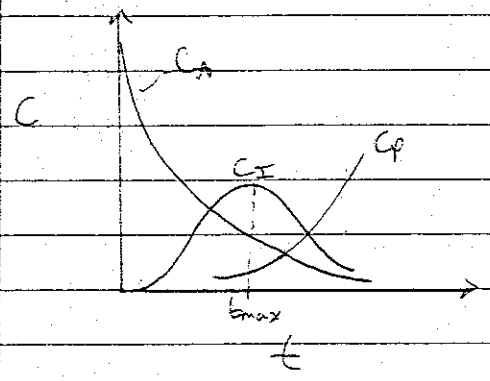
Thermo / Kinetics

1. $A \xrightarrow{k_1} I \xrightarrow{k_2} P$

what variables influence the amount of intermediate formed?

$r_A = -k_1 C_A$ $\quad r_I = k_1 C_A - k_2 C_I$



at $\frac{dC_I}{dt} = 0$ $\quad C_I = max$

Influencing variables are k_1, k_2, C_A

for exothermic rxn. $E_A > E_I$ $\quad E_I > E_A$

high T $\quad$ low T

high T favors rxn. with high E, and low T favors rxn with low E.

$\frac{dC_A}{dt} = -k_1 C_A \qquad C_A = C_{A0} \exp(-k_1 t)$

$\frac{dC_I}{dt} = k_1 C_{A0} \exp(-k_1 t) - k_2 C_I$ solve using integrating factor

Want to maximize conc. of CA use PFR until t_{max}

For a PFR

$$F_{A_0}\frac{dX_A}{dV} = -r_A = -k_1 C_A \qquad C_A = C_{A_0}(1-X_A)$$

$$= k_1 C_{A_0}(1-X_A)$$

$$\frac{dF_I}{dV} = r_I = k_1 C_A - k_2 C_I$$

$$\frac{dF_I}{dV} = k_1 C_{A_0} e^{-k_1 t} - k_2 C_I$$

2) for ΔH_{rxn} = exothermic

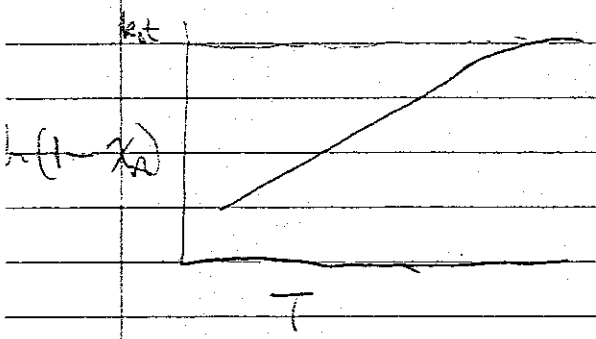
plot X_A & r_A as a function of T

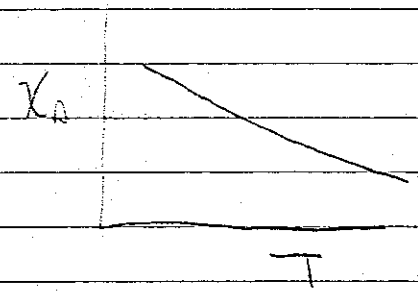
$$r_A = k C_A = k_0 \exp\left(\frac{-E_A}{RT}\right) \qquad -\frac{dC_A}{dt} = kC_A \qquad C_A = C_{A0}(1-X_A)$$

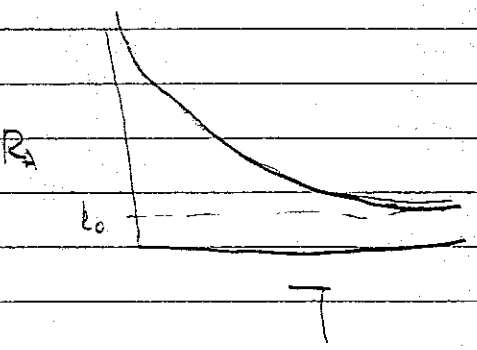
$$\frac{C_{A0}\, dX_A}{dt} = k_0 \exp\left(\frac{-E_A}{RT}\right) C_{A0}(1-X_A)$$

$$-\ln(1-X_A) = k_0 \exp\left(\frac{-E_A}{RT}\right) t$$

$$\ln(1-X_A) = -k_0 \exp\left(\frac{+E_A}{RT}\right) t$$

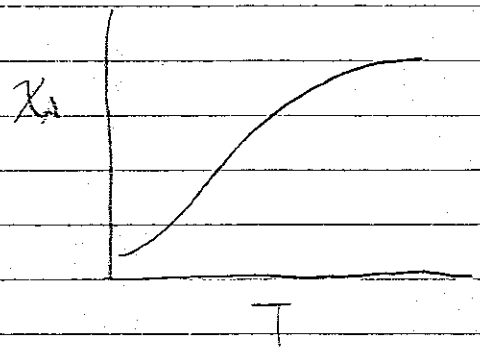


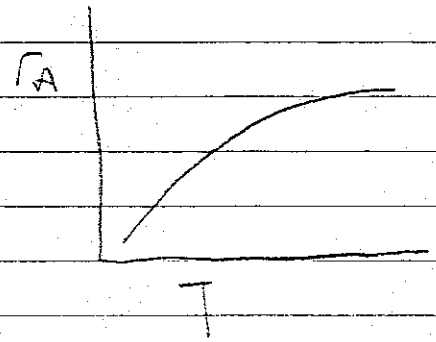




ΔH_{rxn} = endothermic

$r_A = k \exp\left(\frac{-E_a}{RT}\right)$





3. When can the steady-state approximation be used

PSSH ~ breaks down at low & high T

assume: that intermediate are consumed rapidly

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

$$r_A = -k_1 C_A \qquad r_I = k_1 C_A - k_2 C_I$$

non-dimensionalize $C^* = \frac{C_A}{C_{A0}}$ $C' = \lambda \frac{C_I}{C_{A0}}$

$$\frac{dC'}{dt} = k_1 C^* - \frac{k_2}{\lambda} C' \qquad \text{Let } \lambda = \frac{k_2}{k_1}$$

$$\frac{k_1}{\lambda} \frac{dC'}{d\tilde{t}} = k_1 C^* - k_1 C'$$

$$\frac{1}{\lambda} \frac{dC'}{d\tilde{t}} = C^* - C' \qquad \text{when } \lambda \to \infty$$

$$\frac{dC'}{d\tilde{t}} \approx 0 \qquad k_2 \gg k_1$$

4) What is chemical potential?

$$\mu_i \equiv \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}}$$ chemical work

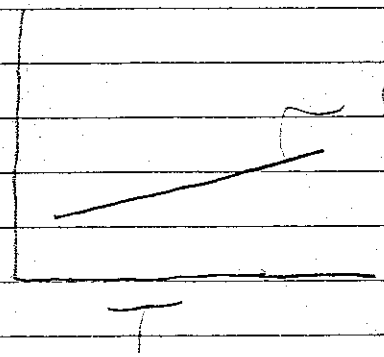
at eq. $\mu^\alpha = \mu^\beta = \mu^\delta$

5) Experimentally how would you determine ΔH_f, ΔG_f, ΔS_f?

$dU = dQ + dW$ $\quad dH = dU - VdP$

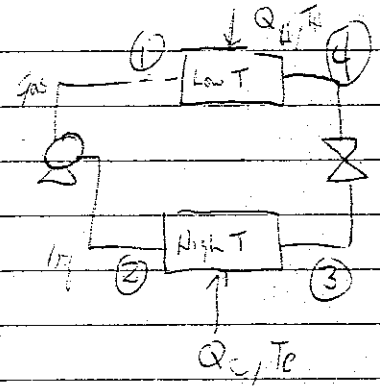
$dH = TdS + VdP$

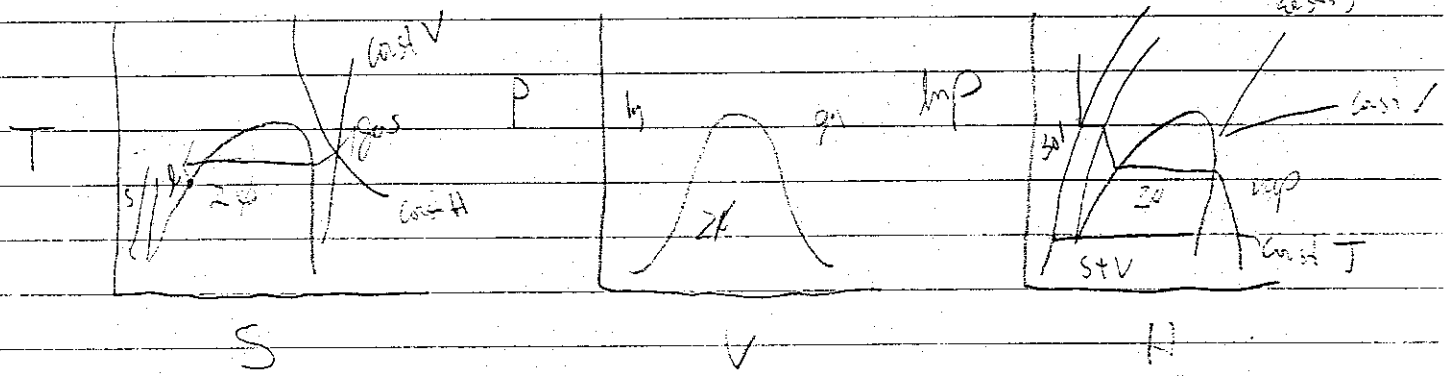
also from

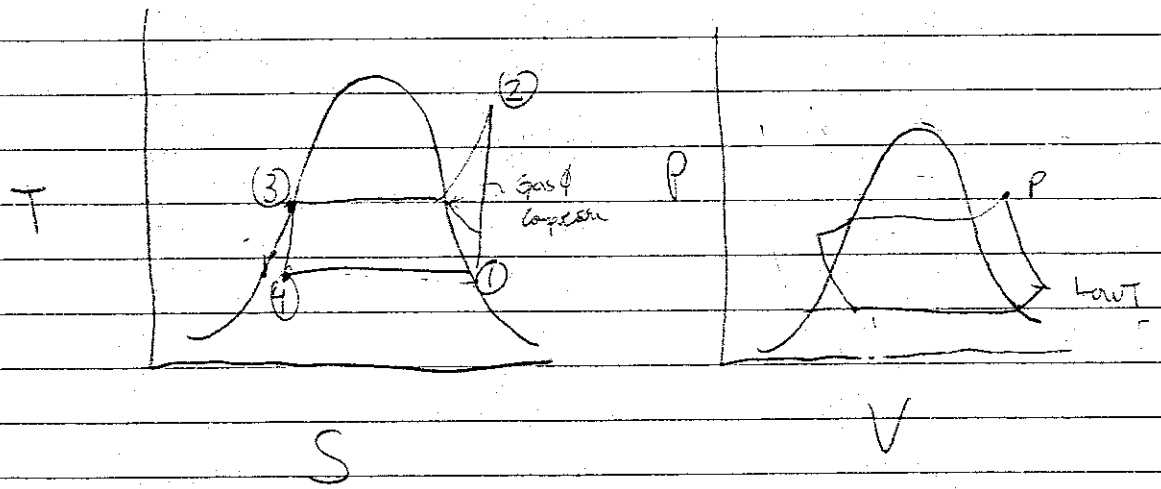


$\frac{dP}{dT} = \frac{\Delta H^{sl}}{T\Delta V^{sl}}$ if ΔV^{sl} is known

6. How does a refridgerator work?

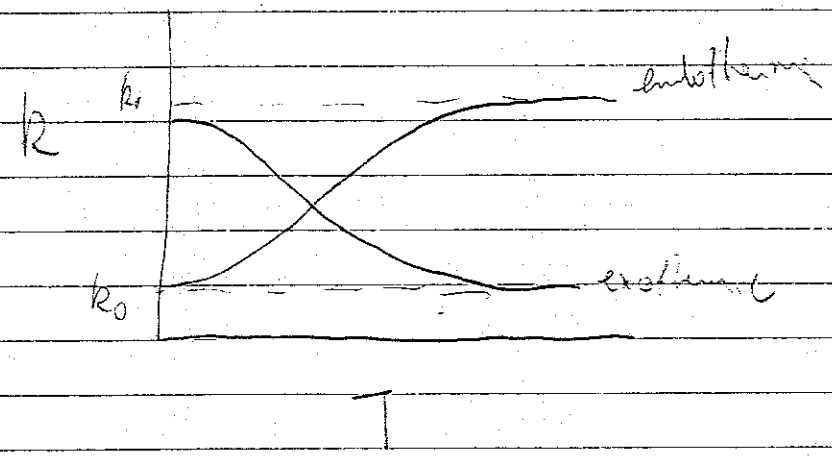






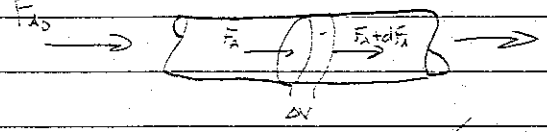
To how does k vary with T

$$k = k_0 \exp\left(\frac{-E_A}{RT}\right)$$



8. Derive the design eqns. for a PFR, CSTR, and Batch reactor.

PFR:



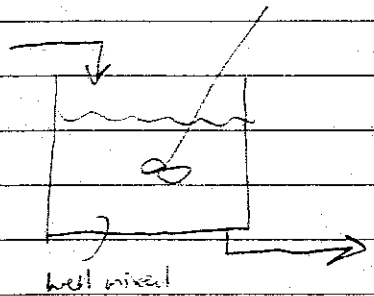
$In - Out + Gen. = accumulation$ (s.s.)

$$F_A - (F_A + dF_A) - r_A dV = 0$$

$$-\frac{dF_A}{dV} = -r_A \qquad F_A = F_{A0}(1-X_A) \qquad dF_A = -F_{A0}\,dX_A$$

$$F_{A0}\frac{dX_A}{dV} = -r_A$$

CSTR

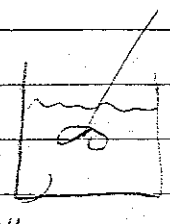


$In - Out + gen = accum$ (s.s.)

$$F_{A0} - F_{A0}(1-X_A) - r_A V = 0$$

$$F_{A0} X_A = r_A V$$

Batch



$In - Out + gen = accum$

$$\frac{dN_A}{dt} = r_A V \qquad N_A = VC_A = VC_{A0}(1-X_A)$$

$$dN_A = -VC_{A0}\,dX_A \quad (N_{A0})$$

$$N_{A0}\frac{dX_A}{dt} = -r_A V$$

9. Space time τ $\qquad \tau = \frac{1}{s} = \frac{C_{A0} V}{F}$

Space velocity $\sim \frac{1}{s}$

Mean Residence time

residence time distribution

$$\bar{t} = \int_0^\infty E(t)\, t\, dt$$

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)\, dt} \qquad \text{CSTR} \sim \frac{e^{-t/\tau}}{\tau}$$

$$\text{PFR} = \delta(\tau - t)$$

10. Clapeyron eqn.

$$dG^\alpha = -S^\alpha dT + V^\alpha dP$$

$$dG^\beta = -S^\beta dT + V^\beta dP$$

$$dG^\alpha - dG^\beta = -S^\alpha dT + S^\beta dT + V^\alpha dP - V^\beta dP$$

$$\frac{dP}{dT} = \frac{(S^\beta - S^\alpha)}{(V^\beta - V^\alpha)} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}}$$

$G = H - TS \qquad G^\alpha = G^\beta$

$H^\alpha - TS^\alpha = H^\beta - TS^\beta$

$H^\alpha - H^\beta = T(S^\alpha - S^\beta)$

$\frac{\Delta H^{\beta\alpha}}{T} = \Delta S^{\alpha\beta}$

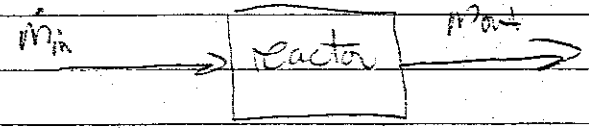
$\frac{dP}{dT} = \frac{\Delta H^{\beta\alpha}}{T \Delta V^{\beta\alpha}}$

Classius - Clapeyron

assume $V^g >> V^l \qquad V^g = \frac{RT}{P}$

$\frac{d \ln P}{d\left(\frac{1}{T}\right)} = -\Delta H^{vap}$

11. Adiabatic flame temp.



First Law:

$$\sum_i n_{i_0} \hat{H}_i(T_{feed}) - \sum_i n_i \cdot \hat{H}_i(T_{ad}) = -n_r \Delta H_{rx}$$

n_r = moles reacted

12. Which type of reactors best for

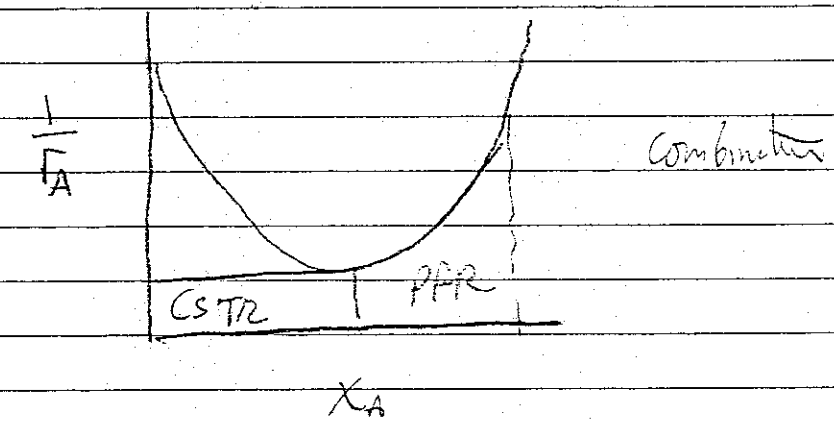
series $A \xrightarrow{k_1} I \xrightarrow{k_2} P$ (PFR)

↑ want to keep conc. high

parallel $A \xrightarrow{k_1} R$, $A \xrightarrow{k_2} P$ (depends on k_1 & k_2)

↑ need good T control (CSTR)

Autocatalytic $A + R \rightarrow R^3 + R$



13. 1st Law energy is conserved (you can't get something for nothing)

2nd Law $\Delta S_{tot} > 0$ (you can't break even any way you like it)

3rd Law $S = 0$ at $T = 0$