molcs/hr} \rightarrow \text{gas}$$
 $y_{2P} = 0.82$
 $y_{2B} = 0.18$
 $T_2 = 240\text{K}$
 $P_2 =$

$$\dot{N}_3 = \text{?} \rightarrow \text{liquid}$$
 $x_{3P} = 0.43$
 $x_{2B} = 0.57$
 $T_3 = 240\text{K}$
 $P_3 = P_2$

From Antoine
 With VLE, you have
 $T_{\text{Liq}} > T_{\text{bub}} > T_{\text{condenser}}$

- no chemical rxns
- VLE
- multiple condensate species

} Can use bubble point and dewpt Eqs



$$P_2 = x_B P_B^{\text{sat}} + x_P P_P^{\text{sat}} \quad \text{Bubble Point Eq}$$

How to Solve

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

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

$$\text{Butane} \quad B = 1149.36$$

$$\text{Propane} \quad A = 4.53678$$

$$B = 1175.581$$

$$C = -2.071$$

$$C = 24.906$$

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

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

(ii) Use bubble point equation to solve for P_L

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

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

If you are given $x_i, y_j, P \rightarrow$ calculate T

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

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

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

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

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

Unit 6



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 ($\Delta E_p = mgz$)

(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

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

For open systems

dot just means energy/time

Energy Exchange

(i) **Heat**: Energy that flows in or out of a system due to change in temperature (ΔT)

Q : when heat is added to the system

$-Q$: when heat is removed from the system

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

W : when work is being done by system on surroundings \leftarrow gas expanding on cylinder

$-W$: when work is done by surroundings on the system

Note distinction from ECHB228

First Law of Thermodynamics

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

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

Freeze Process isolated here

$$W = W_{\text{shaft}} + W_{\text{flow}}$$

↑ Fluid loss to push fluid in front of ↑ Fluid loss to push fluid out of the way

↑ Pushing fluid pushing on each other

$$W_{\text{flow}} = \Delta(PV)$$

↑ This is just change in enthalpy

$$\Delta U + \Delta E_k + \Delta E_p = Q - W_{\text{shaft}} - \Delta(PV) \Rightarrow \boxed{\Delta U + \Delta(PV) + \Delta E_k + \Delta E_p = Q - W_{\text{shaft}}}$$

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 for this class as we like the steady state

Units

• H for a closed system \leftarrow $\frac{kg}{mole}$

(i) H \leftarrow $\frac{kg}{mole}$ = \bar{H} or \hat{H}

Remark: Specific properties we say property that is on a process

(ii) H \leftarrow $\frac{kg}{mole}$ or $H \leftarrow \frac{kg}{mol}$

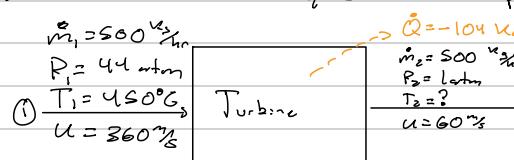
or per mol basis

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

Always keep track of your units

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

Basic ECHB228-examples



$$Q = -104 \text{ kJ/kg-hr}$$

Law of conservation of mass still applies

$m_1 = 500 \text{ kg/hr}$

$P_1 = 1 \text{ atm}$

$T_1 = ?$

$u_1 = 60 \text{ kJ/kg}$

New governing equation will be 1st Law of Thermodynamics

Start with Governing equation and simplify

$$(i) 1^{\text{st}} \text{ Law: } \Delta H + \Delta E_k + \Delta E_p = Q - W$$

↑ Negligible pressure change

↑ Large change in enthalpy

Both given

Want to find 1st Law using process variables from the PFD

$$\Delta H + \Delta E_k = Q - W$$

$$\left\{ \begin{array}{l} \Delta E_k = \frac{1}{2} m (u_2^2 - u_1^2) \\ \Delta H = \frac{kg}{hr} = m_2 \bar{H}_2 - m_1 \bar{H}_1 = m (\bar{H}_2 - \bar{H}_1) \end{array} \right.$$

Steam Turbine

Most of the time \bar{H}

for phase change, channel

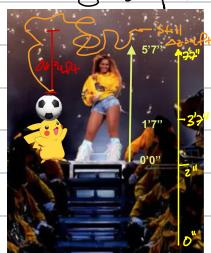
reactions will be much

greater than ΔE_k or ΔE_p

Want to know: $T_2 \leftarrow ?$

State Properties

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



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

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

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

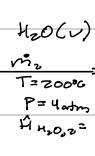
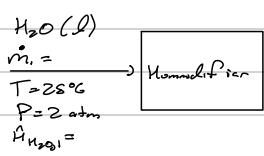
$$\text{Path 3)} \Delta z = 7'7'' - 3'7'' = 4 \text{ ft!}$$

Reference state is arbitrary

Reference states must be consistent within a single Δz calc!

Enthalpy

Example: Homoclinic / Steam Generator



$$\Delta T$$

$$\Delta P$$

$$\Delta \text{phase}$$

\hat{H} is defined by 3 factors:

(i) Temperature

(ii) Pressure

(iii) Phase

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

(iii) Can choose any T, P, 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, phase) so we can calculate \hat{H} associated with each hypothetical step



$1. \Delta T @ \text{const phase } P$

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

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

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

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

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

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

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

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

Want to know

$$\begin{aligned} \Delta \hat{H}_{\text{process}} &= \hat{H}_{\text{out, } E + OH} - \hat{H}_{\text{in, } E + OH} \\ &= [\hat{H}_{\text{out, } E + OH} - \hat{H}_{\text{ref}}] - [\hat{H}_{\text{in, } E + OH} - \hat{H}_{\text{ref}}] \end{aligned}$$

\rightarrow Assume inlet conditions as ref state

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

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

ΔT 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.

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

Δ 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_{200} (Latm)

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

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

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

For ideal gases: $C_P = C_V + R$

For liquids/solids: $C_P \approx C_V$

ΔP at constant T and phase (isothermal expansion or compression)

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

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

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

$P \neq \text{constant}$

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

γ 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 1st 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 \dot{Q} mostly
 \dot{W}_s , ΔE_p , and $\Delta E_k \approx 0$ in this course usually $\Delta E_k \approx 0$ usually $\Delta E_p \approx 0$
adibatic means $\dot{Q} = 0$
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)?

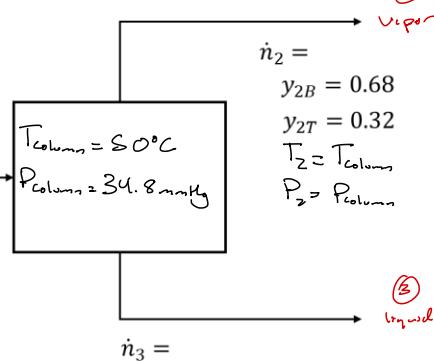
$$\dot{H} \left(\frac{\text{kJ}}{\text{min}} \right) = \dot{n} \left(\frac{\text{mol}}{\text{min}} \right) \dot{h} \left(\frac{\text{kJ}}{\text{mol}} \right)$$

1. Draw and fully label a PFD

Temperature & pressure matter for VLE and energy balances!

DOF Analysis
not required
post-column

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



Pay attention
to phases & temp
and pressures

Want to know
 \dot{Q} $\left(\frac{\text{kJ}}{\text{min}} \right)$

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

Material Balances

$$\begin{aligned}B: \dot{n}_1 x_{1B} &= \dot{n}_2 y_{2B} + \dot{n}_3 x_{3B} \\ T: \dot{n}_1 x_{1T} &= \dot{n}_2 y_{2T} + \dot{n}_3 x_{3T} \\ \text{Total: } \dot{n}_1 &= \dot{n}_2 + \dot{n}_3\end{aligned}$$

How to Solve

- (1) Rearrange Total to plug $\dot{n}_1 = \dot{n}_2 + \dot{n}_3$ into T_1 sole for \dot{n}_3
- (2) Solve Total balance for \dot{n}_2

4. Choose a reflux state (per specie)
Choose L (at -10°C , 760 mmHg) $A_1 = 0$
usually the most common
B (at -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 $A_{1T}, A_{1B} = 0$

3. Write First Law

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

no ΔB or ΔU
no moving parts

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

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

$$\begin{aligned}&= \sum \dot{n}_i \dot{h}_i - \sum \dot{n}_i \dot{h}_i \\ &= \sum \dot{n}_i \dot{h}_i - \sum \dot{n}_i \dot{h}_i \\ &= \sum \dot{n}_i x_i \dot{h}_i - \sum \dot{n}_i x_i \dot{h}_i\end{aligned}$$

Final outlet 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

Stream 2 Stream 3

$\dot{n}_3 x_{3B}$ or $\dot{n}_3 x_{3T}$ just
within 1 b-line

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

$T(l, -10^\circ C, 760 \text{ mmHg}) * \text{ref state } \hat{H}_{1,T=0}$

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

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

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

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

On Table B2 Write the equations for each thermal step

$$C = \text{solid} \quad l = \text{liquid} \quad g = \text{vapour}$$

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

$$\hat{H}_b = \hat{H}_{\text{vap}} = 34.8 \frac{\text{kJ}}{\text{mol}} \quad \Delta P \text{ const } T \& P$$

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

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

$$\text{Defn } C_p \text{ expressions}$$

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

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

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

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

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: $B(l, 50^\circ C, 34.8 \text{ mmHg})$]

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

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

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

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

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

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

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

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

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

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

$B(l, -10^\circ C, 760 \text{ mmHg}) \quad \Delta T, \text{const phase } P$

$\hat{H}_g B(l, T_{\text{boil},B} = 80^\circ C, 760 \text{ mmHg})$

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

$\hat{H}_h B(v, T_{\text{boil},B} = 80^\circ C, 760 \text{ mmHg})$

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

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

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

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

$$\hat{H}_{2B} = \hat{H}_g + \hat{H}_h + \hat{H}_i + \hat{H}_j$$

$$\Rightarrow \hat{H}_{2B} = \int_{-10^\circ C}^{80^\circ C} C_{P,B,l}(T) dT + \Delta \hat{H}_{v,p,B} + \int_{80^\circ C}^{50^\circ C} C_{P,B,v}(T) dT + O$$

$$\text{where } \Delta \hat{H}_{v,p,B} = 9.8 \frac{\text{kJ}}{\text{mol}}$$

$$C_{P,B,v} = 74.06 \times 10^3 + 32.95 \times 10^5 T$$

1 L = 0.03 kg

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

Form Variables

Table B2 Form 1

To calculate \hat{H}_{3T} [shn. 3: $T(1, 50^\circ C, 34.8 \text{ mm Hg})$]

$T(1, -10^\circ C, 760 \text{ mm Hg})$

\downarrow $\Delta T @ \text{const } P_1 \text{ phase}$

$A_x T(1, 50^\circ C, 760 \text{ mm Hg})$ \rightarrow liquid

\downarrow $\Delta P @ \text{const } T_1 \text{ phase}$

$H_L T(1, 50^\circ C, 34.8 \text{ mm Hg})$

$$\hat{H}_{3T} = \hat{H}_K + \hat{H}_L$$

$$\Rightarrow \hat{H}_{3T} = \int_{-10^\circ C}^{50^\circ C} C_{P_{\text{ref}}} dT + V_{T, 1} \Delta P \left(\frac{1 \text{ atm}}{760 \text{ mm Hg}} \right) \left(\frac{0.102 \text{ kJ}}{1 \text{ atm L}} \right)$$

Robust done above

where

$$V_{T, 1} = \frac{\partial V}{\partial P_T}$$

How to solve

- (i) Solve material balances as described above
- (ii) Calculate all \hat{H}_i for all species in streams 1, 2, 3
- (iii) Plug in all x_i , y_i , \dot{m}_i and \hat{H}_i into the energy balance



Unit 7



Energy Balances on Reactive Processes

General Procedure for Energy Balances

- Draw and fully label PFD
- Solve material balance OR determine if its solvable
- Write the general E-balance equation (first law)
- Cancel terms & justify why
- Draw the theoretical path for each species**
- Write relevant equations for each theoretical step**
- Look up all thermodynamic constants**
- Solve OR explain how you would solve

Chemical Reactions: Process that involves breaking and forming chemical bonds

Exothermic Reactions

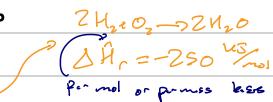
- Energy is released
- ↳ Combustion of Fuels, Haber process for producing ammonia

Endothermic Reactions

- Energy is absorbed
- ↳ photosynthesis

Heat of Reactions

- Entropy change with stoichiometric quantities of reactants at some T & P react to form products at the same T & P



Heat of Reaction for Chemical Engineers

- $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \quad \Delta H_r(T_1, P_1) = -250 \frac{\text{kJ}}{\text{mol}}$ exothermic or endothermic? exothermic! energy released
- $\Delta H = \Delta H_r(T, P)$ is enthalpy change associated with a chemical reaction
- ↳ used when we don't have stoichiometric amounts of each reactant or don't have 100% conversion

No Reactants

$$\Delta H = \sum n_{i,out} \bar{H}_{i,out} - \sum n_{i,in} \bar{H}_{i,in}$$

Reactant Present

→ 2 methods to handle

Single reactor, "Heat of reaction method"

$$\Delta H = \sum \Delta \bar{H}_{r,i} + \sum n_{i,out} \bar{H}_{i,out} - \sum n_{i,in} \bar{H}_{i,in}$$

\nwarrow Heat of reaction

Heat of Reaction Method

- Use when:
- Given a $\Delta \bar{H}_r$ ($\Delta \bar{H}_{\text{reaction}}$)
 - Can easily look $\Delta \bar{H}_r$ up
e.g. combustion rxn $\Leftrightarrow \Delta \bar{H}_{\text{combustion}}$ in Table B.1
 - Calculate $\Delta \bar{H}_r$ reaction by Hess's Law

First Law of Thermodynamics

$$1^{\text{st}} \text{ Law, open system: } Q - W_s = \Delta U + \Delta E_U + \Delta E_P$$

$$1^{\text{st}} \text{ Law, closed system: } Q - W = \Delta U + \Delta E_U + \Delta E_P$$

$$\text{Remember } \Delta \dot{H} = \Delta \dot{U} + \Delta \dot{P}V$$

- Calculate ΔU and $\Delta \dot{H}$ associated with:
 - ΔP at constant T and state
 - ΔT at constant P and state
 - Phase changes at constant T and P
 - Chemical reactions at constant T and P

Example: Combustion of NH_3 proceeds according to the following reaction:

$$4 \text{ NH}_3 + 5 \text{ O}_2 \rightarrow 4 \text{ NO} + 6 \text{ H}_2\text{O} \quad \text{with } \Delta H^\circ_{\text{rxn}} = -900 \text{ kJ/mol}$$

- 100% conversion of NH_3

- Continuous steady-state process

1) PFD

$$\dot{n}_{\text{NH}_3} = 100 \text{ mol/s}$$

$$\dot{n}_{\text{O}_2} = 200 \text{ mol/s}$$

$$T_1 = 25^\circ\text{C}$$

$$P_1 = 1 \text{ atm}$$

Reactor

↓

$$\begin{aligned} \dot{n}_{\text{H}_2\text{O}} &= \dot{n}_{\text{CO}_2} = \\ \dot{n}_{\text{NO}} &= \dot{n}_{\text{NH}_3} = 0 \\ T_2 &= \\ P_2 &= 2 \text{ atm} \end{aligned}$$

Want to know: Heat evolved (emitted) from the reactor: $\dot{Q} (\text{kJ/s})$

2. Material Balance D.o.F

3 Unknowns (\dot{n}_{NO} , $\dot{n}_{\text{H}_2\text{O}}$, \dot{n}_{CO_2})

+ 1 Overall React. Eq.

- 4 Indep. Mat. Balances (N_2 , H_2O , O_2 , NH_3 ; N_2 specie)

0 D.o.F can solve for all \dot{n}_i and \dot{E}

omitted here to
is units L-S, see text

*Side mission: Material Balances describe how to solve for all \dot{n}_i & \dot{E} *

3. Energy Balance

$$\Rightarrow \text{1st Law: } \dot{Q} - \dot{W}_s = \dot{\Delta H} + \dot{E}_x + \dot{E}_p \Rightarrow \dot{Q} = \dot{\Delta H}$$

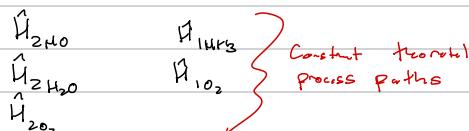
Heat of Reaction Method Spec. Ref.

$$\dot{Q} = \dot{\Delta H} = \dot{\Delta H}_{\text{rxn}} \cdot \dot{E} + \sum_{\text{out}} \dot{n}_i \bar{H}_i - \sum_{\text{in}} \dot{n}_i \bar{H}_i$$

$$\text{Expand: } \dot{Q} = \dot{\Delta H} = \dot{\Delta H}_{\text{rxn}} \cdot \dot{E} + \left[\dot{n}_{\text{H}_2\text{O}} \bar{H}_{\text{H}_2\text{O}} + \dot{n}_{\text{NO}} \bar{H}_{\text{NO}} + \dot{n}_{\text{CO}_2} \bar{H}_{\text{CO}_2} \right] - \left[\dot{n}_{\text{NH}_3} \bar{H}_{\text{NH}_3} + \dot{n}_{\text{O}_2} \bar{H}_{\text{O}_2} \right]$$

= Given

= Calculated from material balances



we choose a different set of reference states for
reactions, should be consistent w/ $\dot{\Delta H}_{\text{rxn}}$!!

4. Reference States

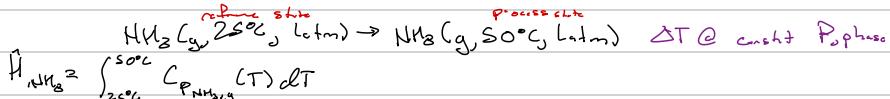
Heat of Reaction Method: Reference states are molecules at the same T & P as the $\dot{\Delta H}_{\text{rxn}}$ You must take this!

$\Rightarrow \text{NH}_3, \text{O}_2, \text{NO}, \text{H}_2\text{O}(g, 25^\circ\text{C}, 1 \text{ atm})$ are our reference states

molar specific \bar{H} can be used for $\dot{\Delta H}_{\text{rxn}}$

So construct thermodynamic process paths for all species in all streams to calculate $H_{1,i}$ and $H_{2,i}$ for all species i

{Inlet Species - Stream 1}



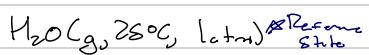
$$\text{where } C_{PNH_3,g} = \dots \quad \text{Table B.2}$$

$$H_{O_2} = \int_{25^\circ C}^{50^\circ C} C_{PO_2,g}(T) dT \quad \text{same thermol process}$$

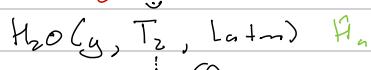
$$\text{where } C_{PO_2,g} = \dots \quad \text{Table B.2}$$

World Ref. Ref.
Today, class the last

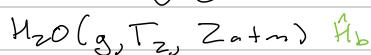
{Outlet Species - Stream 2}



$$0! \rightarrow ① \quad \Delta P = \text{del } G$$



$$\downarrow ②$$



$$H_{2H_2O} = 0 + \int_{25^\circ C}^{T_2} C_{PH_2O,g} dT$$

$$\text{where } C_{PH_2O,g} = \dots \quad \text{Table B.2}$$

$$H_{2O} = 0 + \int_{25^\circ C}^{T_2} C_{PO_2,g} dT$$

$C_{PO_2,g}$ with only one component
reactivity curve on how & assesses

$$H_{2H_2} = 0 + \int_{25^\circ C}^{T_2} C_{PH_2} dT$$

$$\text{where } C_{PH_2}$$

T_2 is unknown... How can we find it?

• EoS? T, P, ρ, v relationship

\hookrightarrow doesn't know v , cannot use hys if v unknown we can't use some EoS from Unit 4

• Raoult's Law? No VLE

\hookrightarrow Maxwell relation for any g.s. phase present

• In real world, measure T_2 or V_2 to have enough information

Q is unsolvable here!!

Sometimes...

Q is given say $100 \text{ kJ/hr} \rightarrow$ solve T_2

Isothermal is now equal to adiabatic

$Q = 0 \rightarrow$ adiabatic

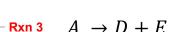
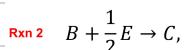
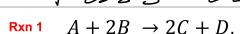
$T_1 = T_2 \rightarrow$ isothermal but $Q \neq 0$ as heat transfer to keep temp const.

What if you want ΔH_{rxn}

\rightarrow Heat of Combustion (ΔH°_c) Table B.1

or from chemistry class...

Hess's Law



$$\Delta H_1^\circ = 2\Delta H_2^\circ + \Delta H_3^\circ$$

Hess's Law: If the stoichiometric equation for rxn 1 can be

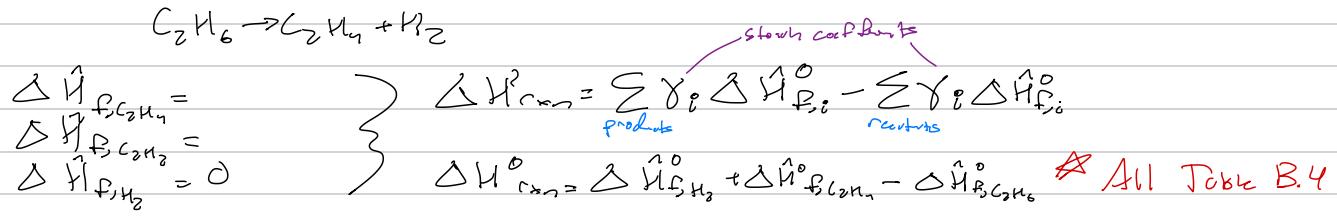
obtained by algebraic operations on stoichiometric equations for rxns 2, 3, ... then $\Delta H_{rxn,1}^\circ$ can be obtained by performing the same operations on $\Delta H_{rxn,3}^\circ, \Delta H_{rxn,2}^\circ$

Heat of Formation with Hess's Law

- Enthalpy change associated with forming 1 mole of a compound from its elements at 298K and 1 atm

Note: $\Delta \hat{H}_{f, H_2} = 0$ because H₂ is a pure element or diatomic species

Example Calculate ΔH_r using Hess's Law and standard heats of formation for.



Summary

(i) Heat of Rxn Method

- generally preferred for sig figs
- where ΔH_{rxn}

$$\Delta \hat{H} = \underbrace{\sum \Delta \hat{H}_{rxn}}_{\substack{\text{account + Prod} \\ \text{b. } K_{ij}/D_{ij} \\ \text{cl. enthal. bonds}}} + \underbrace{\sum n_i \hat{H}_i}_{\substack{\text{out} \\ \text{in}}} - \underbrace{\sum i_i \hat{H}_i}_{\substack{\text{account + fr. } D_p \\ \text{D and D phase}}}$$

- Ref state: Conditions of ΔH_{rxn} from $\Delta H_{rxn}^o (298K, 1\text{ atm, pure})$
- corresponds to rxns

Heat of Formation Method

Heat of Formation

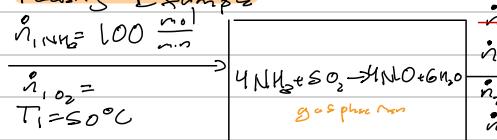
- Enthalpy change associated with forming 1 mole of a compound from its elements at 298K and 1 atm

Generally preferred for multiple reactions when ΔH_{rxn} is unknown

$$\Delta \hat{H} = \sum_{\text{out}} n_i \hat{H}_i - \sum_{\text{in}} n_i \hat{H}_i \quad \text{against } T, P, \text{ phases and chemical rxns}$$

- Reference state: element or diatomic species (298K, 1 atm, phase) phase corresponds to ΔH°_f

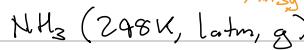
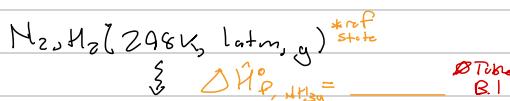
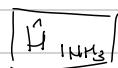
Reactivity Examples



$$\begin{array}{l} \text{1st Law: } Q - \dot{Q}_s = \Delta \hat{H} + \Delta E_P + \Delta E_K \\ \Rightarrow Q = \Delta \hat{H} = \sum_{\text{out}} n_i \hat{H}_i - \sum_{\text{in}} n_i \hat{H}_i \end{array}$$

$$Q = \left[n_{\text{O}_2} \hat{H}_{\text{O}_2} + n_{\text{H}_2\text{O}} \hat{H}_{\text{H}_2\text{O}} + n_{\text{HNO}_3} \hat{H}_{\text{HNO}_3} \right] - \left[n_{\text{NH}_3} \hat{H}_{\text{NH}_3} + n_{\text{H}_2} \hat{H}_{\text{H}_2} \right]$$

Reference State: $\text{H}_2, \text{N}_2, \text{O}_2$ (298K, 1 atm, g)

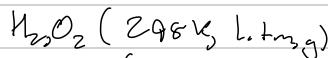
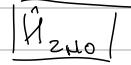
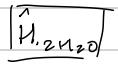


$\downarrow \Delta T, \text{ const } P, \text{ phase}$

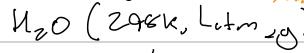


$$\hat{H}_{\text{O}_2} = \text{O} + \int_{298\text{K}}^{50^\circ\text{C}} C_{P_{\text{O}_2}} dT$$

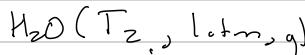
$$\Delta \hat{H}_{\text{NH}_3} = \Delta \hat{H}_{\text{F, NH}_3} + \int_{298\text{K}}^{50^\circ\text{C}} C_{P_{\text{NH}_3}} dT$$



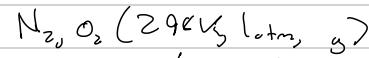
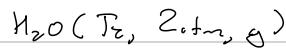
$\downarrow \Delta \hat{H}_{\text{F, H}_2\text{O}_2} = \text{_____} \quad \text{Table B1}$



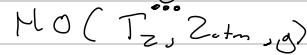
$\downarrow \Delta T, \text{ const } P, \text{ phase}$



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

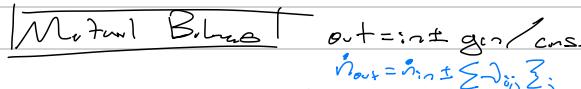


$\downarrow \Delta \hat{H}_{\text{F, H}_2\text{O}_2} = \text{_____} \quad \text{Table B1}$

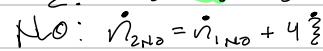
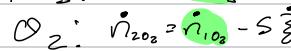
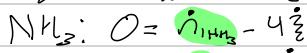
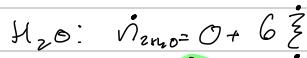


$$\hat{H}_{\text{MO}} = \Delta \hat{H}_{\text{F, MO}} + \int_{298\text{K}}^{T_2} C_{P_{\text{MO}}} dT + \text{O}$$

$$\hat{H}_{\text{H}_2\text{O}} = \Delta \hat{H}_{\text{F, H}_2\text{O}} + \int_{298\text{K}}^{T_2} C_{P_{\text{H}_2\text{O}}} dT + \text{O}$$



How to Solve



Unit 8 - Comprehensive Practice

ECHE 260: Intro to Chemical Systems

Homework #9 (50 points)

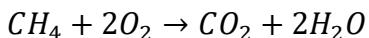
Due Friday, December 6, 2018

Assignments are due in person at the beginning of the class period on the due date. No late assignments will be accepted. Homework should follow the general formatting guidelines posted in Canvas.

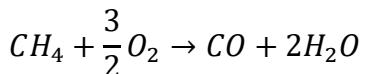
Incomplete combustion of methane

Topics: Reactive material balances, reactive energy balances, steam tables, non-ideal gas law

Natural gas, also known as methane (CH_4), is a byproduct of landfills. The methane is often burned in a furnace or flare and the byproducts are vented to the atmosphere. The combustion of methane follows the equation:



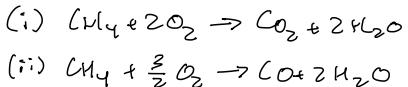
In an undesired side reaction, the incomplete combustion of methane leads to the production of carbon monoxide:



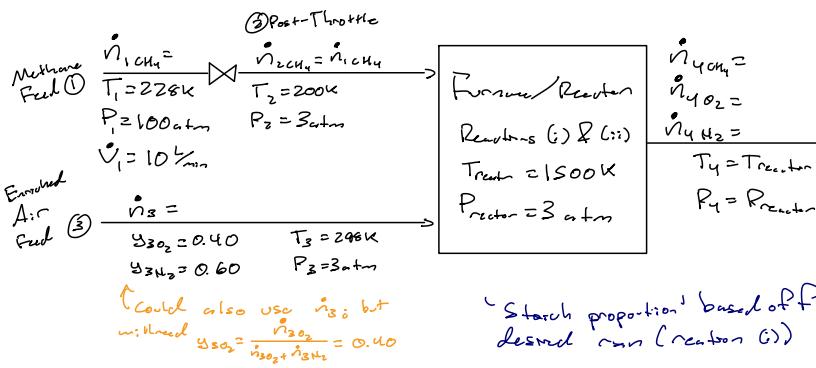
In a furnace, methane undergoes a combustion reaction with enriched air (40mol% O_2 and 60 mol% N_2). The entire process operates continuously at steady state. Methane is fed to a throttling valve which reduces the pressure, then continues to the reactor. The flowrate of methane to the throttling valve is at a pressure of 100 atm, temperature of 228 K and volumetric flowrate of 10 L/min. The temperature after throttling is 200 K and the pressure is 3 atm. In a separate feed stream, enriched air is delivered directly to the reactor at 298K and 3 atm. Oxygen and methane are fed to the reactor in a stoichiometric proportion and the reactor operates at 1500 K and 3 atm. The fractional conversion of methane is 0.50 and the selectivity of carbon dioxide to carbon monoxide is 10.

One of the process engineers at the landfill wants to know if the heat produced from the furnace would be sufficient to heat water needed elsewhere in the facility. Cold water is available from the city at 20°C and a flowrate of 8 L/min. Using the general procedure from class, perform the necessary material and energy balances to answer this question. The desired final temperature of the water is 60°C. Be clear in your process and approach.

Incomplete Combustion of Methane



PF D)



Additional Info

~~(*)~~ $\frac{\dot{n}_{2\text{CH}_4}}{\dot{n}_{3\text{O}_2\text{N}_2}} = \frac{1}{2}$ Methane & oxygen in stoichi proportion w/ respect to desired run

~~(*)~~ $f_{\text{CH}_4} = \frac{\dot{n}_{2\text{CH}_4} - \dot{n}_{4\text{CH}_4}}{\dot{n}_{2\text{CH}_4}}$ mols reacted / mols fed

~~(*)~~ $\Delta \frac{\text{CO}}{\text{CO}} = \frac{\dot{n}_{4\text{CO}_2}}{\dot{n}_{4\text{CO}}} = 1.0$ compare relative production of products in product stream

~~(*)~~ $PV = \dot{n}_{\text{CH}_4} RT_{1,2}$ This can be done if gass want to

Want to know: $|Q_{\text{water}}| \leq |Q_{\text{reactor}}|$

Energy Balance on Reactor

$$1^{\text{st Law:}} \dot{Q}^{\text{in}} + \dot{E}_{\text{Ex}}^{\text{in}} + \dot{\Delta U} = \dot{Q}^{\text{out}} - \dot{V}^{\text{in}}$$

no changes in position or velocity no moving parts

$$\dot{Q} = \dot{\Delta U} = \sum_{\text{out}} \dot{H}_i \dot{n}_i - \sum_{\text{in}} \dot{H}_i \dot{n}_i \quad (\text{Hartoff Formulas Method})$$

Ref State: Elements or Pictures @ 298 K, 1 atm
 $\text{H}_2, \text{H}_2, \text{O}_2$ (298 K, 1 atm, g)
 C (298 K, 1 atm, s) $\xrightarrow{\text{Cessel}}$

$$\text{Reactn Temp} = 1226.85^\circ\text{C}$$

$$\text{Reactn Pressure} = 3 \text{ atm}$$

$$\text{Reform Temp} = 24.85^\circ\text{C}$$

$\dot{H}_{\text{uH}_2\text{O}}$

$$\text{H}_2, \text{O}_2 (298 \text{ K, 1 atm, g})$$

$$\text{Table B.1} \quad \Delta \dot{H}_{\text{f}, \text{H}_2\text{O}}^{\circ} = -241.83 \frac{\text{kJ}}{\text{mol}}$$

$$\text{H}_2\text{O} (298 \text{ K, 1 atm, g})$$

$$\downarrow \Delta T @ \text{const } P_{\text{phase}}$$

$$\Delta \dot{H}_{\text{a}} \text{ H}_2\text{O} (1500 \text{ K, 1 atm, g})$$

$$\downarrow \Delta P @ \text{const } T_{\text{phase}}$$

$$\Delta \dot{H}_{\text{b}} \text{ H}_2\text{O} (1500 \text{ K, 3 atm, g})$$

$$\dot{H}_{\text{uH}_2\text{O}} = \Delta \dot{H}_{\text{f}, \text{H}_2\text{O}}^{\circ} + \int_{298 \text{ K}}^{1500 \text{ K}} C_{\text{PH}_2\text{O}, \text{g}} dT + 0$$

where $C_{\text{PH}_2\text{O}, \text{g}} = \frac{23.46}{10^5} + \frac{0.6880T}{10^5} + \frac{0.7604T^2}{10^8} - \frac{3.548T^3}{10^{12}}$

\dot{H}_{uCO}

$$\text{O}_2 (298 \text{ K, 1 atm, g}), \text{C} (298 \text{ K, 1 atm, s})$$

$$\text{Table B.1} \quad \downarrow \quad \Delta \dot{H}_{\text{f}, \text{CO}}^{\circ} = -110.52 \frac{\text{kJ}}{\text{mol}}$$

$$\text{CO} (298 \text{ K, 1 atm, g})$$

$$\downarrow \Delta T @ \text{const } P_{\text{phase}}$$

$$\Delta \dot{H}_{\text{c}, \text{CO}} (1500 \text{ K, 1 atm, g})$$

$$\downarrow \Delta P @ \text{const } T_{\text{phase}}$$

$$\Delta \dot{H}_{\text{d}, \text{CO}} (1500 \text{ K, 3 atm, g})$$

$$\dot{H}_{\text{uCO}} = \int \Delta \dot{H}_{\text{f}, \text{CO}, \text{g}}^{\circ} + \int_{298 \text{ K}}^{1500 \text{ K}} C_{\text{PCO}, \text{g}} dT + 0$$

$$\text{where } C_{\text{PCO}, \text{g}} = \frac{28.45}{10^5} + \frac{0.4110T}{10^5} + \frac{0.3548T^2}{10^8} - \frac{2220}{10^{12}} T^3$$

$$\text{Table B.2}$$

Remaining C_p expressions found on next page \downarrow

$$\dot{H}_{\text{uCO}_2} = \Delta \dot{H}_{\text{f}, \text{CO}_2, \text{g}}^{\circ} + \int_{298 \text{ K}}^{1226.85 \text{ K}} C_{\text{PCO}_2, \text{g}} dT + 0$$

$$\dot{H}_{\text{uCH}_4} = \Delta \dot{H}_{\text{f}, \text{CH}_4}^{\circ} + \int_{298 \text{ K}}^{1500 \text{ K}} C_{\text{PCH}_4} dT + 0$$

$$\dot{H}_{\text{uO}_2} = \Delta \dot{H}_{\text{f}, \text{O}_2}^{\circ} + \int_{298 \text{ K}}^{1226.85 \text{ K}} C_{\text{PO}_2} dT + 0$$

$$\dot{H}_{\text{uN}_2} = \Delta \dot{H}_{\text{f}, \text{N}_2}^{\circ} + \int_{298 \text{ K}}^{1226.85 \text{ K}} C_{\text{PN}_2} dT + 0$$

\hookrightarrow could also (just do init species) do the $\rightarrow G$ method for calculation

Because: $\text{H}_2 (298 \text{ K, 3 atm, g})$ Just temperature!
 $\text{you do it!} \quad \downarrow \quad \text{H}_2 (1500 \text{ K, 3 atm, g})$

\hat{H}_f for H_2CO was derived above. The rest of the \hat{H}_f are shown here:

For all reactive species: Ref state N_2, O_2 (298K, 1atm, g), C (298K, 1atm, solid)

$$\hat{H}_f^{\text{CO}} = \Delta H_f^{\circ} + \int_{298K}^{T_4} C_{P,\text{CO},g} dT$$

C, O (298K, 1atm, g or solid) Ref State



$$\hat{H}_f^{\text{CH}_4} = \Delta H_f^{\circ} + \int_{298K}^{T_4} C_{P,\text{CH}_4,g} dT$$

C, H_2 (298K, 1atm, g or solid) Ref State



$$\hat{H}_f^{\text{O}_2} = \Delta H_f^{\circ} + \int_{298K}^{T_4} C_{P,\text{O}_2,g} dT$$

O_2 (298K, 1atm, g or solid) Ref State



$$\hat{H}_f^{\text{CO}_2} = \Delta H_f^{\circ} + \int_{298K}^{T_4} C_{P,\text{CO}_2,g} dT$$

C, O_2 (298K, 1atm, g or solid) Ref State



$$C_{P,\text{CO},g} = 28.95 \times 10^{-3} + 0.4110 \times 10^{-5} T + 0.36 \times 10^{-7} T^2$$

$$C_{P,\text{CH}_4,g} = 19.87 \times 10^{-3} + 5.02 \times 10^{-5} T + 1.27 \times 10^{-8} T^2$$

$$C_{P,\text{O}_2,g} = 29.10 \times 10^{-3} + 1.158 \times 10^{-5} T + -0.608 \times 10^{-8} T^2$$

$$C_{P,\text{CO}_2,g} = 36.11 \times 10^{-3} + 4.235 \times 10^{-5} T + -2.887 \times 10^{-8} T^2$$

Table
B.2
*all
for OC
except
 CH_4

$$\Delta H_f^{\circ,\text{CO}} = -110.52 \text{ kJ/mol}$$

$$\Delta H_f^{\circ,\text{CH}_4} = -74.9 \text{ kJ/mol}$$

$$\Delta H_f^{\circ,\text{O}_2} = 0 \text{ kJ/mol}$$

$$\Delta H_f^{\circ,\text{CO}_2} = -393.5 \text{ kJ/mol}$$

Table
B.1

For non-reactive species (N_2)

We can chose our ref. state to be anything we want for N_2 because there is no chemical rxn that it is tied to.

So, ref state $\text{N}_2(g, T_4, P_4)$ and $\hat{H}_f^{\text{N}_2} = 0$

Now we just need to write the \hat{H}_f for N_2 in the inlet

$$\hat{H}_f^{\text{N}_2} = 0 \text{ because assumed } T_4, P_4 \text{ as the ref state.}$$

$$\hat{H}_f^{\text{N}_2} = \int_{1500K}^{T_3} C_{P,\text{N}_2} dT$$

We already wrote a C_{P,N_2} expression above.

Stream 2 (200K, 3 atm, g)



$\text{C}(298\text{K}, \text{Latm}, \text{g}), \text{H}_2(298\text{K}, \text{Latm}, \text{g})$

$$\text{Table B.1} \downarrow \quad \Delta \dot{H}_{\text{f,CH}_4}^{\circ} = -74.88 \frac{\text{kJ}}{\text{mol}}$$
 $\text{CH}_4(298\text{K}, \text{Latm}, \text{g})$

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

$\text{CH}_4(200\text{K}, 1 \text{ atm}, \text{g})$

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

$\text{CH}_4(200\text{K}, 3 \text{ atm}, \text{g})$

$$\dot{m}_{\text{CH}_4} = \Delta \dot{H}_{\text{f,CH}_4}^{\circ} + \int_{200\text{K}}^{200\text{K}} C_{P,\text{CH}_4,\text{g}} dT + 0$$

where

$$C_{P,\text{CH}_4,\text{g}} = \frac{19.87}{10^3} + \frac{5.021}{10^6} T + \frac{1.268}{10^8} T^2 + \frac{-11}{10^{12}} T^3$$

Molar Balances

D.o.F Furnace

8 Unknowns ($\dot{n}_{\text{ZCH}_4}, \dot{n}_{\text{O}_2}, \text{all } \dot{n}_{\text{CO}_i}$)

+2 Chemical Reactions ($\dot{\Sigma}_1, \dot{\Sigma}_2$)

-6 Molar Balances (6 species \dot{n}_{CO_i})

-3 Additional B.Gs ($\dot{\Sigma}_1, \dot{\Sigma}_2, \dot{\Sigma}_3$)

1 D.o.F \Downarrow

D.o.F Value

- 1 Unknown (\dot{n}_{CH_4})
- +0 Chemical Reactions
- 0 Molar Balances
- 1 Additional Eq (0)

0 D.o.F \Downarrow

Plan: Solve Value for $\dot{n}_{\text{CH}_4} \rightarrow$ Solve Furnace For all Flowsrates!

Additional Info

$$\cancel{\textcircled{1}} \quad \frac{\dot{n}_{\text{ZCH}_4}}{\dot{n}_{\text{Z}\Sigma\text{O}_2}} = \frac{1}{2} \quad \text{methane & oxygen in stoichi proportion w/ respect to shared rxn}$$

$$\cancel{\textcircled{2}} \quad f_{\text{CH}_4} = \frac{\dot{n}_{\text{ZCH}_4} - \dot{n}_{\text{YCH}_4}}{\dot{n}_{\text{ZCH}_4}} \quad \text{mols reacted / mols fed}$$

$$\cancel{\textcircled{3}} \quad \alpha_{\text{CO}_2} = \frac{\dot{n}_{\text{YCO}_2}}{\dot{n}_{\text{CO}_2}} = 10 \quad \text{comps relative production depends in a product stream}$$

$$\cancel{\textcircled{4}} \quad P_i V_i = \dot{n}_{i,\text{CH}_4} R T_i z \quad \text{This can include: } P_{\text{gas}} \text{ you want}$$

Solve Value System

$$\cancel{\textcircled{1}} \quad P_i V_i = \dot{n}_{i,\text{CH}_4} R T_i z$$

$$\Rightarrow \dot{n}_{i,\text{CH}_4} = \frac{P_i V_i}{R T_i z}$$

$$\cancel{\textcircled{2}} \quad \dot{V} = \frac{RT_2}{P_2} = \frac{0.0821 \text{ L atm}}{\text{mol K}} (228\text{K})$$

$$\cancel{\textcircled{3}} \quad z \neq 1, \text{ otherwise } \quad \dot{V} = \frac{P_2 V_2}{100 \text{ atm}} = 0.188 \frac{\text{L}}{\text{mol}} \quad \text{Not :dol!}$$

would have to use Koenigs for a mixture

$$P_r = \frac{P}{P_0} = \frac{100 \text{ atm}}{45.8 \text{ atm}} = 2.18$$

$$T_r = \frac{T}{T_0} = \frac{228\text{K}}{140.7\text{K}} = 1.62$$

$\cancel{\textcircled{4}} \quad \text{Table B.1}$

\Rightarrow From Graph: $z = 0.95$

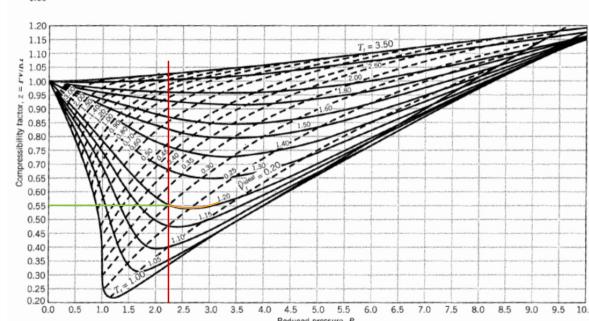


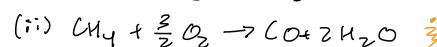
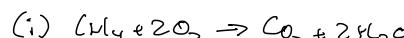
Figure 5.4-3 Generalized compressibility chart, medium pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 176. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

Solve Furnace / Reactor

Molar B.L.s

Stoichiometric:

$$\dot{n}_{\text{out},i} = \dot{n}_{i,\text{in},i} + \sum \dot{n}_{i,j}$$



$$\text{CH}_4: \dot{n}_{4,\text{CH}_4} = \dot{n}_{2,\text{CH}_4} - \dot{\Sigma}_1 - \dot{\Sigma}_2$$

$$\text{O}_2: \dot{n}_{4,\text{O}_2} = \dot{n}_{3,\text{O}_2} - 2\dot{\Sigma}_1 - \frac{3}{2}\dot{\Sigma}_2$$

$$\text{CO}: \dot{n}_{4,\text{CO}} = \dot{\Sigma}_1$$

$$\text{N}_2: \dot{n}_{4,\text{N}_2} = \dot{n}_{3,\text{N}_2}$$

$$\text{H}_2\text{O}: \dot{n}_{4,\text{H}_2\text{O}} = \dot{\Sigma}_1 + 2\dot{\Sigma}_2 + 2\dot{\Sigma}_3$$

$$\text{CO}_2: \dot{n}_{4,\text{CO}_2} = \dot{\Sigma}_1$$

$$\cancel{\textcircled{1}} \quad \frac{\dot{n}_{2,\text{CH}_4}}{\dot{n}_{3,\text{O}_2}} = \frac{1}{2} \quad \cancel{\textcircled{2}} \quad \alpha_{\text{CO}_2} = \frac{\dot{n}_{4,\text{CO}_2}}{\dot{n}_{4,\text{CO}}} = 10$$

$$\cancel{\textcircled{3}} \quad f_{\text{CH}_4} = \frac{\dot{n}_{2,\text{CH}_4} - \dot{n}_{4,\text{CH}_4}}{\dot{n}_{2,\text{CH}_4}}$$

Stream 3 (298K, 3 atm, g)

$$\dot{m}_{\text{O}_2} = 0 + 0 + 0 = 0 \frac{\text{kg}}{\text{mol}}$$

$$\dot{m}_{\text{H}_2\text{O}} = 0 + 0 + 0 = 0 \frac{\text{kg}}{\text{mol}}$$

nearby ideal gases per species formed @ process temperature

How to solve for the \dot{Q}_{reactor}

1. Evaluate all \dot{H}_i expressions in streams 2, 3, and 4

2. Plug those into energy balance, \dot{Q}_{reactor}

3. Calculate all \dot{n}_i for streams 2, 3, 4; plug those into \dot{Q}_{reactor}

\hookrightarrow Requires full material balance section