

<< Units & Dimensions

- > dimensions - property that's measured
- > units - what quantifies dimension
 - important } calculation to carry units
 - } define results

→ System of Units

- American Engineering (AE) system
 - foot, pound-mass, seconds
- SI unit
 - meter, kg, K, s
- cgs unit
 - cm, g

<< Dimensionless Groups

- dimensionless groups - ratio of quantities that have dimensions cancel out
- generalize / scale solutions
- Reynold's number is dimensionless

$$Re = \frac{D v \rho}{\mu}$$

= $\frac{\text{internal force}}{\text{viscous force}}$

D - diameter ρ - density
 v - velocity μ - viscosity

- consistency - balanced units dimension on both sides
- most equations has balanced dimensionality
- some engineered equation does not have balanced dimensionality
- Arrhenius Equation

- $k = A \exp\left(\frac{-E_a}{RT}\right)$ is inconsistent
- $k [=] s^{-1}$ $E_a [E] \frac{J}{mol}$ $R [=] \frac{J}{mol \cdot K}$
- A dimensionless $T [=] K$
- Antoine's' Equation
- $\log_{10} P^* = A - \frac{B}{T+C}$ is inconsistent
- $P^* [=] \text{mmHg}$
- $T [=] {}^\circ C$

<< Measurements

→ Force

$$\gg F = ma$$

- $1 N = 1 \text{kg m/s}^2$
- $1 \text{lb}_f = 32.174 \text{ lb}_m \text{ft/s}^2$

→ Mass & Volume

• volume varies with T, P, composition

$$\gg \text{density} - \rho = \frac{m}{V} = \frac{\text{mass}}{\text{volume}}$$

$$\gg \text{specific volume} \quad \hat{V} = \frac{\text{volume}}{\text{mole}}$$

$$\tilde{V} = \frac{\text{volume}}{\text{mass}}$$

<< Measurements (cont.)

→ Specific gravity

$$\rightarrow SG = \frac{\rho}{\rho_{H_2O}} \quad \text{• pref usually water at } 4^\circ C$$

$$\cdot \text{Benzene SG at } T=60^\circ C \text{ means } SG = \frac{\rho_{\text{benzene (}T=60^\circ C\text{)}}}{\rho_{H_2O} (T=60^\circ C)}$$

→ Flow Measurements.

$$\rightarrow \text{mass flow rate } \dot{m} = \frac{dm}{dt} = \frac{\text{mass}}{\text{time}}$$

$$\rightarrow \text{volumetric flow rate } \dot{V} = \frac{dV}{dt} = \frac{\text{volume}}{\text{time}}$$

' gas \dot{V} is complicated, affected by T, P

$$\cdot \text{density } \rho = \frac{m}{V} = \frac{\dot{m}}{\dot{V}}$$

→ Solving Problems of \dot{m}, \dot{V} - specify T, P for given \dot{V} - specify equivalent \dot{V} at standard condition { scientific $0^\circ C, 1 \text{ atm}$ - SCFM = standard cubic feet per minute (ft^3/min)**EX1** 600 SCFM that's not natural gas- $600 \text{ ft}^3/\text{min}, 0^\circ C, 1 \text{ atm}$ **EX2** Natural gas has flow rate 1000 SCFM. Actual condition are $140^\circ F, 2.5 \text{ atm}$, what is actual flow rate.- $1000 \text{ SCFM} = 1000 \text{ ft}^3/\text{min}, 59^\circ F, 1 \text{ atm}$

- Assume ideal gas

$$\frac{P_1 \dot{V}_1}{T_1} = \frac{P_2 \dot{V}_2}{T_2} \Rightarrow \dot{V}_2 = \frac{P_1 \dot{V}_1 T_2}{P_2 T_1}$$

→ Mole

$$\rightarrow \text{mole} = \frac{\text{mass}}{\text{molecular weight}} = \frac{m}{M} \quad (\text{g/mol, lb-mol, ton-mol})$$

EX3 Convert 5 lb_mO₂ to moles

$$5 \text{ lb}_m O_2 \times \frac{453.6 \text{ g}}{1 \text{ lb}_m} \times \frac{1 \text{ g-mol}}{32 \text{ g}} = 70.9 \text{ g-mol}$$

$$\cdot \frac{kg}{mol} = \frac{kg}{kmol} = \frac{mg}{mmol}$$

<< Measurements

→ Mass Fraction & Mole Fraction

$$\geq X_A = \frac{m_A}{m} = \frac{\text{mass of } A}{\text{total mass}}$$

• process streams usually contains more than one component.

$$\geq y_A = \frac{n_A}{n} = \frac{\text{mole of } A}{\text{total mole}}$$

• convert $x_A \leftrightarrow y_A$ using assuming a basis of calculation

→ Concentrations

$$\geq \text{concentration} = \frac{\text{useful amount}}{\text{another useful amount}}$$

$$\text{e.g. } \frac{\text{mol}}{\text{L}}, \frac{\text{mol solute}}{\text{mol solvent}}$$

$$\frac{\text{lb}}{\text{ft}^3}, \text{ ppm, ppb}$$

- mol fraction → gas
- mass fraction → liquid, solid

EX4 Ne in air 0.001818 Mol%

$$\text{- mol frac } y = 0.00001818 = 18.2 \times 10^{-6} = 18.2 \text{ ppm}$$

EX5 blood sample with 68 ppm creatinine. What is mass fraction?

• assume 1kg basis of blood

$$\frac{68 \times 10^{-6} \text{ kg creatinine}}{1 \text{ kg blood}}$$

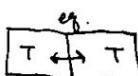
How many mg of creatinine in 1kg blood?

$$68 \times 10^{-6} \text{ kg} \times \frac{10^6 \text{ mg}}{1 \text{ kg}} = 68 \text{ mg creatinine}$$

→ Temperature

• temperature - measure of KE of molecule in substance

• 0th law of thermo - two bodies are in thermo equilibrium if they have same temp.



• temp. scales

$$\left. \begin{array}{l} \text{Fahrenheit } (\circ F) - T_f = 32^\circ F, T_b = 212^\circ F \\ \text{Celsius } (\circ C) - T_f = 0^\circ C, T_b = 100^\circ C \\ \text{Rankine } (\circ R) - T(R) = T(\circ F) + 459.67 \\ \text{Kelvin } (K) - T(K) = T(\circ C) + 273.15 \end{array} \right\} \text{absolute scales}$$

$$T(\circ F) = 1.8 T(\circ C) + 32$$

EX6

$$\begin{array}{|c|} \hline 5 \text{ lbm H}_2\text{O} \\ 50^\circ F \\ \hline \end{array} \xrightarrow{Q} \begin{array}{|c|} \hline 5 \text{ lbm H}_2\text{O} \\ 70^\circ F \\ \hline \end{array}$$

$$Q = \dot{m} c_p \Delta T = (1 \text{ lbm}/(1 \text{ lbm} \cdot ^\circ F))(5 \text{ lbm})(70 - 50)^\circ F \\ = 100 \text{ btu}$$

use abs
temp scale

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

<< Measurements

→ Pressure

- pressure = $\frac{\text{force}}{\text{area}}$

- $P [=] \frac{N}{m^2} = Pa$

- > atmospheric pressure - current pressure, P_{atm}

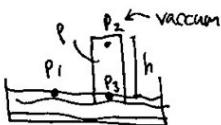
- > absolute pressure - actual pressure, $P=0$ in vacuum, P_{abs} , psia ($P_{abs} \geq 0$)

- > gauge pressure - pressure rel to atmospheric pressure, P_g , psig (P_{gauge} can be neg.)

$$P_{abs} = P_{atm} + P_{gauge}$$

- Standard atm $P = 1 \text{ atm} = 14.696 \text{ psi} = 1.01325 \times 10^5 \text{ Pa} = 1.01325 \text{ bar} = 760 \text{ mm Hg}$

EX1



$$P_1 = P_{atm}$$

$$P_3 = \rho g h$$

$$P_2 = 0$$

$$P_1 = P_2 + P_3 \leftarrow \text{hydrostatic pressure}$$

<< Data Representation

→ Sig. fig

- least accurate variable determines result's sig fig

EX2

2300 - 2 sig fig

0.035 - 2 sig fig

2300. - 4 sig fig

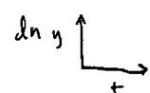
0.03500 - 4 sig fig

2300.0 - 5 sig fig

23040 - 4 sig fig

→ Visualization

- log scale



$$y = ax^b$$

$$\ln y = \ln a + b \ln x$$

$$y = ae^x$$

$$\ln y = \ln a + x$$

→ Fitting data



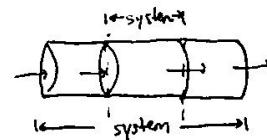
- linear regression

- method of least squares

→ better fit

<< Intro to Material Balances

total accumulation within system	=	total flow into the system	-	total flow out of the system	+	total generation in system	-	total consumption in system															
→ system - control volume arbitrarily defined volume in space & time																							
• boundaries classification																							
<table border="1"> <thead> <tr> <th>type of system</th> <th>mass transfer</th> <th>no</th> <th>no</th> <th>yes</th> </tr> <tr> <th></th> <th>energy transfer</th> <th>yes</th> <th>no</th> <th>yes</th> </tr> </thead> <tbody> <tr> <td></td> <td></td> <td>closed system</td> <td>closed, insulated system</td> <td>open system</td> </tr> </tbody> </table>									type of system	mass transfer	no	no	yes		energy transfer	yes	no	yes			closed system	closed, insulated system	open system
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	energy transfer	yes	no	yes																			
		closed system	closed, insulated system	open system																			



• time classification

→ steady state - system is not changing wrt time

- constant T, P, V

- minor fluctuation around mean ok

→ unsteady state - system changing wrt time

- accumulation ≠ 0

• process classification

- semibatch & batch - unsteady state

- continuous process - ideally steady state in between, unsteady for start & end

- e.g. distillation column

→ material balance equations

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

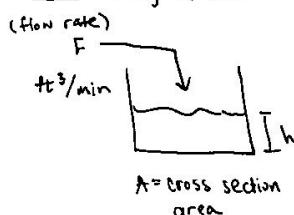
↑
 create
 ↑
 source

↑
 destroy
 ↑
 sink

$$\text{accumulation} = \frac{d\int}{dt} \left[\begin{array}{l} \text{mass} \\ \text{energy} \\ \text{atoms} \end{array} \right] \quad \left. \begin{array}{l} \text{within boundary} \\ \text{of the system} \end{array} \right\}$$

rate can be (+) or (-)

Ex 1 Filling a tank



$$\frac{d[\rho A h(t)]}{dt} = \rho F(t) - 0 + 0 - 0$$

$$\rho A \frac{dh}{dt} = \rho F(t)$$

$$\frac{dh}{dt} = \frac{F(t)}{A}$$

$$h(0) = h_0$$

$$h(t) = \frac{F}{A} t + h_0$$

Assumption: F, ρ, A constant

<< Intro to Material Balance

- common simplifying assumption

- steady state

$$\left\{ \begin{array}{l} \text{accum} = 0 \\ \frac{d(\cdot)}{dt} = 0 \end{array} \right.$$

- integrated form $\int_{t_1}^{t_2} \rightarrow F(t_2) - F(t_1)$

→ Material Balance Equation (cont.)

- in/out term

- flow	}	mass	330, 465, 435
- diffusion			
- conduction	}	energy	340, 325, 326
- radiation			
- convection			
- work			

- create & destroy term

- conserved
 - atoms
 - mass total
 - energy
- accum = in/out

- mass of component i
- moles
- moles of component i

- volume create/destroy

- gas yes
 - liquid
 - solid \rightarrow small, but not always zero

\Rightarrow equation of states

<< Solving Material Balance

[Ex2] Solutions of balance eq. in general

1. Draw a picture, label

2. State the problem

Find w^3_{salt}

Given $\frac{\text{crude oil}}{\text{H}_2\text{O}} = \frac{F^2}{F^1} = 4$

3. Determine Model components

Assumptions stated

• steady state, continuous

• no oil in water $w^4_{\text{oil}} = 0$

• no water in oil $w^3_{\text{H}_2\text{O}} = 0$

Basis assumed

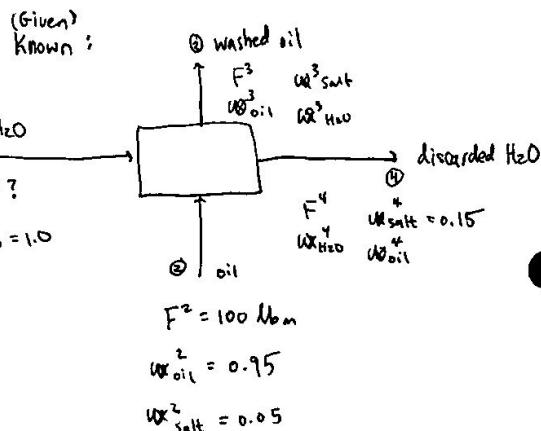
• basis $F^2 = 100 \text{ lb}_m$

Write unknowns

F^1, F^3, F^4

$w^3_{\text{oil}}, w^3_{\text{salt}}, w^3_{\text{H}_2\text{O}}$

$w^4_{\text{H}_2\text{O}}, w^4_{\text{oil}}$



<< Solving Material Balance

Ex:

(cont.)

4. Write out mass balance equation

$$\text{Actual} = \text{in} - \text{out} + \text{gen} - \text{crys}$$

0 0 0 0

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

5. Setup problem

(mass) balance on components

- overall balance

$$F^1 + F^2 = F^3 + F^4$$

- component balances

$$\text{oil} \quad w_{\text{oil}}^2 F^2 = w_{\text{oil}}^3 F^3 + w_{\text{oil}}^4 F^4 \rightarrow 95 = w_{\text{oil}}^3 F^3$$

$$\text{water} \quad w_{\text{H}_2\text{O}}^1 F^1 = w_{\text{H}_2\text{O}}^3 F^3 + w_{\text{H}_2\text{O}}^4 F^4 \rightarrow F^1 = w_{\text{H}_2\text{O}}^4 F^4$$

$$\text{salt} \quad w_{\text{salt}}^2 F^2 = w_{\text{salt}}^3 F^3 + w_{\text{salt}}^4 F^4$$

- Flow ratio

$$\frac{F^2}{F^1} = 4$$

$$\frac{100 \text{ lbm}}{F^1} = 4 \rightarrow F^1 = 25 \text{ lbm}$$

- Mass fraction

$$\text{stream 3: } w_{\text{oil}}^3 + w_{\text{H}_2\text{O}}^3 + w_{\text{salt}}^3 = 1$$

$$\text{stream 4: } w_{\text{oil}}^4 + w_{\text{H}_2\text{O}}^4 + w_{\text{salt}}^4 = 1$$

$$\text{stream 2: } w_{\text{oil}}^2 + w_{\text{salt}}^2 = 1$$

$$\text{stream 1: } w_{\text{H}_2\text{O}}^1 = 1$$

} useful

} not useful relation

- Summary

- 8 variables

- 6 relations (overall, component, mass fraction)

- 8-6 = 2 degrees of freedom \rightarrow need more assumptions

\downarrow * Assume no mixing between oil & water

$$w_{\text{H}_2\text{O}}^3 = 0, \quad w_{\text{oil}}^4 = 0$$

\leftarrow 2 more relations

- 0 degree of freedom now \rightarrow solvable

- Solve Systems of equation

$$F^4 = 29.4 \text{ lbm} \quad w_{\text{salt}}^3 = 0.00615$$

$$F^3 = 95.6 \text{ lbm}$$

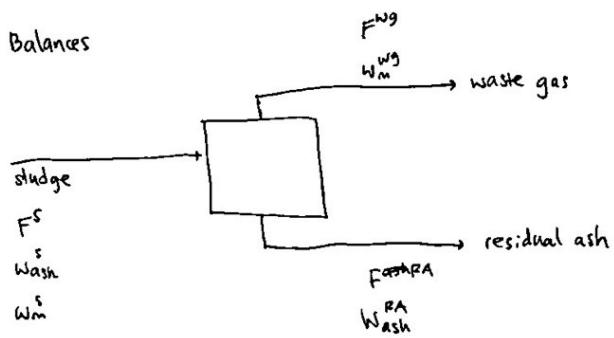
$$F^1 = 25 \text{ lbm}$$

- check soln

- plug back to 2 equations

<< Solving Material Balances

EX 3

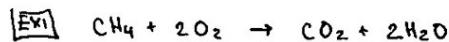


<< Stoichiometry

• general form

$$\sum_{i=1}^n v_i s_i = 0$$

↑ compound
stoich ratio

 $v_i > 0$ product $v_i < 0$ reactant $v_i = 0$ inert (no rxn)

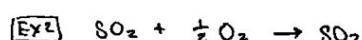
$$v_{\text{CO}_2} = +1 \quad w_{\text{CH}_4} = -1$$

$$v_{\text{H}_2\text{O}} = +2 \quad w_{\text{O}_2} = -2$$

• reactions run in mols

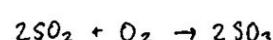
• elements must balance

• stoichiometry does not imply rate



$$w_{\text{SO}_2} = -1 \quad w_{\text{SO}_3} = +1$$

$$w_{\text{O}_2} = -1/2$$



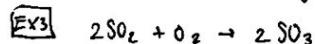
$$w_{\text{SO}_2} = -2 \quad w_{\text{SO}_3} = -2$$

$$w_{\text{O}_2} = -1$$

<< Terminology

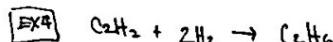
> limiting reactant - compound used up first

> excess reactant - compound will be in excess after what is needed to eliminate the limiting reactant

Feed of 2 mol SO_2 , 3 mol O_2 . find limiting reactant.• Divide by v_i , smallest magnitude is limiting

$$\text{SO}_2 : \left| \frac{2}{-2} \right| = 1 \quad \rightarrow \text{limiting reactant}$$

$$\text{O}_2 : \left| \frac{3}{-1} \right| = 3$$

> fractional excess = $\frac{n_{\text{feed}} - n_{\text{stoich}}}{n_{\text{stoich}}}$ n_{feed} = # moles of excess reactant n_{stoich} = stoichiometric requirement of AFeed of 20 kmol/h C_2H_2 , 50 kmol/h H_2 • stoich ratio $\text{H}_2 : \text{C}_2\text{H}_2 = 2 : 1$ • feed ratio $\text{H}_2 : \text{C}_2\text{H}_2 = 2.5 : 1$ • H_2 fed at greater stoich ratio $\Rightarrow \text{C}_2\text{H}_2$ is limiting

• need 40 kmol/h to react

• H_2 stoich = 40 kmol/h• H_2 feed = 50 kmol/h• fractional excess of $\text{H}_2 = \frac{50-40}{40} = 0.25$

<-- Terminology

> extent of rxn - $\bar{z} = \frac{n_i - n_{i0}}{v_i}$

n_i = mol out of component i

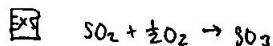
n_{i0} = mol in of component i

v_i = stoich coeff

• only one \bar{z} for every rxn

• mol out = mol in + mol created/destroyed

$$n_i = n_{i0} + v_i \bar{z}$$



Feed 2mol SO_2 , 3mol O_2

	mol in (n_{i0})	mol out (n_i)	mol reacted ($v_i \bar{z}$)
SO_2	2	$2 - \bar{z}$	$-\bar{z}$
O_2	3	$3 - \frac{1}{2}\bar{z}$	$-\frac{1}{2}\bar{z}$
SO_3	0		$+\bar{z}$

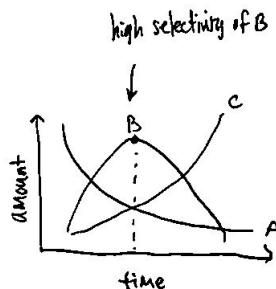
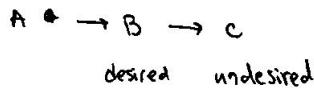
define \bar{z} mol $5 - \frac{1}{2}\bar{z}$
of SO_2

(fraction)
> conversion - $f = \frac{\text{mol reacted}}{\text{mol fed}}$ (usually in terms of limiting reactant)

$$f = \left| \frac{v_i \bar{z}}{n_{i0}} \right|$$

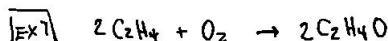
> selectivity = $\frac{\text{amount desired product}}{\text{amount undesired product}}$

Ex6



> Yield = $\frac{\text{amount desired product}}{\text{amount desired product if complete conversion, no side product}} = \frac{\text{actual}}{\text{theoretical}}$

* no standard definition of yield



Feed of 100 kmol C_2H_4 , 100 kmol O_2

in react out

C_2H_4 100 $-2\bar{z}$ $100 - 2\bar{z}$

O_2 100 $-\bar{z}$ $100 - \bar{z}$

$\text{C}_2\text{H}_4\text{O}$ 0 $2\bar{z}$ $2\bar{z}$

C_2H_4 $\left| \frac{100}{2} \right| = 50 \leftarrow \text{limiting reactant}$

O_2 $\left| \frac{100}{-1} \right| = 100$

fractional excess of $\text{O}_2 = \frac{100 - 50}{50} = 1$

conversion = $\left| \frac{v_i \bar{z}}{n_{i0}} \right| = \frac{\bar{z}}{100}$

selectivity = $\frac{\bar{z}}{0} = \infty$

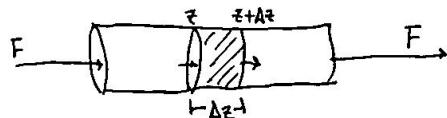
Reaction Balance Tern Approach

- . { molecular H₂
atomic H in H₂
extent of rxn z

→ Molecular Approach

- . not recommended for hand, computer might be needed

[EX1]



- * Assume & facts
 - . steady-state
 - . rxn take place in rate r_{ij}^* species # i rxn # j
 - . density is constant
 - . Flow = $F = \frac{V}{\text{time}}$ = constant
 - . concentration $c_i = \frac{\text{mol}}{\text{Vol}}$
 - . no radial effect

Accumulation = in - out + generation - consumption for $i = 1, 2, 3, \dots$ species

$$0 = Fc_i|_z - Fc_i|_{z+\Delta z} + \left(\sum_{j=1}^m r_{ij}^* \right) \underbrace{\pi R^2 \Delta z}_{V} \quad \text{for } i\text{th species}$$

$$\lim_{\Delta z \rightarrow 0} \frac{c_i|_z - c_i|_{z+\Delta z}}{\Delta z} = \frac{\pi R^2}{F} \sum_{j=1}^m r_{ij}^*$$

$$\frac{dc_i}{dz} = \frac{\pi R^2}{F} \sum_{j=1}^m r_{ij}^* \quad \text{for } i\text{th species}$$

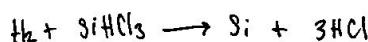
Given initial condition $c_i(0) = c_{i,0}$, give coupled system of ODEs.

Only use when have a simple system with one rxn to solve by hand

→ Atomic Approach

[Ex2]

Growing silica rod



Given:

$$\begin{aligned} \textcircled{1} &\longrightarrow \boxed{\text{ }} \longrightarrow \textcircled{2} \text{ gas} & F_3 &=? \\ F_1 &= 6.22 \text{ kmol} & x_3^{\text{HCl}} &=? \\ x_1^{\text{H}_2} &= 0.58 & x_3^{\text{SiHCl}_3} &=? \\ x_1^{\text{SiHCl}_3} &= 0.42 & x_3^{\text{H}_2} &= 0.233 \\ F_2 &=? & x_3^{\text{Si}} &= 0 \\ x_2^{\text{Si}} &=? \end{aligned}$$

simplifies to

[in = out]

generation = 0

consumption = 0

atom is not destroyed

- * Assume
 - . steady-state
 - . time basis: t = 1h

Ex2 (cont.)

• mol fraction balance

$$x_3^{\text{HCl}} + x_3^{\text{SiHCl}_3} + x_3^{\text{H}_2} = 1$$

• atomic balance

$$\text{H} \quad (2(0.58) + 1(0.42)) 6.22 = (1 \cdot x_3^{\text{HCl}} + 1 \cdot x_3^{\text{SiHCl}_3} + 2 \cdot x_3^{\text{H}_2}) F_3$$

$$\text{Cl} \quad (3(0.42)) 6.22 = (x_3^{\text{HCl}} + 3 \cdot x_3^{\text{SiHCl}_3}) F_3$$

$$\text{Si} \quad (0.42)(6.22) = \cancel{x_3^{\text{HCl}}} \downarrow \cancel{x_3^{\text{H}_2}} + x_3^{\text{SiHCl}_3} F_3$$

Solve the system:

$$\left. \begin{array}{l} F_3 = 8.04 \text{ kmol} \\ F_2 = 1.82 \text{ kmol} \\ x_3^{\text{SiHCl}_3} = 0.099 \\ x_3^{\text{HCl}} = 0.678 \end{array} \right\} \text{for } t=1 \text{ h basis}$$

- Note : atomic balance at steady state : in = out
- atom not created/destroyed
- generation = consumption = 0

• For multiple rxn ,

$$n_i = n_{i,0} + \sum_{j=1}^r D_{ij} \tilde{\gamma}_{ij}$$

↔ Extent of Reaction

Ex3 Same problem in Ex2.

• Define $\tilde{\gamma}$ as mol H₂ reacted

	before	react	after
H ₂	$F_1 \cdot \frac{x_3^{\text{H}_2}}{(0.58)}$ (6.22)	- $\tilde{\gamma}$	$3.61 - \tilde{\gamma}$
SiHCl ₃	$(6.22)(0.42)$	- $\tilde{\gamma}$	$2.61 - \tilde{\gamma}$
Si	-	+ $\tilde{\gamma}$	$\tilde{\gamma}$
HCl	-	+ $3\tilde{\gamma}$	$3\tilde{\gamma}$

$\leftarrow n_{\text{H}_2} = 3.61 - \tilde{\gamma} = F_3 x_3^{\text{H}_2}$

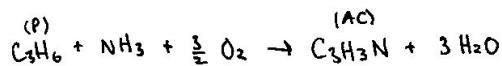
$\leftarrow n_{\text{SiHCl}_3} = 2.61 - \tilde{\gamma} = F_3 x_3^{\text{SiHCl}_3}$

$\leftarrow n_{\text{Si}} = \tilde{\gamma} = F_2 x_2^{\text{Si}}$

$\leftarrow n_{\text{HCl}} = 3\tilde{\gamma} = F_3 x_3^{\text{HCl}}$

« Solving Rxn Stoichiometry

[Ex1] Production of Acrylonitrile



fractional conversion = ?

given product : 5% $\text{C}_3\text{H}_3\text{N}$ feed : 20% C_3H_6 , 20% NH_3 , 60% air $y_{\text{P}}^1 = 0.20$ y_{P}^2 $y_{\text{NH}_3}^1 = 0.20$ $y_{\text{NH}_3}^2$

$$y_{\text{air}}^1 = 0.60 \quad \left\{ \begin{array}{l} y_{\text{N}_2}^1 = 0.474 \\ y_{\text{O}_2}^1 = 0.126 \end{array} \right.$$

 $y_{\text{O}_2}^2$ $y_{\text{N}_2}^2$ $y_{\text{AC}}^2 = 0.05$

★ Assume steady state

★ air is dry air (No H_2O)· 21% O_2 , 79% N_2 ★ Basis : $F^1 = 100 \text{ mol}$

	in ($n_{i,0}$)	react ($\nu_i \bar{z}$)	out ($n_i = n_{i,0} + \nu_i \bar{z}$)
(P) C_3H_6	20	-3	$20 - 3$
NH_3	20	-3	$20 - 3$
O_2	12.6	$-\frac{3}{2} \bar{z}$	$12.6 - \frac{3}{2} \bar{z}$
N_2	47.4	0	47.4
(AC) $\text{C}_3\text{H}_3\text{N}$	0	3	3
H_2O	0	$3 \bar{z}$	$3 \bar{z}$
total	100	$+ \frac{1}{2} \bar{z}$	$100 + \frac{1}{2} \bar{z}$

Fractional conversion

$$f_{\text{O}_2} = \left| \frac{\nu_i \bar{z}}{n_{i,0}} \right| = \left| \frac{(-\frac{3}{2}) (5.13)}{12.6} \right| \times 100\%.$$

= 61%

Known : $y_{\text{AC}}^2 = 0.05 = \frac{\text{mol AC}}{\text{total mol}}$

$$0.05 = \frac{3}{100 + \frac{1}{2} \bar{z}} \Rightarrow \bar{z} = 5.13$$

Limiting Reactant Analysis

C_3H_6	$\left \frac{100(0.2)}{-1} \right = 20$
NH_3	$\left \frac{100(0.2)}{-1} \right = 20$
O_2	$\left \frac{100(0.126)}{-1.5} \right = 9.4 \leftarrow \text{O}_2 \text{ limiting}$

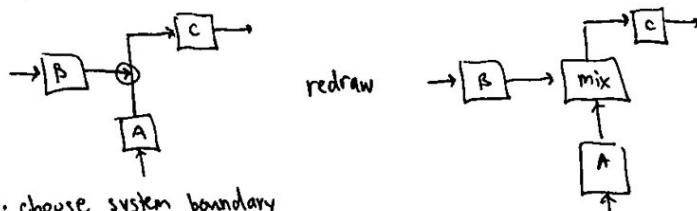
<< Combustion

- > flue gas - product that leaves the combustion furnace
 - on wet basis - all gases + water
 - on dry basis - all gases except water
 - > complete combustion - only products are CO_2 and H_2O
 - > theoretical air - required air for complete combustion (O_2)
 - > excess air - beyond complete combustion
- %, excess = $\frac{\text{actual air} - \text{theoretical}}{\text{theoretical}} \times 100\%$.

<< Multiple Units Process

- same approach as single-unit process

1. draw picture



• choose system boundary

2. label knowns, unknowns

3. state assumption, basis

4. identify problem

5. identify strategy

- relations
- system total
- component: stream, unit
- overall / subsystem?
- how to solve?
 - analytic
 - numerical
 - ASPEN / Python

6. Write soln - based on assumption

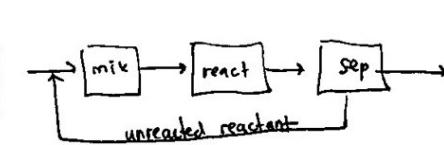
7. check answer

<< Recycle, Purge, Bypass

- recycle - why need this?

- high conversion {
 - (+) use up feed
 - (-) may not be positive, used up too much raw material
- {
 - (+) large energy effect
 - (+) high cost
 - (-) poor selectivity

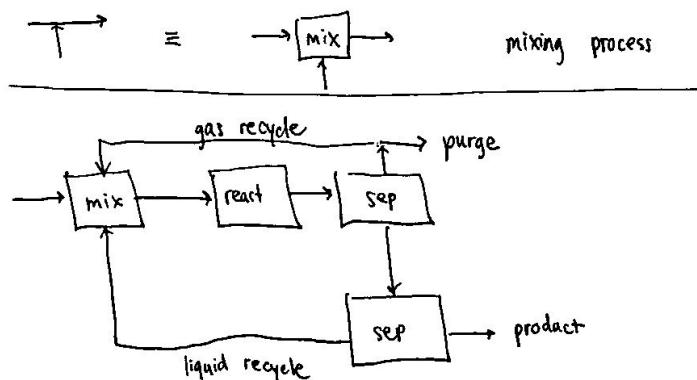
- soln: separate + recycle!



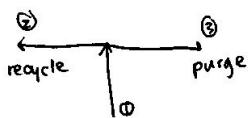
• separate & recycle

↔ Recycle, Bypass, Purge

→ Classic block diagram



→ Purge



$$y_i^1 = y_i^2 = y_i^3$$

$$F^3 = (\text{purge fraction}) F^1$$

$$F^2 = (1 - \text{purge fraction}) F^1$$

→ Recycle Solutions

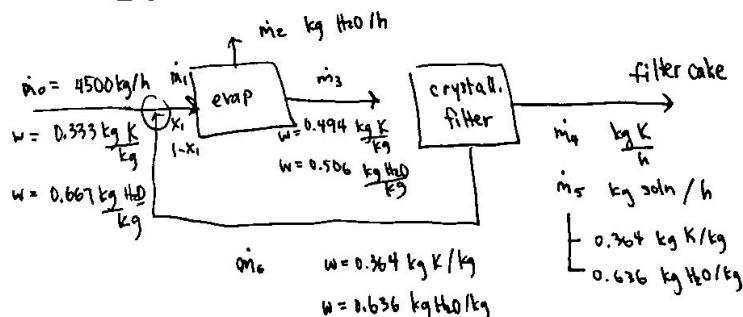
1. Decompose / direct solution

2. Simultaneous equations

3. "tear" stream approach

EX1 Evaporative Crystallization Process

$K: K_2CrO_4$



to be fully labeled,
need to write flow rate
of both solid & liquid stream

Q: calculate rate of evaporation, rate of production of crystalline K_2CrO_4 feed rate for

evaporator & crystallizer, recycle ratio

① Degree of Freedom Analysis

i) Overall system :

3 unknowns : m_2, m_4, m_5

- 2 balances : 2 species (H_2O, K_2CrO_4)

- 1 additional relation : Given $m_4 = 95\%$, total filter cake mass

0 dof. \Rightarrow can determine m_2, m_4, m_5

ii) recycle - fresh feed mixing part

3 unknowns - \dot{m}_6 , x_1 , \dot{m}_1

- 2 balances

1 d.o.f.

iii) evaporator

3 unknowns - \dot{m}_1 , x_1 , \dot{m}_3 (\dot{m}_2 known in i)

- 2 balances

1 d.o.f.

iv) crystallizer / filter

2 unknowns - \dot{m}_3 , \dot{m}_5 (\dot{m}_4 , \dot{m}_7 known in i)

2 balances

0 d.o.f. \Rightarrow can solve for \dot{m}_3 , \dot{m}_5

② Solve it!

i) overall system

$$\cdot \text{total: } \dot{m}_4 = 0.95(\dot{m}_4 + \dot{m}_7)$$

$$\dot{m}_5 = 0.05263 \dot{m}_4$$

$$\cdot K_2CrO_4: \left(0.333 \frac{\text{kg Cr}}{\text{kg}}$$

$$\right) (4500 \text{ kg/h}) = \dot{m}_4 + 0.364 \dot{m}_5$$

$$\left. \begin{cases} \dot{m}_4 = 1470 \text{ kg K}_2CrO_4 \text{ crystals/h} \\ \dot{m}_5 = 77.5 \text{ kg soln/h} \end{cases} \right\}$$

$$\cdot \text{total: } 4500 \text{ kg/h} = \dot{m}_2 + \dot{m}_4 + \dot{m}_5$$

$$\dot{m}_2 = 2950 \text{ kg H}_2O \text{ evaporated/h}$$

ii) crystallizer

$$\cdot \text{total: } \dot{m}_3 = \dot{m}_4 + \dot{m}_5 + \dot{m}_6$$

$$\dot{m}_3 = 1550 \text{ kg/h} + \dot{m}_6$$

$$\left. \begin{cases} \dot{m}_3 = 7200 \text{ kg/h} \\ \dot{m}_6 = 5650 \text{ kg/h} \end{cases} \right\}$$

$$\cdot \text{water: } 0.506 \dot{m}_3 = 0.636 \dot{m}_5 + 0.636 \dot{m}_6$$

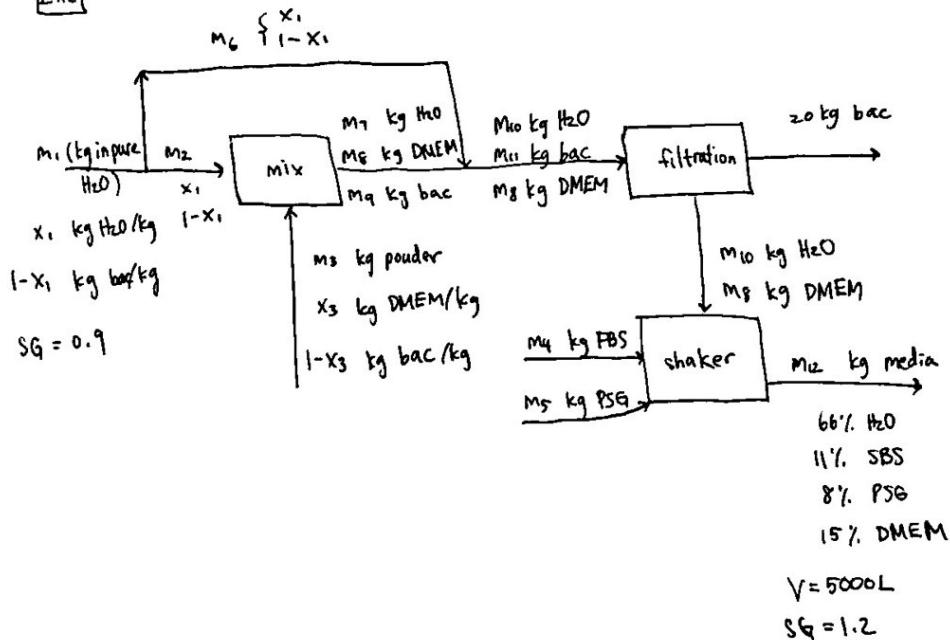
$$\text{recycle ratio} = \frac{\text{Mass of recycle}}{\text{Mass of fresh feed}} = \frac{\dot{m}_6}{4500} = 1.26 \frac{\text{kg recycle}}{\text{kg fresh feed}}$$

→ Recycle, Bypass, Purge

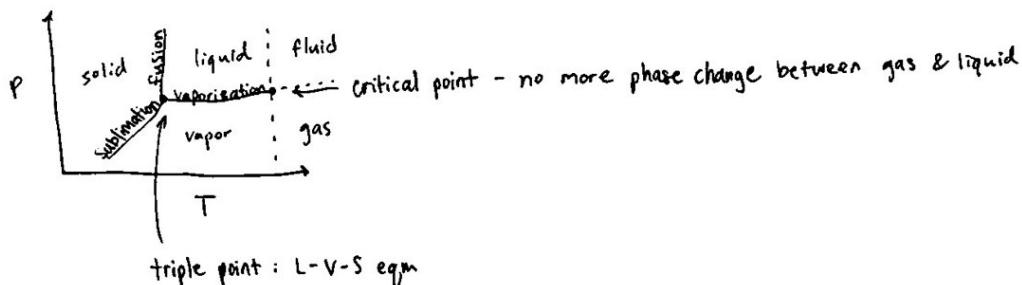
→ Tear stream approach

- simulate each process in sequence following physical flow of stream
- when needed, guess stream from forward/backward ~~of~~ processes (recycle / bypass)
- iterate to get convergence
 - every process
 - every stream
- tools : Excel, ASPEN, Python

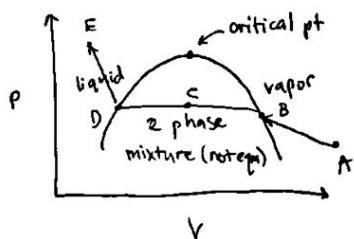
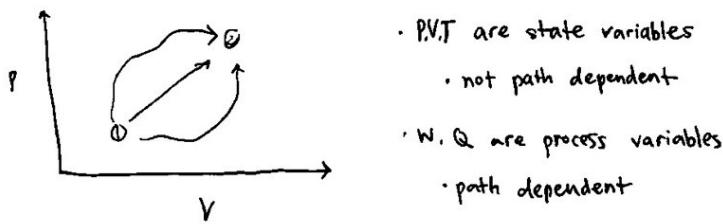
Ex2



<< PVT Behavior of Pure Substance



- > sublimation curve - S-V eqm
- > vaporization curve - V-L eqm
- > fusion curve - S-L eqm
- > fluid - matter that continuously deform in response to a force
 - can be liquid, vapor, gas
 - vapor \neq gas
- > gas - substance that has a defined single thermodynamic state at room temp.
- > fluid phase - no condensation is possible by constant P (isobaric) cooling
no condensation is possible by constant T (isothermal) compression
- > gas phase - can be condensed by isobaric cooling, but not isothermal compression



- > supercritical fluid - fluid where $\begin{cases} T > T_c \\ P > P_c \end{cases}$
- > critical temp T_c - highest temp where species can be in 2 phases
- > critical pressure P_c - corresponding pressure to T_c
- > superheated vapor - vapor present in a gas in less than its saturation amount
 - (A) compress isothermally
- > saturated vapor - substance exists entirely as a vapor at its saturation temperature
 - (B) compress isothermally
- > mixture of vapor & liquid (C)
 - $V_c = V_o(1-x) + V_B x$, $x = \frac{\text{liquid}}{\text{total}}$
 - compress isothermally
- > supersaturated liquid - a liquid about to vaporize
 - (D) compress isothermally
- > subcooled liquid - (compressed)

- At critical point,

$$\left. \frac{\partial P}{\partial V} \right|_{T_c} = 0$$

- Critical point only function of material

• Volume $\left\{ \begin{array}{l} \hat{V} = \frac{\text{vol}}{\text{mass}} \\ \hat{V} = \frac{\text{vol}}{\text{mol}} \end{array} \right.$

<< Equation of State

- in general, a function of P, T, \hat{V} : $f(P, T, \hat{V}) = 0$

- total derivative of V - volume of fluid which is function of T, P, n

$$d\hat{V} = \left. \frac{\partial V}{\partial T} \right|_{P, x_i} dT + \left. \frac{\partial V}{\partial P} \right|_{T, x_i} dP + \underbrace{\sum_{i=1}^n \left. \frac{\partial \hat{V}}{\partial x_i} \right|_{T, P} dx_i}_{0 \text{ for pure substance}}$$

<< Liquid & Solids

- incompressible, independent T

$$\left. \begin{array}{l} \frac{\partial V}{\partial P} \Big|_T = 0 \\ \frac{\partial V}{\partial T} \Big|_P = 0 \end{array} \right\} \Rightarrow \partial V = 0$$

- volume expansivity

$$\beta = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P$$

- isothermal compressibility

$$K = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T$$

$$\frac{dV}{V} = \beta dT - K dP \quad (\text{if } \beta, K \text{ constant})$$

$$\ln\left(\frac{V_2}{V_1}\right) = \beta(T_2 - T_1) - K(P_2 - P_1)$$

<< Ideal Gas

- $PV = nRT$

$$(V = \frac{N}{n})$$

- $PV = RT$

} ideal when

- P is low (best P << 1 atm)
- T > 0°C

- partial pressure $p_i = y_i P$

- Dalton's law $P = \sum p_i = \sum y_i P$

<< Two Parameter Equation of States

- corresponding states: all gases when compared at the same reduced temp & pressure

→ compressibility behave the same.

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

→ Process of

- $\Tr = \frac{T}{T_c}$

- compressibility factor $z = \frac{PV}{RT}$

- for ideal gas $z=1$

- measure of deviation from ideal behavior

- $z = f(\Tr, \Pr)$

- for ideal gases, $\Pr \ll 1$

<< Two Parameter Eqn of States

→ van der Waals (1873)

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

$$a, b = f(T_c, P_c)$$

→ Redlich-Kwong (1949)

$$P = \frac{RT}{V-b} - \frac{a}{T^{\frac{1}{2}}(V)(V+b)}$$

use for nonpolar gas

<< Three Parameter Eqn of States

→ Peng-Robinson

<< Higher Order Eqn

→ virial

→ Benedict Webb Rubin

· 8 param

· accurate for L,V of light hydrocarbon

· read table & graph

<< Equation of States of Mixtures

→ Kay's method

· mixing rules

$$T_c' = \sum_{i=1}^n y_i T_{ci}$$

[EX] air : N₂, O₂

$$\begin{aligned} T_c' &= (0.21)(154.4\text{ K}) + (0.79)(126.1\text{ K}) \\ &\approx 132.1\text{ K} \end{aligned}$$

$$P_c' = \sum_{i=1}^n y_i P_{ci}$$

$$T_r' = \frac{T}{T_c'}$$

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

<< Vapor Pressure

→ Antoine's Eqn

$$\log P^* = A - \frac{B}{T+C}$$

A, B, C constants

T in °C

P* in mmHg

→ Clapeyron Eqn

$$\frac{dP^*}{dT} = \frac{\hat{A}_{\text{Hvap}}}{T(V_g - V_c)}$$

cubic equation of state

· 3 roots for \hat{V}

$\hat{V}_{\text{sat, vapor}}$ - largest

$\hat{V}_{\text{sat, liquid}}$ - smallest

V middle has no significance

<< Gibbs Phase Rule

- For system in eqm.

$$f = 2 + c - p - r$$

↑ ↑ ↗
 degree of freedom # component # phases
 (T)

rxn (independent)

- # of intensive variables that must be specified
 - > intensive variable - does not depend on system size
 - density, specific gravity, temperature, mass frac., mol frac.
 - > extensive variable - depend on system size
 - mass, mol, volume

Ex1 liquid H₂O + vapor H₂O at boiling eqns

$$F = 2 + 1 - 2 - 0 = 1 \quad \rightarrow \text{need 1 intensive variable specified}$$

EX2 pure substance at triple point

$f = 2 + 1 - 3 = 0 \Rightarrow$ at triple point, nonreactive pure substance has 0 def.

Vapor-Liquid Eqn (VLE.)

→ pure V or L component in a noncompressible gas

- $T > T_c$
 - ideal gas law apply
 - at eqn between V and L of component A,

$$\boxed{P_A^* = y_A P = P_A}$$

- if $p_A^* = p_A$
 - \Rightarrow gas is saturated
 - \Rightarrow gas is at dew point

→ Saturation - any gas-vapor combination

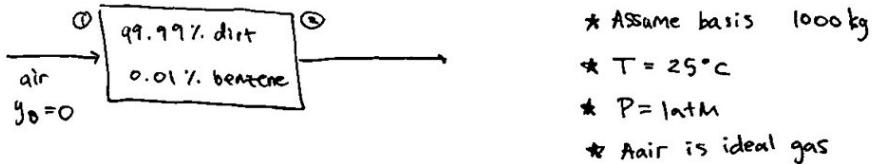
→ humidity - Specifically for air-water combination

$$\begin{aligned} &> \text{relative saturation} - h_r \\ &> \text{relative humidity} - S_r \end{aligned} \} = \frac{P_i}{P_i^*(T)} \times 100\%.$$

$$\left. \begin{array}{l} > \text{absolute saturation - } h_a \\ > \text{absolute humidity - } S_a \end{array} \right\} = \frac{P_i M_i}{(P - P_i) M_{\text{dry}}} = \frac{\text{mass vapor}}{\text{mass dry gas}}$$

$$\begin{aligned} &> \text{molal saturation} \\ &> \text{molal humidity} \end{aligned} \} = \frac{\text{mol vapor}}{\text{mol dry gas}} = \frac{P_i}{P - P_i}$$

Ex3 Dirt contain 0.01% wt benzene. Remove benzene with air. $V_{\text{air}} = ?$



* Air leaving dirt is saturated with benzene $P_B^* = P_B^*$

* Benzene vapor is ideal gas

• By Antoine's eqn,

$$\log P_B^* = A - \frac{B}{T+C} = 6.89272 - \frac{1203.51}{25^\circ\text{C} + 219.5888}$$

$$P_B^* = 95 \text{ mmHg}$$

$$y_B = \frac{P_B^*}{P} = \frac{95 \text{ mmHg}}{760 \text{ mmHg}} = 0.125$$

$$y_A = 1 - y_B = 0.875$$

$$\text{Note that } n_B = y_B n, \quad n_A = y_A n \quad \Rightarrow \quad n_A = \frac{y_A}{y_B} n_B$$

$$n_B = (0.01\%) (1000 \text{ kg}) = 0.1 \text{ kg B} = 1.2 \times 10^{-3} \text{ kmol B}$$

$$n_A = \frac{0.875}{0.125} (1.2 \times 10^{-3} \text{ kmol B}) = 8.4 \times 10^{-3} \text{ kmol air}$$

By ideal gas law $PV = nRT$

$$V_A = \frac{n_A RT}{P} = \frac{(8.4 \times 10^{-3} \text{ kmol}) \left(\frac{10^3 \text{ g/mol}}{1 \text{ kmol}} \right) (82.06 \frac{\text{cm}^3 \text{ atm}}{\text{g mol} \cdot \text{K}}) (298 \text{ K})}{1 \text{ atm}} = 205 \times 10^3 \text{ cm}^3 \text{ air}$$

→ Two immiscible phases

• total vapor pressure is sum of each liquid vapor pressure

$$P = P_A^* + P_B^*$$

→ Henry's law

• when $x_A \rightarrow 0$ (dilute soln of A)
(liquid)

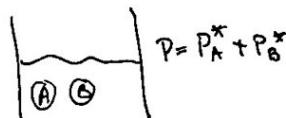
$$P_A = y_A P = H_A x_A$$

↑ mol frac of gas ↙ Henry's law constant

→ Raoult's law

- assume ideal gas, liquid

$$P_i = y_i P = x_i P_i^*(T)$$



[EX1] Calculate pressure & gas phase composition in a system containing a liquid that is 0.3 mol% N₂ and 99.7 mol% H₂O in eqm with N₂ and H₂O vapor at 80°C.

Soh:

- For N₂ use Henry's law since we have dilute gas in liquid

$$P_{N_2} = X_{N_2} H_{N_2} \quad , \text{ where } H_{N_2}(80^\circ\text{C}) = 12.6 \times 10^4 \text{ atm/mol frac}$$

$$= (0.003)(12.6 \times 10^4) = 37.8 \text{ atm}$$

- For H₂O use Raoult's law since not dilute in H₂O in liquid

$$P_{H_2O} = X_{H_2O} P_{H_2O}^*$$

$$P_{H_2O}^*(80^\circ\text{C}) = 355.1 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.467 \text{ atm} \quad (\text{Table B.3})$$

$$P_{H_2O} = (0.997)(0.467 \text{ atm}) = 0.466 \text{ atm}$$

- Find total pressure

$$P = P_{N_2} + P_{H_2O} = \boxed{378.5 \text{ atm}}$$

- For mol frac of gas, use Raoult's law

$$y_i P = P_i$$

$$y_{H_2O} = \frac{P_{H_2O}}{P} = \frac{0.467 \text{ atm}}{378.5 \text{ atm}} = \boxed{1.23 \times 10^{-3} \frac{\text{mol H}_2\text{O}}{\text{mol gas}}}$$

$$y_{N_2} = 1 - y_{H_2O} = \boxed{0.999 \frac{\text{mol N}_2}{\text{mol gas}}}$$

[EX2] An equimolar liquid mixture of benzene and toluene is in eqm with its vapor at 30°C.

What is the system pressure and the composition of vapor?

Soh:

- Henry's law can't be used since equimolar is not dilute.

- Raoult's law needed.

- Antoine's eqn for vapor pressure

$$\log P_B^* = A - \frac{B}{T+C} = 6.906 - \frac{1211}{30+220.8}$$

$$\xrightarrow{\text{Table B.4}} \Rightarrow P_B^* = 119 \text{ mmHg}$$

$$\log P_T^* = 6.9553 - \frac{1343.9}{30+219.38} \Rightarrow P_T^* = 36.7 \text{ mmHg}$$

- Raoult's law

$$P_B = X_B P_B^* = (0.5)(119 \text{ mmHg}) = 59.5 \text{ mmHg}$$

$$P_T = X_T P_T^* = (0.5)(36.7 \text{ mmHg}) = 18.3 \text{ mmHg}$$

$$P = P_B + P_T = \boxed{77.9 \text{ mmHg}}$$

- Raoult's law

$$y_B = \frac{P_B}{P} = \boxed{0.764 \frac{\text{mol B}}{\text{mol}}}$$

$$y_T = 1 - y_B = \boxed{0.236 \frac{\text{mol T}}{\text{mol}}}$$

① Antoine

↑

② Water → ③ Table B.3

④ dilute → ⑤ Henry's law

↓

⑥ Raoult's law

<< Recap

- pure liquid $y_i P = P_i^*$ (y for gas, x for liquid)
- immiscible liquids $P_i^* + P_j^* = P^*$
- Henry's law
(dilute liquid component) $y_i P = x_i H_i$
- Raoult's law $y_i P = x_i P^*$ (ideally) $\bar{\Phi}_i = 1, \gamma_i = 1$
 $y_i \bar{\Phi}_i P = x_i \gamma_i P^*$ (real)
 $\begin{matrix} \uparrow & \uparrow \\ \text{fugacity} & \text{activity} \\ \text{coeff} & \text{coeff} \end{matrix}$

partition/distribution coefficient

$$\frac{y_i}{x_i} = K_i = \frac{x_i P^*}{\bar{\Phi}_i P} \underset{\substack{\uparrow \\ \text{partition coeff}}}{\approx} \frac{P_i^*}{P}$$

- If $P^* > P, K_i > 1$
- If $P^* < P, K_i < 1$

<< VLE Calculation

> bubble point - T at which first bubble of vapor forms at constant P

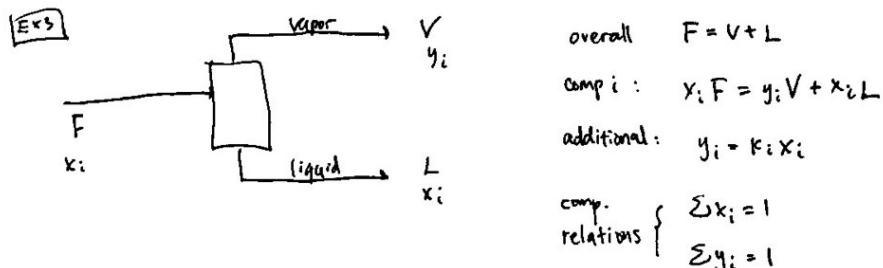
> dew point - T at which vapor becomes saturated

at bubble point, $y_i = K_i x_i$

- if $\sum K_i x_i < 1$, subcooled liquid
- if $\sum K_i x_i = 1$, saturated liquid
- if $\sum K_i x_i > 1$, vapor exist in system

at dew point, $y_i = K_i x_i$

- if $\sum \frac{y_i}{x_i} < 1$, superheated vapor
- if $\sum \frac{y_i}{x_i} = 1$, saturated vapor
- if $\sum \frac{y_i}{x_i} > 1$, liquid exist in system



<< Partition Coefficients

partition coeff

$$y_i = K_i x_i \quad \begin{cases} K_i > 1, \text{ favor gas phase} \\ K_i < 1, \text{ favor liquid phase} \end{cases}$$

obtain through

{ experiment
relationships

Raoult's law

$$y_i \cancel{\equiv} P = \gamma_i x_i P_i^* \quad (\cancel{\equiv} : 1, \gamma_i = 1)$$

$$\frac{y_i}{x_i} = K_i = \frac{P_i^*}{P}$$

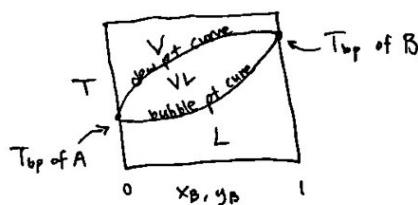
Henry's law

$$K_i = \frac{H_i}{P} \propto$$

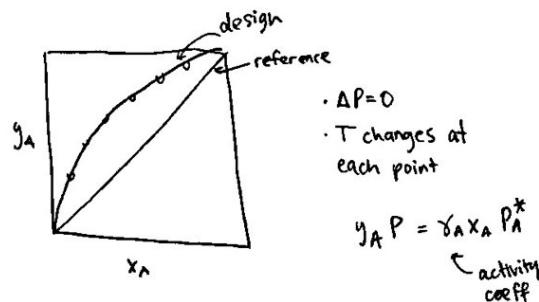
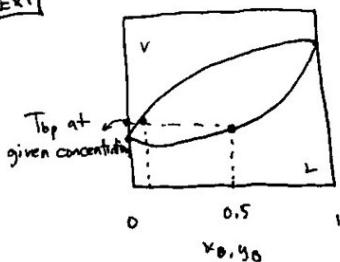
<< Binary VLE Diagram

For mixture of A and B

$$\rightarrow \Delta P = 0$$



(EX1)



- $\Delta P = 0$
- T changes at each point

$$y_A P = \gamma_A x_A P_A^*$$

activity coeff

End of Multiphase System

← Intro to Thermo

- Accumulation of energy in system = total transfer of energy into system through syst. boundary - total transfer of energy out of syst thru syst boundary + total energy generated in the syst - total energy consumed in system
- Accumulation = in - out + generation - consumption

• 1st law of thermo - energy cannot be created or destroyed

→ Types of energy

- internal energy

- U
- \hat{U}
extensive
energy/mol
- \tilde{U}
intensive
energy/mass

- energy of molecules
 - translational
 - vibrational
 - rotational

• no zero state - ΔU matters, U not so much

• state function $\hat{U}(T, V)$

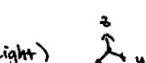
- kinetic energy, E_k

- $E_k = \frac{1}{2} M v^2$

- $\tilde{E}_k = \frac{1}{2} m v^2$ energy / mass

- $\dot{E}_k = \frac{1}{2} \dot{m} v^2$ energy / time → power for flowing fluid

- potential energy, E_p

- $E_p = mgz$ (z is height) 

- $\tilde{E}_p = gz$

- $\dot{E}_p = \dot{m} gz$ for flowing fluid

- total energy

- $E = U + E_k + E_p$

<< Intro to Thermo

→ Energy transfer

→ heat

→ heat - energy transfer due to a temperature diff between syst & surrounding

- Q [Btu]

- \dot{Q} [J/s]

- \hat{Q} [cal/kgmol]

- \tilde{Q} [Btu/kg]

} path function, process variable

} path dependent

• conduction of heat

- $Q = A k (T_2 - T_1)$

A - cross sectional area

k - thermal conductivity

• convection of heat

- $\dot{Q} \propto \Delta T$

• radiation of heat

- $\dot{Q}_{rad} \propto (T_1^4 - T_2^4)$

<< Intro to Thermo

→ Energy Transfer
→ Work

> work - energy transfer that is not heat

- generally, $W = F_s$

- work is path dependent

- types of work

- | | |
|---|---------------|
| <ul style="list-style-type: none"> deformation expansion/contraction electrical Magnetic spring forces mechanical | flow |
|---|---------------|

> shaft work W_s - rate of work done on a process fluid by a moving part within system

> flow work W_{fl} - rate of work done on fluid at system inlet minus at outlet

→ Sign Convention

- \oplus heat transferred into system
- \oplus work done on system

→ Enthalpy

> enthalpy H - $H = U + PV$

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

- no zero state
- state fn
- useful in flow system

<< Types of Systems

- Energy balance for closed system

$$\frac{dE}{dt} = E_{in} - E_{out} = E_f - E_{in}$$

$$\Delta E = Q + W$$

$$\Delta U + \Delta E_k + \Delta E_p = Q + W$$

- | | |
|------------------|---|
| $\Delta E_k = 0$ | if not accelerating |
| $\Delta E_p = 0$ | if not rising / falling |
| $\Delta U = 0$ | if no phase change, chem rxn, T change |
| $Q = 0$ | if insulated system, or syst & surr T same, (adiabatic) |
| $W = 0$ | if no moving parts, no radiation, electric current (no flow in closed system) |

<< Types of Systems

- Energy balance for open system

$$\frac{dE}{dt} = \sum_i^{\text{all streams}} \left[\int (\tilde{U}_i + \tilde{E}_{K,i} + \tilde{E}_{P,i} + p\tilde{V}_i) dm_i \right] + \dot{Q} + \dot{W}_s$$

\dot{Q} all work except
 \dot{W}_s , accounted
 by $p\tilde{V}_i$

- integral balance:

$$\Delta(\tilde{E}) = \sum_i [\tilde{H}_i + \tilde{E}_K + \tilde{E}_P] m_i + \dot{Q} + \dot{W}_s$$

- steady state system:

$$0 = \sum_i [\tilde{H}_i + \tilde{E}_K + \tilde{E}_P] m_i + \dot{Q} + \dot{W}_s$$

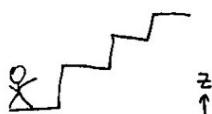
$$\Delta \dot{H} + \Delta \dot{E}_K + \Delta \dot{E}_P = \dot{Q} + \dot{W}_s$$

- simplification

- $\dot{W}_s = 0$ no moving parts
- $\Delta E_P = 0$ stream enter and leave at same level of height
- $\dot{Q} = 0$ if syst & surr. T same
- $\Delta E_K = 0$ if linear velocity of all stream are same

Ex1

7.2



- * Assume 1 flight of stairs = 14 ft (google)
- * Assume average person = 150 lb
- * Assume all cal burned will be from work in creating potential energy from climbing the stairs

$$\Delta U + \Delta E_k + \Delta E_p = Q + W$$

$$\Delta E_p = mg \Delta z$$

$$m = 150 \text{ lb}$$

$$g = 32.174 \text{ ft/s}^2$$

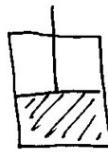
$$1090 \text{ food cal} \times \frac{1000 \text{ cal}}{1 \text{ food cal}} = 1.09 \times 10^6 \text{ cal} = E_p$$

$$1.09 \times 10^6 \text{ cal} = (150 \text{ lb}) (32.174 \text{ ft/s}^2) n_{\text{flight}} \left(\frac{14 \text{ ft}}{1 \text{ flight}} \right) \left(\frac{1 \text{ lb}_f}{32.174 \text{ ft lbm/s}^2} \right) \left(\frac{0.23901 \text{ cal}}{0.7376 \text{ ft lbF}} \right)$$

$$n_{\text{flight}} = 1602 \text{ flights}$$

Ex2

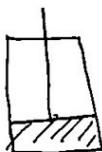
7.12



$$V_i = 5 \text{ L}$$

$$T_i = 30^\circ\text{C}$$

$$P_i = 5 \text{ bar}$$



$$P_f = 3.80 \text{ bar}$$

$$V_f = ?$$

$$T_f = ?$$

closed system

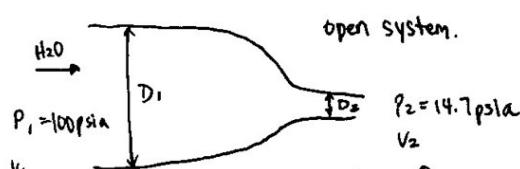
$$(a) \Delta U + \Delta E_k + \Delta E_p = Q + W$$

$$\Delta U = Q + W$$

$$(b) \text{ If iso thermal, } \Delta U = 0$$

$$Q = -W = -7.65 \text{ L-bar} \times \frac{8.314 \text{ J}}{0.08314 \text{ L-bar}} = -765 \text{ J} \quad (\text{heat leaving syst})$$

Ex3 Water flow through a nozzle where $D_1 \gg D_2$. How fast will H_2O come out?



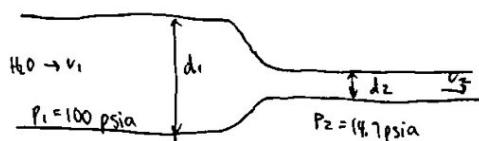
open system.

★ ASSUME

$$\tilde{\Delta H} + \Delta \tilde{E}_k + \Delta \tilde{E}_p = Q + W$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + V\Delta P$$

EX1 Find v_2 .



Assume $Q=0$

$\dot{W}_s=0$

fluid incompressible
slow reversible

$$\text{Open system } \Delta \tilde{E}_k + \Delta \tilde{E}_p + \Delta \tilde{H} = \dot{Q} + \dot{W}_s$$

$$\Delta \tilde{E}_k + \Delta \tilde{H} = 0$$

$$\Delta \tilde{E}_k = -\frac{1}{\rho} \Delta P$$

$$\frac{1}{2} (v_2^2 - v_1^2) = -\frac{\Delta P}{\rho}$$

$$\left\{ \begin{array}{l} \Delta H = dU + d(PV) \\ \Delta \tilde{H} = \dot{Q} + \Delta(P\tilde{V}) \\ \tilde{V} = \frac{1}{P} \end{array} \right. \quad \tilde{V} = \frac{1}{P}$$

$$\Delta \tilde{H} = \frac{1}{\rho} \Delta P$$

If $d_1 \gg d_2$,

then $v_1 \approx v_2$

so $v_1^2 \rightarrow 0$

$$v_2^2 = -\frac{2 \Delta P}{\rho}$$

$$v_2 = \sqrt{\frac{(14.7 - 100) \text{ psia}}{62.4 \frac{\text{lbfm}}{\text{ft}^3}} \frac{144 \text{ in}^2}{1 \text{ ft}^2} \frac{\frac{1 \text{ lbf}}{1 \text{ in}^2}}{1 \text{ psia}}} = \frac{1 \text{ lbf}}{32.174 \frac{\text{lbfm ft}}{\text{ft}^2 \text{s}^2}} = 112 \text{ ft/s}$$

--- Mechanical Energy Balance

• Assume steady state

$$(\tilde{H}_{\text{out}} + \tilde{E}_k + \tilde{E}_p) \dot{m}_{\text{out}} - (\tilde{H}_{\text{in}} + \tilde{E}_k + \tilde{E}_p) \dot{m}_{\text{in}} = \dot{Q} + \dot{W}_s$$

• If incompressible,

$$\tilde{V} = \frac{1}{P}, \quad \Delta \tilde{H} = \Delta \tilde{U} + \frac{1}{\rho} \Delta P$$

• So

$$(\Delta \tilde{U} + \frac{\Delta P}{\rho} + \frac{1}{2} \Delta V^2 + g \Delta z) = \frac{\dot{Q}}{\dot{m}} + \frac{\dot{W}_s}{\dot{m}}$$

• Friction loss - $\tilde{F} = \Delta \tilde{U} - \frac{\dot{Q}}{\dot{m}}$

• General balance

$$\boxed{\frac{\Delta P}{\rho} + \frac{1}{2} \Delta V^2 + g \Delta z + \tilde{F} = \frac{\dot{W}_s}{\dot{m}}}$$

• Bernoulli equation

$$\left(\tilde{F} \approx 0 \right)$$

$$\dot{W}_s = 0$$

$$\boxed{\frac{\Delta P}{\rho} + \frac{1}{2} \Delta V^2 + g \Delta z = 0}$$

$\Delta U, \Delta H$ Calculation

• U, H have no zero state, only changes $\Delta U, \Delta H$

• $\tilde{H}(1\text{atm}, 30^\circ\text{C}) = 37.5 \text{ J/mol}$ implies

$$\tilde{H}(1\text{atm}, 30^\circ\text{C}) - \tilde{H}(\text{Pref}, T_{\text{ref}}) = 37.5 \text{ J/mol}, \text{ with } \tilde{H}(\text{Pref}, T_{\text{ref}}) = 0$$

• Calculate using tables & charts

Ex2 $P = 1\text{atm}$

$$T = 340^\circ\text{F} \quad \tilde{H} = 1320 \text{ btu/lbm}$$

$$T = 360^\circ\text{F} \quad \tilde{H} = 1380 \text{ btu/lbm}$$

Find $\tilde{H}(T = 344^\circ\text{F})$.

$$= 1320 + \frac{1380 - 1320}{360 - 340} (344 - 340)$$

$$= 1332 \text{ btu/lbm}$$

• Pressure effect on U, H

• condensed phase (L,S) if incompressible,

$$\left(\frac{\partial U}{\partial P}\right)_T = 0 \quad \Rightarrow \quad \Delta \tilde{U} = \tilde{V} \Delta P \quad (\text{usually negligible compared to temp effect})$$

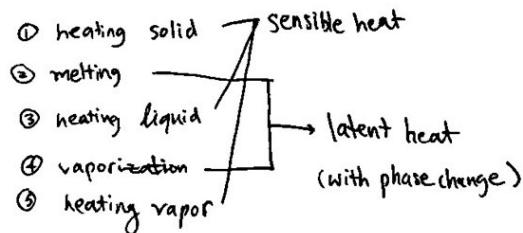
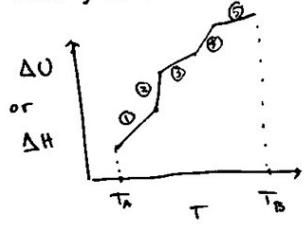
• ideal gas

$$\left(\frac{\partial \tilde{U}}{\partial P}\right)_T = 0 = \left(\frac{\partial \tilde{H}}{\partial P}\right)_T$$

• for real gas, the pressure effect tends to be small ($P < 10 \text{ bars}$)

• Temperature effect on U, H

Ex3 Heating Solid



$$\Delta \hat{U} = \sum \Delta \hat{U}_i$$

$$\Delta \hat{H} = \sum \Delta \hat{H}_i$$

• For condense phase, $\Delta \hat{U} \approx \Delta \hat{H}$

• For vapor phase, $\Delta \hat{U} \neq \Delta \hat{H}$

• sensible heat calculation

$$\hat{c}_v = \left(\frac{\partial \tilde{U}}{\partial T}\right)_v \quad ; \quad \hat{c}_p = \left(\frac{\partial \tilde{H}}{\partial T}\right)_p$$

• condensed phase $\hat{c}_v \approx \hat{c}_p$ good approx for moderate T range

• ideal gas $\hat{c}_v - \hat{c}_p = R$

• For nonconstant C ,

$$\Delta U = \int_{T_1}^{T_2} \hat{c}_v dT$$

$$\Delta H = \int_{T_1}^{T_2} \hat{c}_p dT$$

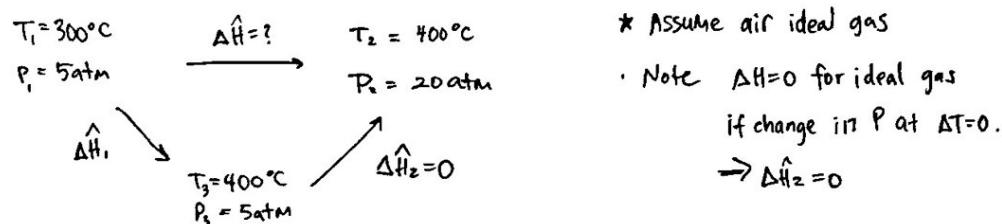
Ideal gas

$$\text{- monoatomic} \quad \hat{c}_p = \frac{5}{2} R \quad \hat{c}_v = \frac{3}{2} R$$

$$\text{- polyatomic} \quad \hat{c}_p = \frac{7}{2} R \quad \hat{c}_v = \frac{5}{2} R$$

<< Enthalpy Calculation

Ex1 2kg air at 300°C and 5atm. We heat it to 400°C at 20 atm. What is ΔH?



$$\text{Since } \Delta\hat{H}_2 = 0, \quad \Delta\hat{H} = \Delta\hat{H}_1 + \Delta\hat{H}_2^0 \Rightarrow \Delta\hat{H} = \Delta\hat{H}_1$$

[Method 1] * Assume \hat{c}_p constant, then $\hat{c}_p = \frac{7}{2}R$ (polyatomic gas)

$$\begin{aligned}\Delta H &= M \int_{T_1}^{T_2} \hat{c}_p dT = M \frac{7}{2} R \int_{300}^{400} dT = M \frac{7}{2} R (400 - 300) {}^\circ C \\ &= \frac{7}{2} (8.314 \text{ kJ/(kg·mol·}{}^\circ\text{C)}) \left(\frac{1 \text{ kg mol}}{29 \text{ kg}} \right) (2 \text{ kg}) (100 {}^\circ\text{C}) \\ &= 200 \text{ kJ}\end{aligned}$$

[Method 2] By Table B.8, $\hat{h}_1 = 8.17 \text{ kJ/mol}$ @ 300°C } with reference state
 $\hat{h}_3 = 11.24 \text{ kJ/mol}$ @ 400°C }

$$\Delta H = M \Delta\hat{H} = 2000 \text{ g} \left(\frac{1 \text{ kg mol}}{29 \text{ g}} \right) (11.24 - 8.17) \text{ kJ/mol = 211.7 kJ}$$

[Method 3] By Table B.2, read air c_p param

* Assume $\hat{c}_p = a + bT + cT^2$ second-order relationship

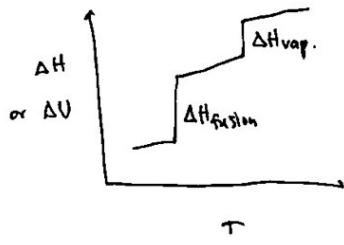
$$\begin{aligned}\Delta H &= M \int_{T_1}^{T_2} \hat{c}_p dT = M \int_{T_1}^{T_2} (a + bT + cT^2) dT \\ &= M \int_{T_1}^{T_2} 28.94 \times 10^{-3} + 0.4147 \times 10^{-5} T + 0.3191 \times 10^{-8} T^2 dT \\ &= M \left[28.94 \times 10^{-3} T + 0.4147 \times 10^{-5} \frac{T^2}{2} + 0.3191 \times 10^{-8} \frac{T^3}{3} \right]_{300}^{400} \\ &= 2000 \text{ g} \left(\frac{1 \text{ kg mol}}{29 \text{ g}} \right) (11.976 - 8.897) \text{ kJ/(mol·}{}^\circ\text{C)} \\ &= 212.3 \text{ kJ}\end{aligned}$$

<< Enthalpy of Mixtures

- Mixture - if we have binary mix A+B
 - works best at ideal gas
 - works well { real gases
similar liquid

$$\begin{aligned}\Delta H_{\text{mix}} &= M_A \int_{T_1}^{T_2} c_{pA} dT + M_B \int_{T_1}^{T_2} c_{pB} dT \\ &= M \left[w_A \int_{T_1}^{T_2} c_{pA} dT + w_B \int_{T_1}^{T_2} c_{pB} dT \right] \\ &= M \left[w_A \int_{T_1}^{T_2} a_A + b_A T + c_A T^2 dT + w_B \int_{T_1}^{T_2} a_B + b_B T + c_B T^2 dT \right] \\ &= m \int_{T_1}^{T_2} (w_A a_A + w_B a_B) + (w_A b_A + w_B b_B) T + (w_A c_A + w_B c_B) T^2 dT\end{aligned}$$

<< Latent Heat Calculations



- associated with phase change
- usually obtained from tables
- estimation technique

Clayperon Eqn

$$\frac{dp^*}{dT} = \frac{\tilde{\Delta}H_{\text{vap}}}{T(\tilde{V}_g - \tilde{V}_l)}$$

Assume $\tilde{V}_g \gg \tilde{V}_l$, ideal gas, $\tilde{\Delta}H_{\text{vap}}$ constant,

Clausius Clayperon Eqn

$$\ln \frac{P_1^*}{P_2^*} = \frac{\Delta H_{\text{vap}}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

- ΔH_{phase} dominates over $\Delta E_k, \Delta E_p \Rightarrow \approx 0$

- Enthalpy of phase change is large over other energy.

EX1 At what rate in kW must heat be transferred to liquid stream of methanol at normal boiling point to generate 1500 g/min of saturated methanol vapor?

* Neglect $\Delta E_k, \Delta E_p$, since have phase change.

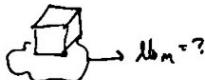
$$\dot{Q} = \dot{n} \hat{\Delta H} \quad (\text{Table B.1 } \hat{\Delta H}_v = 35.27 \text{ kJ/mol})$$

$$\dot{Q} = 1500 \frac{\text{g CH}_3\text{OH}}{\text{min}} \left(\frac{1 \text{ mol}}{32 \text{ g}} \right) \left(\frac{35.27 \text{ kJ}}{1 \text{ mol}} \right) \left(\frac{1 \text{ min}}{60 \text{ s}} \right) \text{ at } T_{bp} = 64.7^\circ\text{C}$$

$$= 27.6 \text{ kW}$$

EX2

8.28



$$\text{latent heat } (\text{Table B.1}) \quad \hat{\Delta H}_m = 6.0095 \text{ kJ/mol}$$

$$\hat{\Delta H}_m = 6.0095 \frac{\text{kJ}}{\text{mol}} \left(\frac{1 \text{ mol}}{18.016 \text{ g}} \right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{0.239 \text{ cal}}{1 \text{ J}} \right) \left(\frac{1 \text{ food cal}}{10^3 \text{ cal}} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 80 \text{ food cal}$$

$$\Delta H = \int_0^{37} C_p dT + \hat{\Delta H}_m \quad (\text{Table B.2 for } C_p)$$

$$= \int_0^{37} 75.4 \times 10^{-3} dT + \hat{\Delta H}_m$$

$$= 2.7898 \frac{\text{kJ}}{\text{mol}} + \hat{\Delta H}_m$$

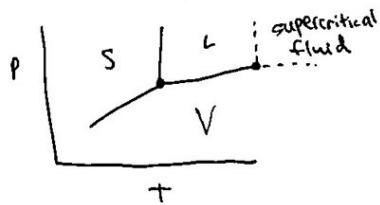
$$= 37 \text{ food cal} + 80 \text{ food cal}$$

$$= 117 \text{ food cal}$$

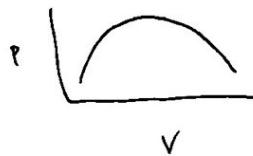
$$1 \text{ lb}_m \times \frac{3500 \text{ food cal}}{1 \text{ lb}_m} \times \frac{1 \text{ kg ice}}{117 \text{ food cal}} \times \frac{2.204 \text{ lb}_m}{1 \text{ kg}} = 66 \text{ lb}_m \text{ ice}$$

Phase Behavior & Equation of State

→ PVT behavior of pure substances



- critical properties
- supercritical fluid T_c, P_c



→ Equation of State

- total derivative

- liquid, solid property

- volume expansivity $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$

- isothermal compressibility $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$

- ideal gas law

- $PV = nRT$

- $PV = nRT$

- two parameters eqn of state

- compressibility eqn of state

- $z = \frac{PV}{nRT}$ ideal gas $z=1$

- $P_r = \frac{P}{P_c}, T_r = \frac{T}{T_c}$

- Van der Waals eqn of state

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

- Redlich-Kwong eqn of state

- Other three parameter eqn of state

- Soren-Riedlich-Kwong

- Peng-Robinson

- Higher Order Eqn of State

- tables

- graphs

→ Eqn of State for Mixtures

- Kay's Method

$$T_c' = \sum y_i T_{ci} \rightarrow T_r' = \frac{T}{T_c}$$

$$P_c' = \sum y_i P_{ci} \rightarrow P_r' = \frac{P}{P_c}$$

→ VLE

- vapor pressure

- Antoine's eqn.

$$\log P^* = A - \frac{B}{T+C} \quad (\text{units!})$$

- Table B.4

- Clapeyron eqn

$$\frac{dP^*}{dT} = \frac{\Delta H_{\text{vap}}}{T(\bar{V}_g - \bar{V}_l)}$$

- Clausius-Clapeyron eqn

$$\ln \left(\frac{P_1^*}{P_2^*} \right)$$

- Gibbs Phase Rule

$$F = 2 + C - P - r$$

<< VLE Calculations

→ Special Cases

- pure in noncondensable gas

$$P_i^* = P_i = y_i P$$

- two immiscible liquid

$$P = P_A^* + P_B^*$$

- Henry's law

$$y_i P = H_i X_i$$

- Raoult's law

$$y_i P = y_i P_i^*$$

→ EqM Constant -

- Partition coeff

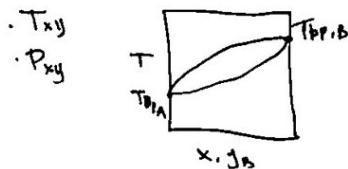
$$K = \frac{y_i}{x_i} = \frac{P_i^*}{P}$$

→ VLE Calculations

- bubble point
- dew point
- isothermal flash

| L17

→ Binary VLE Diagram



→ Humidity

$$\text{relative humidity} = \frac{P_i}{P_i^*(T)} \times 100\%$$

<< Energy Balance Review

→ Intro to thermo

- 1st law of thermo - conservation of energy

• TYPES of energy

- Internal U , state fun, no zero state $U(T, V)$

- Kinetic $E_k = \frac{1}{2}mv^2$

- Potential $E_p = MgZ$

- Total $E = U + E_k + E_p$

• Energy Transfer (across syst boundary)

• Heat Q

- conduction
- convection
- radiation

• Work W

- flow work $W_{fi} = \Delta(PV)$

- shaft work W_s

- moving parts

• Sign Convention

- ⊕ heat add to syst surr → syst

- ⊖ work done on syst surr → syst

path
dependent

• Enthalpy

- $\Delta H = \Delta U + \Delta(PV)$

- useful for flow syst. (closed syst $\Delta H = \Delta U$)

- state fun, no zero state

- $H = H(P, T)$

• System Energy Balance

- closed system

$$\Delta U + \Delta E_k + \Delta E_p = Q + W$$

- open system

$$\dot{\Delta H} + \dot{\Delta E}_k + \dot{\Delta E}_p = \dot{Q} + \dot{W}_s$$

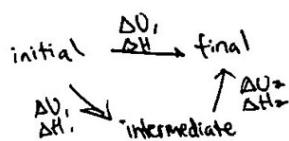
• Mechanical Balance

- open system

- Bernoulli equation

<< Energy Balance w/o Reaction Review

- $\Delta U, \Delta H$ w/o Rxn



- temperature effect

- $\Delta U, \Delta H$ differs by $\Delta(PV)$

- important for gas.

- sensible heat calculation

$$C_p, C_v$$

$$\text{condensed } C_v \approx C_p$$

$$\text{ideal gas } C_p \approx C_v + R$$

$$\text{Table B.2, } C_p = a + bT + cT^2$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT$$

(Mixtures

- sum weighted by fraction -

- latent heat

• tables (Table B1-B4)

• Clausius-Clapeyron eqn

- use tables

- linear interpolation

- pressure effects usually small

- condensed phase (L,S)

- incompressible

$$\Delta V = 0, \Delta H \approx \text{small}$$

- ideal gas

$$\Delta U = 0, \Delta H = 0$$

- real gas

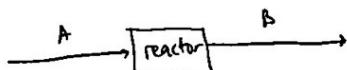
• like ideal gas approx

<< Energy Balance with Rxn

→ Standard Heat of Rxn

- bonds breaking & forming

Consider a single component rxn



$$\dot{Q} = 0 \quad \dot{\Delta E_k} = 0 \quad \dot{\Delta H} = 0$$

$$\dot{W}_s = 0 \quad \dot{\Delta E_p} = 0$$

$$m\tilde{H}_2 - m\tilde{H}_1 = 0$$

$$\tilde{H}_2 - \tilde{H}_1 = 0$$

$$(\tilde{H}_2 - \tilde{H}_{ref}) - (\tilde{H}_1 - \tilde{H}_{ref}) = 0$$

$$(\tilde{H}_2^0 - \tilde{H}_1^0) - (\tilde{H}_{ref}^0, \tilde{H}_{ref}^A) = 0$$

$\underbrace{\Delta H_{rxn}^0}$, standard heat of rxn

ΔH_f^0 of element is 0

- choice of reference

ΔH_f^0 standard heat of formation (1 atm, 25°C)

ΔH_c^0 of combustion product & O₂ is 0

ΔH_c^0 standard heat of combustion (1 atm, 25°C)

<< Recap

- $\Delta\hat{H}_{rxn}^\circ$ - standard heat of rxn at 25°C, 1 atm
- ΔH_f° - standard heat of formation $\rightarrow \Delta H_f^\circ = 0$ for elements
- ΔH_c° - standard heat of combustion $\rightarrow \Delta H_c^\circ = 0$ for O₂ and combustion product

$$\Delta\hat{H}_{rxn}^\circ = \sum n_i (\Delta\hat{H}_f^\circ)_i = - \sum n_i (\Delta H_c^\circ)_i$$

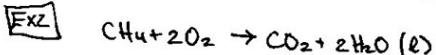
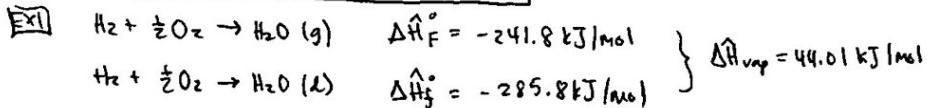


Table B.1 $\Delta H_f^\circ = (-1)(-74.84 \text{ kJ/mol}) + (-2)(0) + (1)(-393.5 \text{ kJ/mol}) + (2)(-285.8 \text{ kJ/mol})$
 $= -890.4 \text{ kJ/mol}$

$$\Delta H_c^\circ = - \left[(-1)(-890.4 \text{ kJ/mol}) + (-2)(0) + (1)(0) + (2)(0) \right]$$
 $= -890.4 \text{ kJ/mol}$

<< Heat of Reaction at Nonstandard Condition

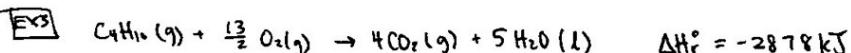
• $\Delta H_{rxn}(T, P) = \Delta H_{rxn}(T_0, P_0) + \bar{z} \Delta H_{rxn}^\circ(T_0, P_0)$

$T_0 = 25^\circ\text{C}, P_0 = 1 \text{ atm}$

• $\Delta H_r > 0$ endothermic

$$\bar{z} = \frac{n_i}{(P_0 V_i)} = \frac{\dot{V}_i}{(P_0 V_i)}$$

(batch) (cont.)

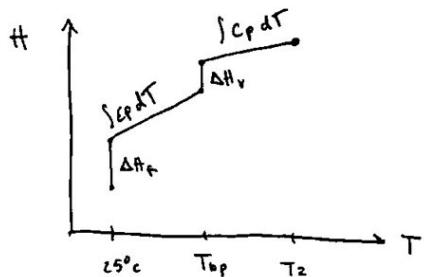


Calculate ΔH (kJ/s) if 2400 mol/s CO₂ produced in the rxn at STP.

$$\bar{z} = \frac{\dot{n}_{CO_2}}{\dot{n}_{CO_2}} = \frac{2400 \text{ mol CO}_2/\text{s}}{4 \text{ mol CO}_2/\text{s}} \times \frac{1 \text{ mol rxn/s}}{1 \text{ mol CO}_2/\text{s}} = 600 \text{ (mol rxn/s)}$$

$$\bar{z} \Delta H_{rxn}^\circ = 600(-2878 \text{ kJ}) = -1.73 \times 10^6 \text{ kJ} \quad \left| \frac{\dot{V}_i}{V_i} \right| = -1.73 \times 10^6 \text{ kJ/s}$$

Ex4 Suppose A is a product and vapor at outlet continuous T₂. A is liquid at T_{ref}.



$$\Delta H_A = \Delta H_r^\circ + \int_{25^\circ\text{C}}^{T_{bp}} C_p(u) dT + \Delta H_{vap} + \int_{T_{bp}}^{T_2} C_p(v) dT$$