CBE 140
Spring 2020
Exam #2 Solutions

- **Problem #1** −12.5

a.) True 2.5
b.) True 2.5
c.) True 2.5
d.) True 2.5
e.) False 2.5

- **Problem 2**

2.5 pt

$x_{Benzene} \approx 0.43$ (anything between 0.4-0.45)
$x_{toluene} \approx 0.57$

$y_{Benzene} \approx 0.62$ (anything between 0.6-0.65)
$y_{toluene} \approx 0.38$

b.) True 2.5 pts
c.) False 2.5 pts

- **Problem 3**

(a) Derive Clausius-Clapeyron

$$\mu^\alpha = \mu^\beta$$

$$\hat{v}^\alpha dP - s^\alpha dT = \hat{v}^\beta dP - s^\beta dT$$

$$\frac{s^\alpha - s^\beta}{\hat{v}^\alpha - \hat{v}^\beta} = \frac{dP^{sat}}{dT}$$

$$\hat{v}^\alpha - \hat{v}^\beta \approx \hat{v}^\alpha$$

$$\hat{v}^\alpha = \frac{RT}{P}$$

$$\Delta S = \frac{\Delta H_v}{T}$$

$$\frac{H_v}{\Delta \hat{V} \cdot T} = \frac{dP^{sat}}{dT}$$

$$\frac{H_v P}{RT^2} = \frac{dP^{sat}}{dT} = \frac{4900\, P^{sat}}{T^2}$$

$$\frac{H_v}{R} = 4900\text{ K}$$

$$\boxed{H_v = (4900\text{ K})\left(8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\left(\frac{1\text{ kJ}}{1000\text{ J}}\right) = 40.7\text{ kJ/mol}}$$

$$\boxed{\frac{dP^{sat}}{dt} = \frac{4900\, P^{sat}}{T^2}}$$

3 pts

4900 → units of Kelvin (temperature)

- (b) $\hat{V}_{vap} = \frac{RT}{P} = \frac{(0.08206 \frac{atm \cdot L}{mol \cdot K})(10°C + 273.15\ K)}{(0.0123\ atm)}$

$\boxed{\hat{V}_{vap} = 1.89 \times 10^3\ L/mol}$

*removed from test. Don't worry about *specific volume*

$\hat{V}_{vap} >> \hat{V}_{liq}$, so we are able to modify the Clausius - Clapeyron equation.

$\boxed{\Delta H_v = 40.7\ kJ/mol}$ 3 pts

(c) $\frac{dP^{sat}}{dt} = \frac{4900\ P^{sat}}{T^2}$

$T_1 = 10°C \rightarrow 283.15\ K$

$T_2 = 30°C \rightarrow 303.15\ K$

$P^1 = 0.0123\ atm$

$P^2 = ?$

$$\int_{P_1}^{P_2} \frac{dP^{sat}}{P^{sat}} = \int_{T_1}^{T_2} \frac{4900\ dt}{T^2}$$

$$\ln\left(\frac{P^{sat}_{12}}{P^{sat}_{11}}\right) = -4900\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = 4900\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{P^{sat}}{0.0123 atm}\right) = 4900\ K\left(\frac{1}{283.15\ K} - \frac{1}{303.15\ K}\right)$$

$\boxed{P^{sat} = 0.0385\ atm \quad at\ T = 30°C}$

3 pts

Question 4

(a) Far from STP ⇒ van't Hoff +3

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{K_2}{13.5}\right) = \frac{60\times10^3 \text{ J/mol}}{8.314 \text{ J/mol K}}\left(\frac{1}{450+273} - \frac{1}{200+273}\right)$$

+1

$$\Rightarrow \boxed{K_{eq}(450°C) = .069 \text{ atm}^{-1}}$$ +1

Common Mistakes:

- Missed sign on ΔH
- Wrong order of T's (i.e., $\frac{1}{T_1} - \frac{1}{T_2}$)
- Used ΔG eqn (+2 for trying...)
- Didn't convert to J

(b) Elementary Kinetics

+2

$$\Rightarrow \frac{-r_{HCl}}{4} = \frac{-r_{O_2}}{1} = \overbrace{k_f P_{HCl}^4 P_{O_2} - k_b P_{Cl_2}^2 P_{H_2O}^2}$$

+0.5 → 4

+1.5

$$\Rightarrow \boxed{\frac{-r_{HCl}}{4} = k_f y_{HCl}^4 y_{O_2} P^5 - k_b y_{Cl_2}^2 y_{H_2O}^2 P^4}$$

+1 NOT A REASONABLE ASSUMPTION

because elem. kinetics do not capture catalyst behavior

(c) $-r_{HCl} = 0$

$$K_{eq} = \frac{y_{Cl_2}^2 \, y_{H_2O}^2}{y_{O_2} \, y_{HCl}^4} \, \frac{1}{P} \qquad \underline{+5}$$

$\underline{+3}$

$$\left.\begin{aligned} n_{HCl} &= 4 - 4f_{HCl} \\ n_{O_2} &= 1 - f_{HCl} \\ n_{Cl_2} &= 2f_{HCl} \\ n_{H_2O} &= 2f_{HCl} \\ \hline n_{tot} &= 5 - f_{HCl} \end{aligned}\right\} \Rightarrow \begin{aligned} y_{HCl} &= \frac{4(1-f_{HCl})}{5-f_{HCl}} \\ y_{O_2} &= \frac{1-f_{HCl}}{5-f_{HCl}} \\ y_{Cl_2} &= \frac{2f_{HCl}}{5-f_{HCl}} \\ y_{H_2O} &= \frac{2f_{HCl}}{5-f_{HCl}} \end{aligned}$$

$$\Rightarrow \quad K_{eq} = \frac{16 f_{HCl}^4}{\cancel{(5-f_{HCl})^4}} \, \frac{(5-f_{HCl})^5}{256(1-f_{HCl})^5} \, \frac{1}{P}$$

$$\Rightarrow .069 = \frac{16(0.5)^4 (5-0.5)}{256(1-0.5)^5} \, \frac{1}{P}$$

$$\Rightarrow \boxed{P \simeq 8.15 \text{ atm}} \qquad \underline{+2}$$

Common Mistakes

- Errors in Keq expression
- Tried to implement design eqn.

(d) Irrev. ($k_b = 0$)

$$\Rightarrow \boxed{\frac{-r_{HCl}}{4} = k_f \, y_{HCl}^4 \, y_{O_2} \, P^5}$$

+0.5 $\rightarrow$ 4

+4.5

f_{HCl} if $V = 250 \, m^3$, $P = 1 \, atm$, $k = 1 \, \frac{mol}{m^3 s \, atm^5}$?

PFR design eqn:

+3 $$\frac{df_{HCl}}{dV} = \frac{-r_{HCl}}{n_{HCl,o}} = \frac{-r_{HCl}}{4}$$

Plug in $y(f_{HCl})$ terms...
$$= (1) \frac{256 (1 - f_{HCl})^5}{(5 - f_{HCl})^5} \left(\frac{1}{1}\right)$$

+1 $$\Rightarrow \int_0^{f_{HCl}} \frac{(5 - f_{HCl})^5}{256 (1 - f_{HCl})^5} \, df_{HCl} = \int_0^{250} dV$$

$$= 250 \, m^3$$

Wolfram Alpha (e.g.)

$$\Rightarrow \boxed{f_{HCl} \approx 0.72}$$ +1

V for $f_{HCl} = 0.95$?

+4 $\Rightarrow \displaystyle\int_0^{0.95} \frac{(5-f_{HCl})^5}{256(1-f_{HCl})^5}\, df_{HCl} = \int_0^V dV$

$= V$

+1 $\Rightarrow \boxed{V \approx 1.74 \times 10^5\ m^3}$

Common Mistakes

- Incorrect $-r_{HCl,\, irrev.}$
- Integration of design equation BEFORE substituting f_{HCl} terms
- Wrong design equation (e.g. CSTR)

5 a) $n_{CO_2} = 2\times10^5$ mols

$V = 150\,m^3$

$T = -45°C$

Ideal gas law predicts;

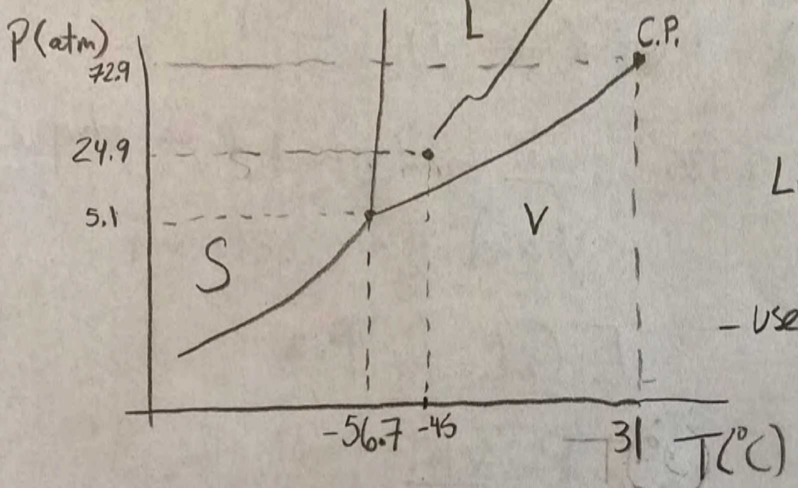
$$PV = nRT \rightarrow P = \frac{nRT}{V}$$

$$P = \frac{2\times10^5(8.205\times10^{-5})(-45+273)}{150\,m^3}$$

$= 24.9$ atm if CO_2 is entirely in gas phase

PT phase diagram:

what I.G.L. predicts → appears firmly in liquid phase (noting diagram is not to scale).



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Likely vapor-liquid equilibrium

↓

- use Antoine's eqn., if $P^* < P_{I.G.L}$ then we are at VLE
- if $P^* > P_{IGL}$, we are fully in vapor phase

$P^*(T=-45°C) = 10^{(A - B/T+C)}$ A, B, C given

$= 6184$ mm Hg $= 119.6$ psi

$= 8.1$ atm

$$\boxed{\begin{array}{c}P^* < P_{IGL}\text{, so} \\ \text{we are at VLE, and} \\ P = P^* = 119.6\text{ psi}\end{array}}$$

) From PT diagram, $T = 40°C > T_c = 31°C$, so this is either vapor or supercritical fluid. Either way, I.G.L. can be used to calculate P:

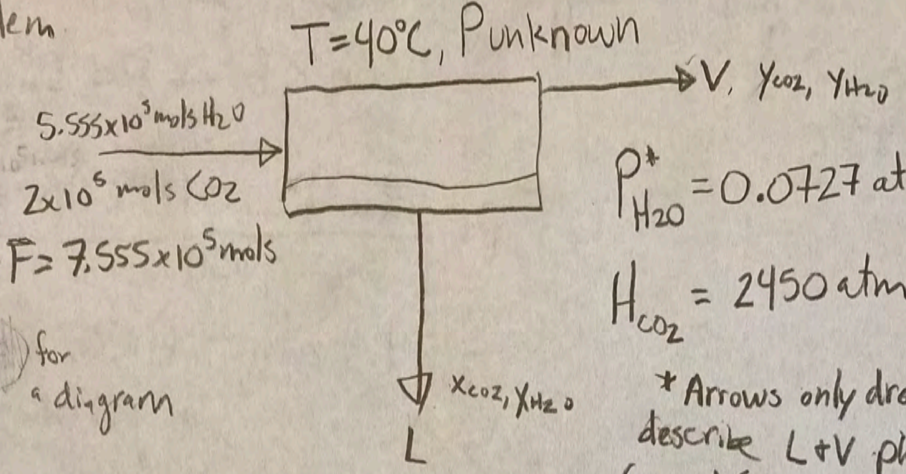
$P = \frac{nRT}{V}$ same calc. as in a: $P = 34.2$ atm

$= 503$ psi

calculated P below P_c (72.9 atm),

$\boxed{\text{So this is a vapor @ } P = 503\text{ psi}}$

5c) Flash problem



$P^*_{H_2O}=0.0727$ atm

$H_{CO_2}=2450$ atm

* Arrows only drawn to describe L+V phases (no real flow exists)

for a diagram

From class:

$$1=\frac{z_{H_2O}}{1+\left(\frac{V}{F}\right)\left(\frac{P^*_{H_2O}}{P}-1\right)}+\frac{z_{CO_2}}{1+\left(\frac{V}{F}\right)\left(\frac{H_{CO_2}}{P}-1\right)}\quad[1]$$

$$z_{H_2O}=\frac{5.555\times10^5}{7.555\times10^5}=0.735$$

$$z_{CO_2}=0.265$$

V — total moles in vapor phase

V and P are unknown

I.G.L. for P:

$$P=\frac{VRT}{\mathcal{V}}$$

$\mathcal{V}$ — total volume of gas phase

Assume that liquid density is $\sim\rho_{H_2O}$

$$1000\,\frac{kg}{m^3}=5.55\times10^4\,\frac{mol}{m^3}=\rho_L$$

Total volume of gas phase: $\mathcal{V}=150\,m^3-\frac{L}{\rho_L}$ L = moles in liquid phase

L = F − V

$$=150\,m^3-\frac{(F-V)}{5.55\times10^4}$$

so, $P=\frac{VRT}{\left(150-\frac{(F-V)}{5.55\times10^4}\right)}$, plug into [1]

5c (cont.)

$$1 = \frac{z_{H_2O}}{1+\left(\frac{V}{F}\right)\left[\frac{P^*_{H_2O}\left(V_T - \frac{(F-V)}{\rho_L}\right)}{VRT} - 1\right]} + \frac{z_{CO_2}}{1+\left(\frac{V}{F}\right)\left[\frac{H_{CO_2}\left(V_T - \frac{(F-V)}{\rho_L}\right)}{VRT} - 1\right]}$$

Only unknown is V (mols in vapor phase).

$z_{H_2O} = 0.735$, $z_{CO_2} = 0.265$, $F = 7.555 \times 10^5$ mols, $P^*_{H_2O} = 0.0727$ atm, $H_{CO_2} = 2450$ atm

$V_T = 150\,m^3$, $\rho_L = 5.555 \times 10^4 \frac{mol}{m^3}$, $R = 8.205 \times 10^{-5} \frac{m^3\,atm}{mol\,K}$, $T = 40 + 273\,K = 313$

Use goal seek to solve for V: 1.93×10^5 mols $= V$

Plug V back into IGL: $P = \frac{1.93 \times 10^5\,\text{mols}\left(8.205 \times 10^{-5}\,\frac{m^3\,atm}{mol\,K}\right)(313\,K)}{150 - \frac{(7.555 \times 10^5 - 1.93 \times 10^5)}{5.55 \times 10^4}}$

$$\boxed{P = 35.4\text{ atm}}$$

$$\boxed{35.4\text{ atm} > 34.2\text{ atm}\ \text{☹ doesn't help}}$$