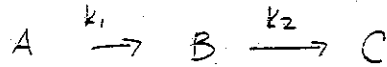## KINETICS

1. Series Reaction
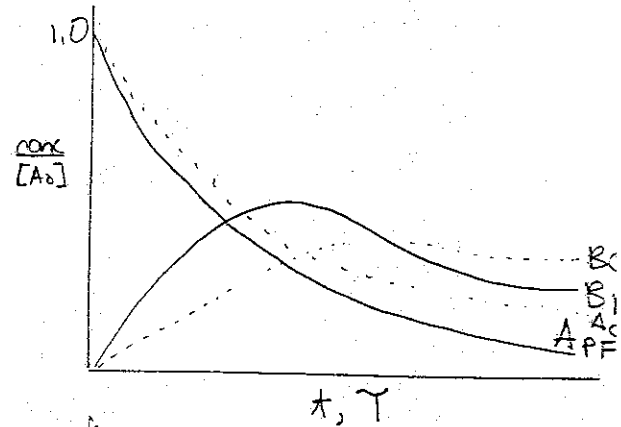
$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

k_1, k_2 determine the amount of intermediate B formed.
If $k_2 \gg k_1$, the B_{max} is small. If $k_2 \ll k_1$, B_{max} is large.

For PFR, Batch

$$B_{max} = A_0 \left(\frac{k_1}{k_2}\right)^{\left(\frac{k_2}{k_2-k_1}\right)}$$

For CSTR

$$B = \frac{k_1 A_0 \tau}{1+k_1\tau} \quad \frac{1}{1+k_2\tau}$$

In C*, • less conversion of A
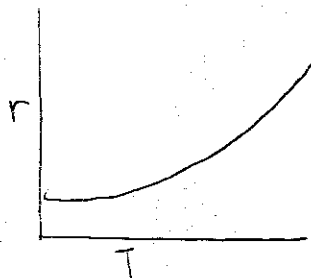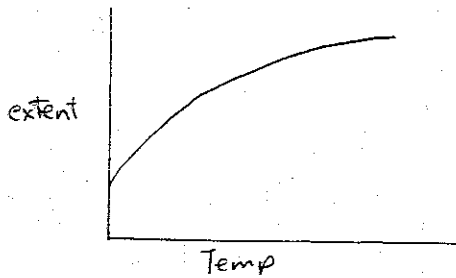• lower conc. of B, intermediate.

Other factors
• order of reaction
• time, or space time
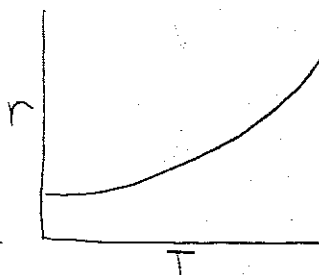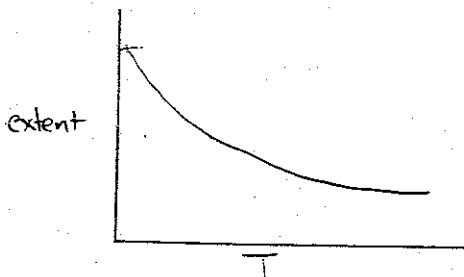• rate constants can be changed with temperature

2. EXOTHERMIC, FIRST ORDER Reaction

Plot extent of reaction and reaction rate as functions of temp.

$$rate = k C_A = A e^{(-Ea/RT)} C_A$$

irreversible

reversible rxn

3   <u>Steady State Approximation</u>   (iv)

PSSA can be used if B is a very reactive intermediate: $k_2 \gg k_1$
The larger k_2 is, the faster B reaches a quasi-steady-state level.

Relaxation time (time required for ε, fractional deviation of B from B_{ss}, to reach $1/e$ of its initial value)

$$t_r = \frac{1}{k_2}$$

- can not use it in initial period
- reaction rate, arrow convention

7.   <u>Rate constant and temperature</u>
     1) Arrhenious
$$K = A \exp\left(\frac{-E_a}{RT}\right)$$

↗ exponential dependance.

$(\downarrow \text{MORE} \downarrow)$

8.   <u>Design Eqns</u> F_{A0}, U_0, C_{A0}

   <u>CSTR</u>   in $-$ out $+$ formed $=$ accum

          F_{A0} $-$ F_A $+$ $r_A V_R$ $= 0$

          $\cancel{F_{A0}}$ $-$ $F_{A0}(\cancel{1}-f_A)$ $+$ $r_A V_R$ $= 0$

          $U_0 C_{A0} f_A$ $+ r_A V_R = 0$

$$\frac{V_R}{U_0} = \boxed{\tau_{C*} = \frac{C_{A0}\, f_A}{(-r_A)}}$$

     <u>constant density:</u>
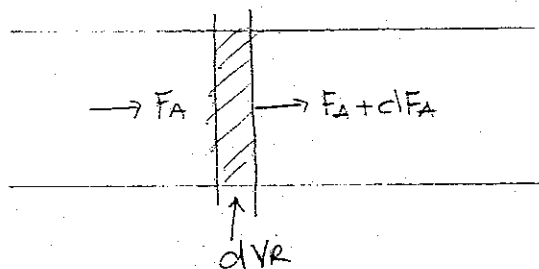 F_{A0} $-$ F_A $+$ $r_A V_R$ $= 0$

          $C_{A0} U_0$ $- C_A U_0$ $+$ $r_A V_R$ $= 0$

$$\boxed{\tau_{C*} = \frac{C_{A0} - C_A}{(-r_A)}}$$

PFR

$$\rightarrow F_A \qquad \rightarrow F_A + dF_A$$

$$dV_R$$
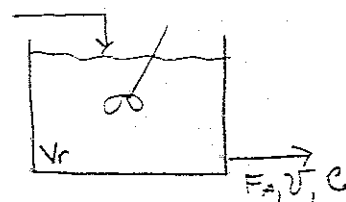
In $-$ out $+$ formed $=$ accum

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

$$-d[F_{A0}(1-f_A)] + r_A dV_r = 0$$

$$\frac{C_{A0} v_0\, df_A}{v_0} + \frac{r_A dV_r}{v_0} = 0$$

$$C_{A0}\, df_A + r_A\, dv = 0$$

$$\boxed{\tau_{PF} = C_{A0} \int_0^{f_A} \frac{df_A}{(-r_A)}}$$

BATCH

$$V_R$$
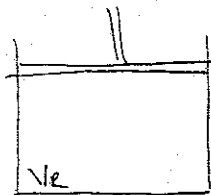
In $-$ out $+$ formed $=$ accum

$$r_A V_R = \frac{dn_A}{dt}$$

$$\frac{r_A V_{R0}(1+\delta_A f_A)}{V_{R0}} = \frac{d(n_{A0}(1-f_A))}{dt}\,^{const}\,\frac{1}{V_{R0}}$$

$$r_A(1+\delta_A f_A) = -C_{A0}\frac{df_A}{dt}$$

$$\boxed{t_B = C_{A0} \int_0^{f_A} \frac{df_A}{-r_A(1+\delta_A f_A)}}$$

Energy Balance: $A \rightarrow B$ ΔH_{rx}

in − out + form − Removal = accumulate

CSTR: in − out + form − Removal = acc

$\sum F_{jo} H_{jo} - \sum F_j H_j + F_{Ao} X_A (-\Delta H_R) + U \cdot A (T_R - T) = 0$

Note, You can
express as this
If $\sum F_j \cdot H_{jo} - \sum F_j H_j$

The reaction term
will be counted
see following page
for prove

Generally pose A feed.

$$F_{Ao} (H_{Ao} - H_A) + F_{Ao} X_A (-\Delta H_R) + UA(T_R - T) = 0.$$

$$F_{Ao} \cdot \widehat{C_p} (-T + T_{Ao}) + F_{Ao} X_A (-\Delta H_R) + U A (T_R - T) = 0$$

$\Delta H_R = \Delta H_R^0 + \widehat{C_p}(T$

* that is $F_{Ao} X_A (-\Delta H_R) = (T - T_c)(\quad)$.   MSS

$F_{Ao} X_A =$

PFR: Difference is heat flow along reactor differ

So, $Q = \int U(T - T_a) dA = \int^V U a (T - T_a) dv$

a: heat exchange area/Reactor Volume.

$$\longrightarrow \boxed{F_{Ao} \cdot \int_T^{T_{Ao}} \cdot C_p \, dT + F_{Ao} X_A (-\Delta H_R) + \int_a^V U a (T_R - T) dv = 0}$$

Different with V:

$U a (T_a - T) - \{ F_{Ao} \cdot C_p \cdot \frac{dT}{dv} \} + (-\Delta H_R) F_{Ao} \cdot \frac{dX_A}{dv} = 0$

start: $F_{Ao} \bar{C_p} T|_V - F_{Ao} \bar{C_p} T|_{V+\delta V} + (-\Delta H_R) F_{Ao} \cdot \Delta X_A - dA \cdot U(T - T_a) = 0$

above $\longleftarrow$ $- F_{Ao} \bar{C_p} \cdot \frac{dT}{dv} + (-\Delta H_R) F_{Ao} \cdot \frac{dX_A}{dv} - U \cdot a (T - T_a) = 0$ $a = \frac{dA}{dv}$

Batch: Formed − Removal = accumulated

$$\boxed{N_{Ao} X_A (-\Delta H_R) - U \cdot A (T - T_a) = \sum n_i \bar{C_{pi}} \frac{dT}{dt}}$$ $\rho \cdot V \cdot C_p \frac{dT}{dt}$

If $X_A = 1$ $N_{Ao} (-\Delta H_R) \, \Xi = \sum n_i \bar{C_{pi}} \Delta T$

$$\boxed{\rho \cdot V \cdot C_p \frac{dT}{dt} = (-\Delta H_R) \cdot \gamma_x \cdot V + Q}$$

Energy Balance:

Use $A \rightarrow \frac{b}{a} B$ for illustrate.

In : F_i, H_{io} : $F_{Ao} H_{Ao} + F_{Bo} H_{Bo}$ $F_A = F_{Ao}(1-X_A)$

out: F_i, H_i : $F_A H_A + F_B H_B$ $F_B = F_{Bo} + \frac{b}{a} \cdot F_{Ao} X_A$

$= F_{Ao}(\theta_B + Y^2 X_A)$

In $-$ out $= F_{Ao}(1+X_A) H_{Ao} + F_{Bo} H_{Bo} - F_{Ao}(1-X_A) H_A - F_{Ao}(\theta_B + Y^2 X_A) H_B$

$= \underline{F_{Ao}[H_{Ao} - H_A + \theta_B(H_{Bo} - H_B)]} + F_{Ao} \underbrace{X(H_A - Y^2 H_B)}_{-\Delta H_R}$

Generally, $F_{Bo} = 0$ for simplify.

In $-$ out $= F_{Ao}(H_{Ao} - H_A) + (-\Delta H_R) F_{Ao} X_A$

heat removed oradded $\dot{Q}$
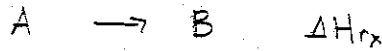
accumulate: $\rho F_{Ao} C_p \frac{dT}{dt}$

In $-$ out $+ -$ Removal $=$ accumulate.

Usually, pure A feed. (if they ask, give derivation above)

$F_{Ao}(H_{Ao} - H_A) + (-\Delta H_R) \cdot F_{Ao} X_A + U \cdot A(T_2 - T) = 0$
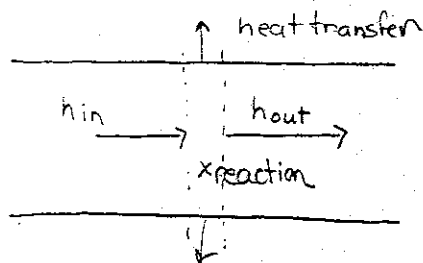
Energy Balances

CSTR
(from 244)

$$A \longrightarrow B \qquad \Delta H_{rx}$$

$$\text{In} - \text{out} + \text{form} = \text{accum}$$

$$\sum_j F_{jo} H_{jo} - \sum_j F_{jo} H_j + V(-\Delta H) r_i + \overset{0}{\cancel{A_K U (T_r - T)}} = 0$$

↑ heat transfer

$$\underbrace{\phantom{\sum_j F_{jo} H_{jo} - \sum_j F_{jo} H_j}}$$

use an average
heat capacity for mixture

$$\upsilon_0 \rho_{f_0} \overline{C_P} (T_0 - T) + V(-\Delta H) r_i + A_K U (T_r - T) = 0$$

PFR

↑ heat transfer

$h_{in} \longrightarrow$ | $h_{out} \longrightarrow$

$x_{reaction}$

↓

$$\text{In} - \text{out} + \text{form} + \text{heat transfer} = 0$$

$$\sum \left(F_i \int_{T_0}^{T_{in}} \overline{C}_{pi} dT \right) - \sum \left(F_i \int_{T_0}^{T_{out}} \overline{C}_{pi} dT \right) + \Delta H_r (r_A) dV_r + U(T_r - T) dA = 0$$

↑ ↑

$$\rightarrow U(T_r - T) dA = U(T_r - T) d\left(\frac{4}{D} V_R \right) = U(T_r - T) \frac{4}{D} F_{A_0} \frac{df_A}{(-r_A)}$$

$$\rightarrow \Delta H_r (r_A) dV_r = \Delta H_r F_{A_0} df_A$$

$$\sum \left(F_i \int_{T_0}^{T_{in}} \overline{C}_{pi} dT \right) - \sum \left(F_i \int_{T_0}^{T_{out}} \overline{C}_{pi} dT \right) + \Delta H_r F_{A_0} df_A + U(T_r - T) \frac{4}{D} F_{A_0} \frac{df_A}{(r_A)} =$$

integrate along reactor length:

$$-\sum \left(F_i \int_{T_0}^{T} \overline{C}_{pi} dT \right) + F_{A_0} \Delta H_r (f_A) + \int_0^{f_A} U(T_r - T) \frac{4}{D} F_{A_0} \frac{df_A}{(-r_A)} = 0$$

BATCH

$$\text{formed} + \text{heat transfer} = \text{accum.}$$

$$\Delta H_R r V_r + UA(T_r - T) = \left(\sum n_i \overline{C}_{pi} \right) \frac{dT}{dt}$$

$$(-\Delta H_R) n_{A_0} \frac{df_A}{dt} + UA(T_r - T) = \left(\sum n_i \overline{C}_{pi} \right) \frac{dT}{dt}$$

Upon integration $t = 0 \rightarrow t$

$$-\Delta H_r n_{A_0} f_A + \int_0^t UA(T_r - T) dt = \sum \left(n_i \int_{T_0}^{T_e} \overline{C}_{pi} dT \right)$$

7 Continued)

2) Temp dependance from thermodynamics

$$A \longrightarrow R \qquad \Delta H_R$$

Van't Hoff

$$\frac{d}{dT}(\ln k) = \frac{E_a}{RT^2}$$

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
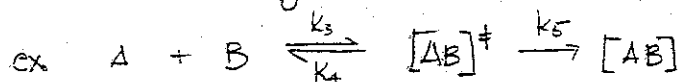
If $T_2 \to \infty$, $k_2 \to k_0$

$$\ln\left(\frac{k_0}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{\infty} - \frac{1}{T_1}\right)$$

$$\boxed{k = k_0 e^{-E/kT}}$$

3) Kinetic Theory of Gases (Collision Theory)

$$k \propto T^{1/2} e^{-E/RT}$$

4) Transition State Theory

$$\text{ex} \quad A + B \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [AB]^{\ddagger} \overset{k_5}{\longrightarrow} [AB]$$

$$K_c = \frac{k_3}{k_4} = \frac{[AB]^{\ddagger}}{[A][B]} \qquad \text{equilibrium}$$

$$k_5 = \frac{kT}{h} \qquad \text{rate of decomp of complex}$$
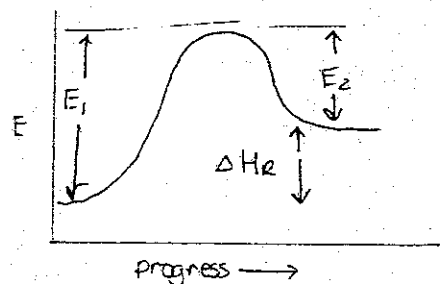
$$r = k_5 [AB]^{\ddagger}$$

$$= \frac{kT}{h} K_c [A][B]$$

From thermodynamics,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K_c$$

$$K_c = e^{\Delta S/R} e^{-\Delta H/kT}$$

$$r = \frac{kT}{h} e^{\Delta S/R} e^{-\Delta H/RT} [A][B]$$

$$r = \left[\frac{k}{h} e^{\Delta S/R} \right] T e^{-\Delta H/RT} (A)(B)$$

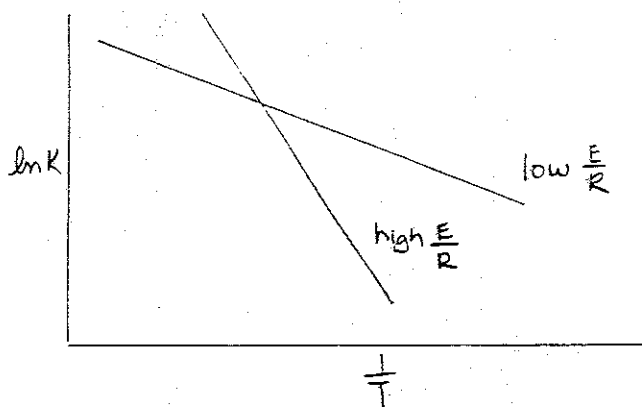$$k^0 \quad \text{assuming } \Delta S^\circ \text{ is not fcn of T}$$

$$r = \underbrace{k_0 T e^{-\Delta H/RT}}_{k} A B$$

notes

1) Arrhenious relation is a good approximation to collision + TST because T on $T^{1/2}$ dependance is less significant than the exponential contribution.

2) TST is generally better than collision theory.

3) Arrhenious plot

$$\ln k = \ln A - \frac{E}{R} \frac{1}{T}$$

1) High E , k more sensitive to T

2) A given reaction is more temperature sensitive at low T than high T.

3) Other theories do not predict a straight line (but close) Above relationships would still hold.

— Arrhenius : it is empirical.

$$k = A \cdot e^{-E_a/RT}$$
$\begin{cases} A \text{ is assumed be } T \text{ independent.} \\ E \text{ is independent of } T \end{cases}$

1> A : collision frequency.

2> Only enough energy molecules will react, Boltzmann distribution introduce $e^{-E_a/RT}$.
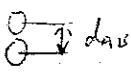
Elementary kinetic theory :

= Collision theory :

Assume : ① only those with high energy collision can react

② hard sphere.

$$k = P \cdot L \, d_{AB}^2 \, \sqrt{\frac{8RT}{\pi M^*}} \, exp\left(-\frac{E_c}{RT}\right) \qquad T \propto T^{\frac{1}{2}} e^{-E/RT}$$

L : Avogadro.

d_{AB} :

M^* : $\frac{M_A \cdot M_B}{M_A + M_B}$

E_c : from Boltzmann distribution.

If $k = B \cdot T^{\frac{1}{2}} \cdot exp\left(\frac{-E}{RT}\right)$ compare with Arrhenius. $E_a = E_c + \frac{1}{2}RT$.
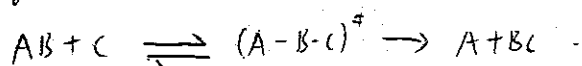
P : steric factor

Transient state theory (TST)

Reacting system is assumed to pass through a configuration of minimum potential energy from reactants to products and <u>the rate of passing through this configuration is reaction rate</u>. The number of activated complex is ~~assumed~~ determined by an equilibrium with reactant molecules.

I̲t̲ is assumed the rate of removal of product by decomposition of activated complex does not affect equilibrium.
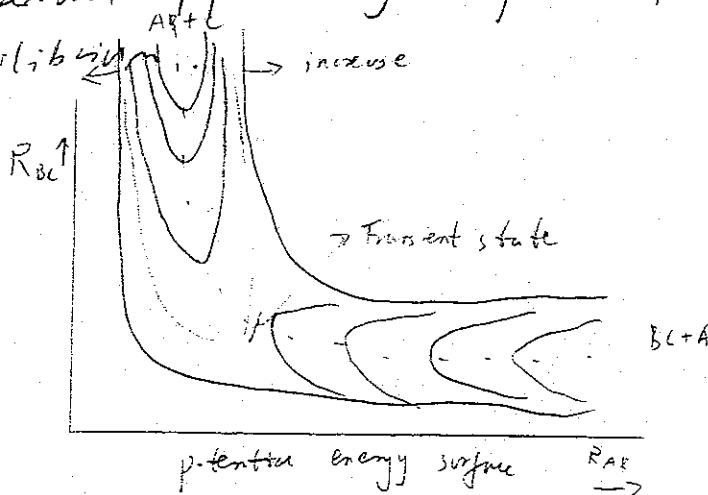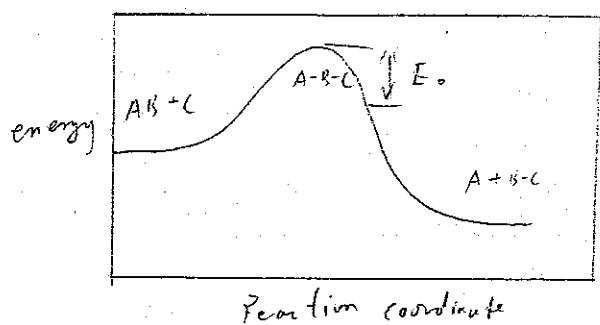
a. Reaction Path ↑

b. Equilibrium of transition complex:

$$AB + C \rightleftharpoons (A-B-C)^{\ddagger} \longrightarrow A + BC$$

$$K_c^{\ddagger} = \frac{\overline{ABC} \; C^{\ddagger}}{C_{AB} \cdot C_C} = \frac{\overline{Q^{\ddagger}}}{\overline{Q^0_{AB}} \cdot \overline{Q^0_C}} = \frac{Q^{\ddagger}}{Q^0_{AB} \cdot Q^0_C} \cdot \exp\left(-\frac{E}{RT}\right)$$

Differ of lowest state for AB, C and ‡

c. Rate of Reaction:

Reaction rate equals rate of passage. $\gamma = V_i \, C_{\ddagger}$ → frequency.

$$\gamma = V_i \cdot \frac{Q^{\ddagger}}{Q^0_{AB} \cdot Q^0_C} \cdot \exp\left(-\frac{E}{RT}\right) C_{AB} \cdot C_C$$

$Q^0_{AB} \cdot Q^0_C$ ~~can be calculated directly~~. $Q^{\ddagger}$: less one degree of vibration freedom

accord for motion along C_{OO}

Nonlinear $3n-7$, linear $3n-6$

$\begin{cases} \text{nonlinear } 3n-7 \\ \text{linear } 3n-6 \end{cases}$

$$(f^{\ddagger}_v)_i = (1 - e^{-hV_i/kT})^{-1} \quad \text{at low } V_i.$$

$$= kT/h\gamma.$$

$(Q^0_{\ddagger})'$: one account for motion along coordinate reaction.

$$\text{So,} \quad \gamma = \left(\frac{kT}{h}\right) \cdot \frac{(Q^0_{\ddagger})'}{Q^0_{AB} \, Q^0_C} \exp\left(-\frac{E}{RT}\right) C_{AB} \cdot C_C$$

In TST,

steric factor P is given by the ratio of preexponential factor to that for binary collision model.

$$P = \frac{(Q_{\ddagger}^0)' / \pi Q_i^0}{f_i^0 / f_t^0}$$

Reaction more complex $\to$ in reln to hard sphere, P decrease.

d. Thermodynamic view:

$$(\Delta G^0)^{\ddagger} = -RT \ln k^{\ddagger} = (\Delta H^0)^{\ddagger} - T(\Delta S^0)^{\ddagger}$$

$$k^{\ddagger} = e^{-\Delta H^{\ddagger}/RT} \cdot e^{(\Delta S^0)^{\ddagger}/R}$$

$$\gamma = \left(\frac{kT}{h}\right) e^{-(\Delta H^0)^{\ddagger}/RT} \underbrace{\frac{e^{(\Delta S^0)^{\ddagger}/R}}{c^0}} C_{AB} C_e \quad \Bigg| \quad \overset{TST:}{\gamma \sim k_0 \cdot T \cdot e^{-\Delta H/RT}}$$

① free-energy barrier, not energy.

② possible for large enthalpy change occur because positive Δs.

③ small steric factor $\sim$ large entropy change
$$\qquad\qquad\qquad\qquad \overset{\wedge}{\text{large structure change.}}$$

$$P \approx \exp\left(\frac{\Delta^{\ddagger} S_m^{\circ}}{R}\right)$$

Comparment: a. in Arr, A indep ‡ of T, actually it did.

b. E reln with T

c. P.

Diffusion, in Thermal:

The property governs spontaneous change is chemical potential.
When unit amount of solute is shift from a region $\mu(1)$ to a
region $\mu(2)$. the work required $W = \mu(2) - \mu(1)$, suppose μ depends
on x. $dw = \mu(x+dx) - \mu(x) = [\mu(x) + (\frac{d\mu}{dx})dx] - \mu(x) = (\frac{d\mu}{dx}) \cdot dx$

In classical mechanics. $dw = -F \cdot dx$

So, $\boxed{F = -\frac{d\mu}{dx}}$ Gradient of chemical potential acts like a force.

$$\mu = \mu^\circ + RT \ln C$$

$$F = -\frac{RT}{C} \cdot \frac{dc}{dx}.$$

Force per unit volume : CF.

Flow if mass J is proportional to CF

$$J(matter) \propto CF = -RT \frac{dc}{dx}$$

9.   Space time - $\Upsilon = \dfrac{V_R}{v_o}$ Amt. of time it takes for one reactor full of contents to be processed.

Space Velocity $S = \dfrac{1}{\Upsilon}$ # reactor volumes to be processed per unit time

Mean Residence Time

average age of a fluid element as it leaves the reactor (avg. time necessary to cover distance from inlet to outlet) $= \dfrac{\int_0^\infty t\, E(t)\, dt}{\int_0^\infty E(t)\, dt}$

11.   Adiabatic Flame Temp - maximum attainable temperature for a process. Usually refers to a combustion process. All heat that is given off is used to heat up products and unreacted reactants. Thus, no heat loss.

For steady state:

$$\Delta h = \cancel{q} - \underset{\text{no work}}{\cancel{w_s}} \qquad = \Delta h_{rxn} + \Delta h_{heating}$$

$$\Delta h_{rxn} = \Sigma \left(h^f_{T_{rx}} \right)_{products} - \Sigma \left(h^f_{T_{rx}} \right)_{react}$$

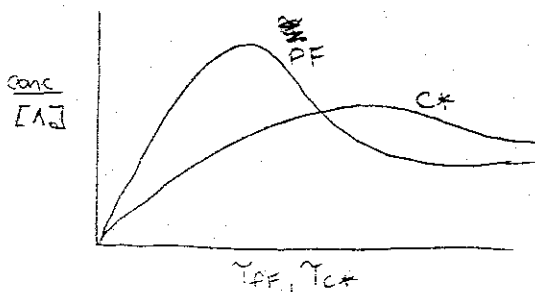$$\Delta h_{heat} = \underset{avg.\ C_p}{\left(\Sigma\, y_i\, C_{p,i} \right)} \left(T_{af} - T_{rx} \right)$$

We can determine T_{af} given:

1) Δh_{rx} or $h^f_{T_{rx}}$ for components
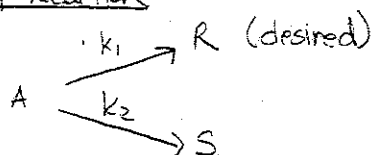
2) Composition

3) $C_{p,i}$

12.   Series reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$
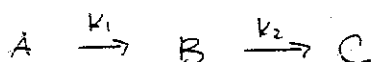
To maximize production of B, use a PFR. PFR always gives a higher yield of B than in CSTR.

conc [A]

PF

C*

$\Upsilon_{PF}, \Upsilon_{C*}$

Also, PFR requires less Υ

Parallel Reaction

$$A \begin{array}{c} \xrightarrow{k_1} R \ (\text{desired}) \\ \searrow_{k_2} S \end{array}$$

- If reactions are of same order, reactor type is irrelevant. Use temps to change product concentration (assuming activation energy is different.)

- If desired pathway has higher order, then keep conc of A high i.e. use PFR or batch.

$$r_S = k_1 C_A^n$$

$$r_r = k_2 C_A^m$$

$$\Rightarrow \frac{r_r}{r_s} = \left(\frac{k_2}{k_1}\right) C_A^{(m-n)}$$

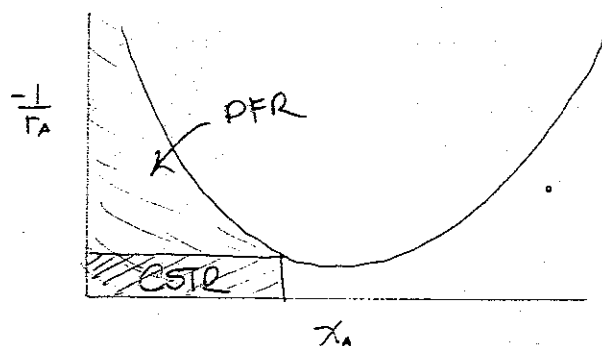- if $m > n$, high C_A gives us a high selectivity $\frac{r_r}{r_s}$

Autocatalytic Reaction

- really looking at, which reactor type needs smallest volume

$$A + (B) \longrightarrow 2B$$
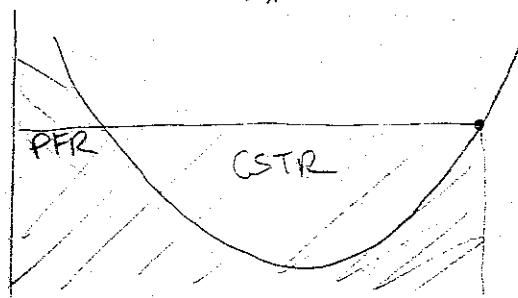
$$-r_A = k C_A^a C_B^\beta$$

qualitatively, rate starts low because C_B is low. Then it increases to a maximum. Beyond this, it decreases as C_A goes down

For $X_A < 0.5$, PFR is least economical use.

Use a CSTR.

recall: area $= \frac{\tau}{C_{A_0}} = \underset{\text{CSTR}}{\underbrace{\frac{f_A}{-r_A}}} = \underset{\text{PFR}}{\underbrace{\int_0^{f_A} \frac{d f}{(-r_A)}}}$

For $X_A > 0.5$ CSTR is least economical.

Use a PFR.

15. Langmuir Hinshelwood

$$A + B \longrightarrow R$$

If surface reaction limited:

$$(-r_A'') = k\,\theta_A\,\theta_B$$

$$(-r_A') = \frac{k\,K_A P_A K_B P_B}{(1 + K_A P_A + K_B P_B)^2}$$

If limited by adsorption of A:

?

19. Series Reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$k_1 = A_1 e^{-E_1/RT}$$

$$k_2 = A_2 e^{-E_2/RT}$$

$$\frac{k_1}{k_2} = \frac{A_1}{A_2} e^{\left(\frac{E_2 - E_1}{RT}\right)}$$

If $E_2 > E_1$, raising the temp would decrease $\frac{k_1}{k_2}$.
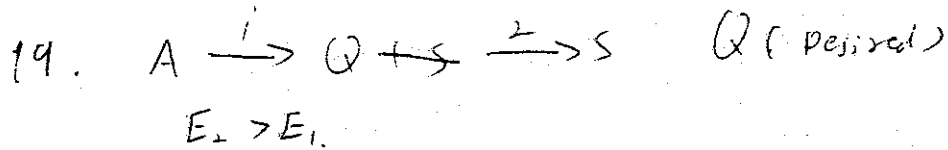
We want the opposite, <u>lower the temp</u>

23. Slope of an $\ln K_{eq}$ vs $\frac{1}{T}$ curve for an:

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{A_1 e^{-E_1/RT}}{A_1 e^{-E_2/RT}} = A' e^{(E_2 - E_1)/RT}$$

$$\ln(K_{eq}) = \ln A' + \frac{(E_2 - E_1)}{R}\,\frac{1}{T}$$

exothermic, $E_2 - E_1$ is pos

19. $A \xrightarrow{1} Q + S \xrightarrow{2} S$ Q (pesired)

   $E_2 > E_1$.

   The initial rate should high to get fast first reaction, but the temperature should diminish as Q accumulate to preferentially slow down the degradation reaction 2.

External limitation: $D_a = \dfrac{\text{maximum rxn rate}}{\text{maximum flux rate through diffusion layer}}$

$\Phi: \dfrac{\text{max rxn rate}}{\text{maximum Diffusion rate}}$

$B_i = \dfrac{k_s R}{D_{eff}}$: $\dfrac{\text{characterize film transport rate}}{\text{characterize intraparticle diff rate}}$.
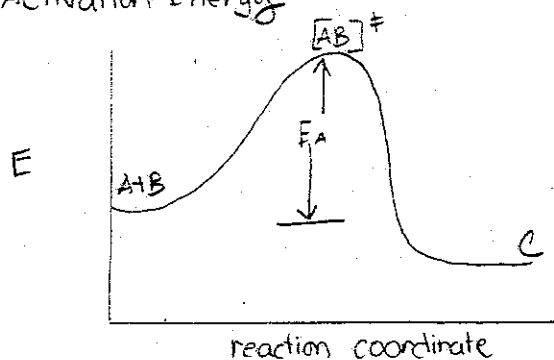
24. If $\Delta G = 0$ at eqm, why isn't $\Delta G_{rxn} = 0$ for any reaction?

$\Delta G = 0$ at equilibrium = chemical potentials are equal.

ΔG_{rxn} is kinetic. Components not in equilibrium, otherwise would not react. Measure of ~~whether~~ driving force for a reaction.

$$\Delta_r G_m = -RT \ln k^\circ + RT \ln J \qquad \prod (a_i)^{\nu_i}$$

25. Activation Energy

reaction coordinate

E_a is minimum energy required for the reaction to occur.

Difference in energy from reactants to transition state.

26. Langmuir Isotherm

- Equation describing the concentration of adsorbed species as a function of partial pressures at a constant temperature

Assumptions:
1) Every site is equivalent

2) Occupation of a specific site is not affected by the occupation of nearby sites.

3) Equilibrium is reached

For example:

$$A(g) \rightleftharpoons A(ads)$$
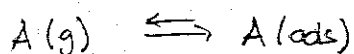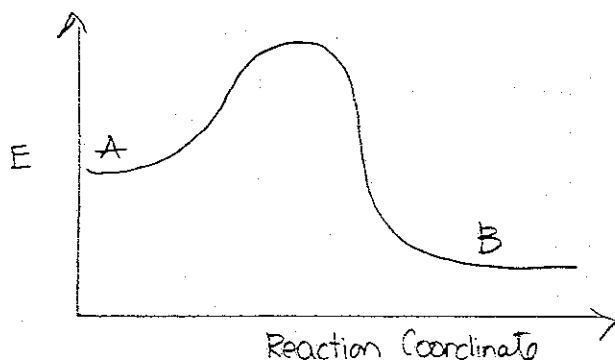
At steady state:

$$r_{ads} = r_{des}$$

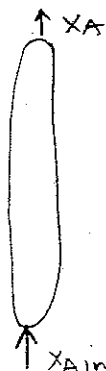$$k_A P_A (1 - \theta) = k_{-A} \theta$$

$$\boxed{\theta = \frac{K_A P_A}{1 + K_A P_A}}$$

33. Reaction Coordinate

Used to represent the course of a reaction as it goes from reactants to products. One can visualize the potential energy of species present at any point of the reaction.

Reaction Coordinate

37. Differential Reactors

used in initial Rate method

ΔX is small so that
$$r_A = \overline{r_{Aavg}}$$
$$\gamma' = \frac{C_{A0} \Delta X_A}{\overline{r_{Aavg}}}$$

Convenient way to determine the rate of reaction as a function of concentration. Differential reactors are small and conversion through the bed is small. Therefore concentration is approx. constant.

$$-r_a = \frac{F_{a0} - F_a}{W} = \frac{\mathcal{V}_0(C_{A0} - C_{Ae})}{W}$$

$$\overline{C_A} = \frac{C_{A0} + C_{Ae}}{2}$$

We can get $-r_a = F(\overline{C_A})$

38. Extent of reaction V. Equilibrium Conversion

Extent of reaction is a measure of the degree of conversion of the reactants. Time dependant <u>extensive variable</u> that is measured in moles. Useful because its not tied to any particular species

$$\xi = \frac{n_i - n_{i0}}{\mathcal{V}_i}$$

Fractional Conversion is an <u>intensive</u> measure of the progress of a reaction. Depends on a particular species chosen as a reference substance. (usually limiting reactant). <u>Equilibrium</u> conversion is dictated by ~~thermodynamics~~ thermodynamics.

$$f = \frac{n_{i0} - n_i}{n_{i0}}$$

42.

Sites are filled up. No sites left for reaction

Consider $\quad -r_A = \dfrac{k_1 \bar{K}_A P_A}{1 + \bar{K}_A P_A + \bar{K}_B P_B}$

$\uparrow$

rate slows as pressure is increased.

43. Apparent Activation Energy

<u>For internal diffusion controlling:</u>

$r'' = \eta k C_A \qquad$ assuming first order
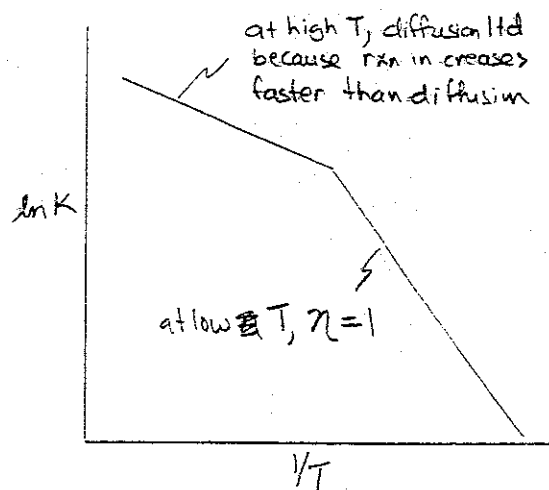
$\eta \to \dfrac{1}{\phi} = \dfrac{1}{f_s \sqrt{\dfrac{k \rho S_a}{D_{eff}}}}$

$r'' = \dfrac{1}{f_s} \sqrt{\dfrac{D_{eff}}{k \rho S}} \, k C_A$

$= \dfrac{1}{f_s} \sqrt{\dfrac{D_{eff}}{\rho S}} \, \boxed{k^{1/2}} C_A$

$\downarrow$

$= A^{1/2} e^{-\frac{E_a/2}{RT}}$

$\boxed{E_{apbs} = \dfrac{E_a}{2}}$

at high T, diffusion ltd because rxn increases faster than diffusion

$\ln K$

at low T, $\eta = 1$

$1/T$

Apparent order & activated energy:

Intraparticle diffusion:

$$\eta \sim \frac{1}{\phi}$$

$$\phi = \frac{V}{S} \cdot \sqrt{\frac{n+1}{2} \cdot \frac{k' \cdot C_s^{n-1} \cdot \rho_s}{D_{eff}}}$$

$$r_{obs} = \frac{1}{\phi} \cdot kC^n \sim k^{\frac{1}{2}} \cdot C^{\frac{n+1}{2}} \cdot \quad (\text{Knudson Region})$$

However, if not, $D_{eff} \sim \frac{1}{p} \sim \frac{\alpha}{RT} \frac{1}{CRT}$
$\qquad\qquad pv = nRT \quad p = CRT$

So, $r_{obs} = \frac{1}{\phi} \cdot kC^n \sim C^{\frac{n}{2}}$

If external mass transfer ltd

The apparent activation energy becomes equal to that of the mass transfer coefficient. This decrease is greater than that for internal mass transfer limitations.
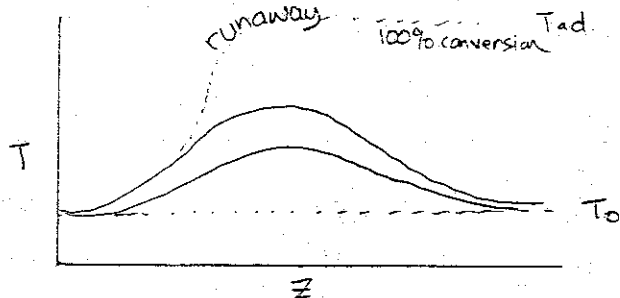
45. Temperature distribution in a PFR

1) Endothermic
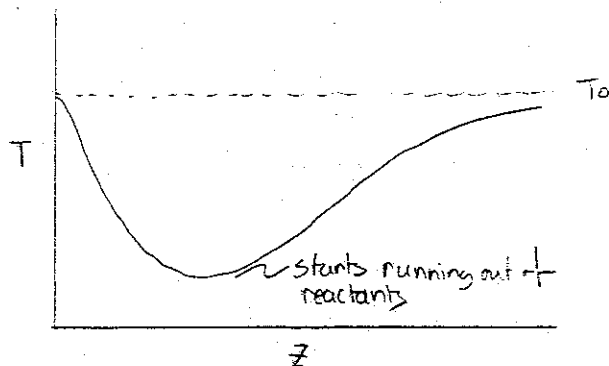
Temp goes down because reaction requires heat. As $T\downarrow$, $k\downarrow$ and reaction rate decreases accordingly.
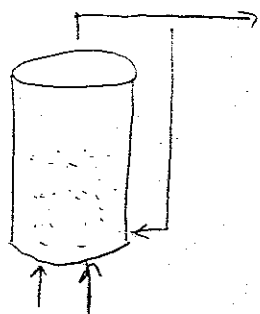
2) Exothermic

Runaway occurs because rxn increases temp which increases rxn ... Gets outta control and heat transfer isn't removing enough heat.

46. Fluidized Bed

Solid particles fluidized by high velocity gas flow.

+ excellent heat and mass transfer
+ catalyst can be extracted

- catalyst attrition and carry over
- reactor wall erosion

• need correct gas velocity for fluidization

• Two phase analysis:
   • bubble phase is PF
   • emulsion phase has mixing

Reaction occurs only in emulsion phase

48. K_{eq}

$$K_{eq} = \frac{[c]^c}{[a]^a [B]^b}$$

or

$$\Delta G = -RT \ln K_{eq}$$

where $\Delta G° = \sum \nu_i \Delta G_f°$ $\Delta G_f°$ are tabulated for standard temps.
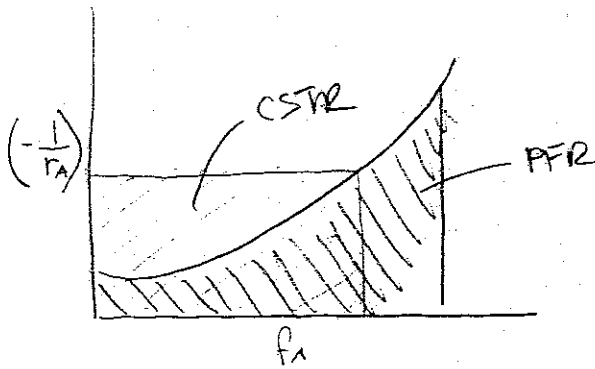
49.

Use a design equation:

$$\tau_{PF} = C_{Ao} \int_0^{f_A} \frac{df_A}{(-r_A)}$$

$$\tau_{PF} = C_{Ao} \int_0^{f_A} \frac{df_A}{K_A C_{Ao} \frac{(1-f_A)}{(1+\delta_A f_A)}}$$

$\uparrow$
solve

60

$$\text{CSTR} \Rightarrow \quad \Upsilon = \frac{C_{A0} f_A}{-r_A} \quad \Rightarrow \quad \left(\frac{-1}{r_A}\right)\left(f_A\right) = \frac{\Upsilon}{C_{A0}}$$

↑
area under
box

$$\text{PFR} \Rightarrow \Upsilon = C_{A0} \int \frac{df_A}{-r_A} \Rightarrow \int \frac{df_A}{-r_A} = \frac{\Upsilon}{C_{A0}}$$
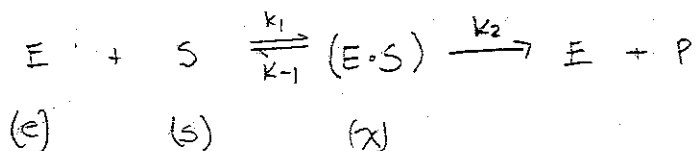
↑
area under
curve

66.   Batch Reactor

$$m\, C_p\, \frac{dT}{dt} = V(\Delta H)(-r_A) + Q_{jacket}$$

Pressure?

once we get $T(t)$ use EOS to get $P(t)$

62   MICHAELIS Mentin Kinetics

$$E \;+\; S \;\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}\; (E \cdot S) \;\xrightarrow{k_2}\; E \;+\; P$$

(e)   (s)   (x)

site balance:

$$e_0 = e + x \quad\Rightarrow\quad e = e_0 - x$$

assume rapid equilibrium:

$$k_1(e)(s) = k_{-1}(x)$$

$$k_1\big[(e_0) - (x)\big](s) = k_{-1}(x) \qquad\qquad \text{Insert site balance}$$

$$k_1(e_0)(s) - k_1(x)(s) = k_{-1}(x)$$

$$(x) = \frac{k_1(e_0)(s)}{k_{-1} + k_1(s)}$$

rate determining step:

$$r = k_2(x)$$

$$= \frac{k_2\, k_1\, e_0\, s}{k_{-1} + k_1(s)}$$

$$\boxed{\; r = \frac{k_2\, e_0\, s}{K_s + s} \qquad\qquad K_s = \frac{k_{-1}}{k_1} \;}$$

63.   Thiele Parameter

Dimensionless parameter used in describing the rate of internal diffusion to the rate of chemical reaction.

$$\phi = \frac{\text{max rxn rate}}{\text{maximum diffusion rate}}$$

$$= (f_i)\sqrt{\frac{K\,P_s}{D_{eA}}} \qquad\qquad \text{for 1st order}$$

$$= (f_i)\left(\left(\frac{n+1}{2}\right)\frac{K\, C_s^{\,n-1}\, P_s}{D_{ea}}\right)^{1/2} \qquad \text{other reaction orders}$$

Question #69

Determination of a 1st order rate constant from an nonideal

experimental data necessary

1) Residence time distribution function for the reactor, d.
2) average conversion of the effluent, $\langle f_a \rangle$

The easiest and probably the most accurate method to determine the rate constant for a 1st order reaction is to employ the segregated flow model. This model assumes that the various fluid elements move through the reactor at different speeds without mixing with one another. Consequently each fluid element behaves as if it were a batch reactor. The conversion attained within the various fluid elements will be equal to those in a batch reactors with holding times equal to the residence time of the different fluid elements.

$$\langle f_a \rangle = \sum_{\substack{all \\ residence \\ times}} \begin{pmatrix} \text{Fraction conversion as a} \\ \text{function of residence time} \end{pmatrix} \times \begin{pmatrix} \text{Fraction of the fluid element having} \\ \text{residence times between } t \text{ and } t+dt \end{pmatrix}$$

$$\langle f_a \rangle = \int_0^\infty f_a(t) \left(\frac{dF(t)}{dt} \right) dt \qquad \overline{x} = \int X \cdot E(t)\, dt$$

$$\uparrow \text{plug in}$$

$$r = -\frac{d(A)}{dt} = (A)_e \frac{df_a}{dt} = K(A)_e (1-f_a) \longrightarrow \quad d\ln(1-f_a) = -K\,dt$$

I.c. $\qquad t = 0 \qquad f_a = 0 \longrightarrow f_a(t) = 1 - e^{-Kt}$

$F(t)$ - is the volume fraction of the fluid at the outlet that has remained in the system for a time less than t, or the probability that an element of volume entering the reactor at time $t=0$ has left it within a period of time t.
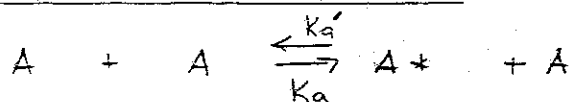
71. UNIMOLECULAR REACTIONS

△ ⟶ ⋀

cyclopropane
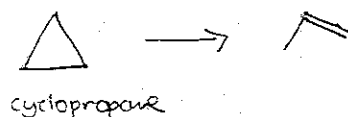
$$rate = k [cyclo]$$

unimolecular because they involve an elementary step where the reactant molecule turns into the product. But the composite mechanism involved bimolecular reactions.

<u>Lindemann-Hinshelwood mechanism</u>

$$A + A \overset{k_a'}{\underset{k_a}{\rightleftharpoons}} A^* + A$$

$$A^* \overset{k_b}{\longrightarrow} P \qquad\qquad RDS$$

<u>PSSH</u>

$$\frac{dA^*}{dt} = 0 = k_a[A]^2 - k_a'[A^*][A] - k_b[A^*]$$

$$[A^*] = \frac{k_a[A]^2}{k_b + k_a'[A]}$$

<u>RDS</u>

$$\frac{d[P]}{dt} = k_b[A^*] = \frac{k_b k_a[A]^2}{k_b + k_a'[A]}$$

The rate of deactivation by A,A* collisions is much greater than kinetic rate

$$k_a'[A^*][A] \gg k_b[A^*]$$

$$k_a'[A] \gg k_b$$

$$\therefore \quad rate = \frac{k_b k_a[A]}{k_a'} \qquad First\ order$$

If pressures were reduced, we would see the full rate law:

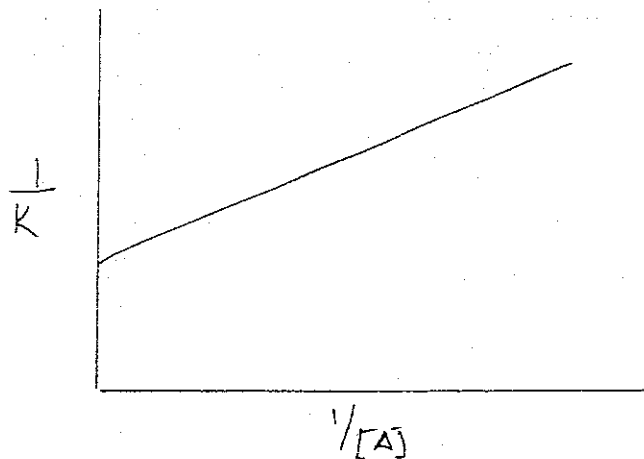$$\text{rate} = \frac{K_a K_b [A]^2}{K_b + K_a' [A]} = K_a [A]^2$$

Plotting K_{eff} vs. pressure:

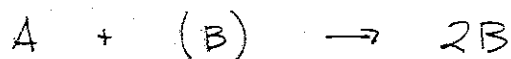$$\text{rate} = \frac{K_a K_b [A][A]}{K_b + K_a'[A]} = K_{eff} [A]$$

$$K_{eff} = \frac{K_a K_b [A]}{K_b + K_a'[A]}$$

$$\frac{1}{K_{eff}} = \frac{1}{K_a [A]} + \frac{K_a'}{K_a K_b}$$
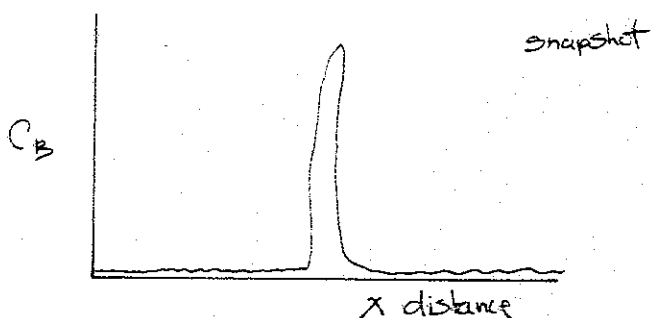

We would expect same plot for $\frac{1}{K}$ vs. P

Autocatalytic Reactions

$$A + (B) \longrightarrow 2B$$

$$\frac{1}{A_0 + B_0} \ln \frac{A_0 B}{B_0 A} = K t_B = K \tau_{PF} \qquad (\text{constant } \rho)$$

Concentration profiles

Plug Flow

snapshot

C_B vs X distance

- Plug flow reactors are not ideal because B is not kept in the system
- Use CSTR or BSTR

BATCH ~~BSTR~~

C_B

$\times \ C_B = C_A = 0.5(C_{A0} + C_{B0})$

t_B

initiation time

- rate $\frac{dC_B}{dt_B}$ = slope

$\left(-\frac{1}{r_A}\right)$

PFR. least economical use

$C*$

most economical use

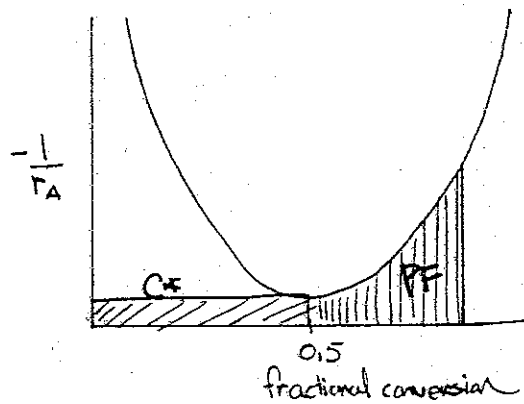O ____ f ___ 0.5 ___ 1
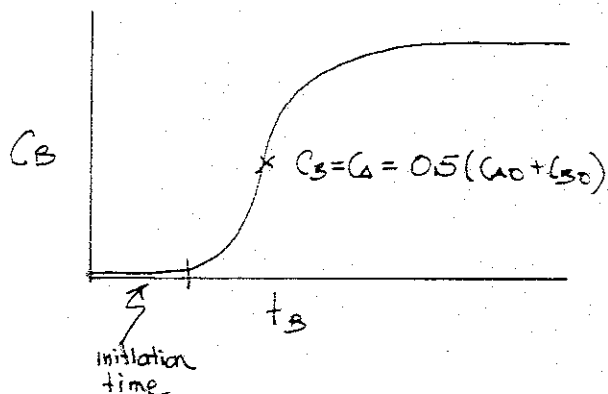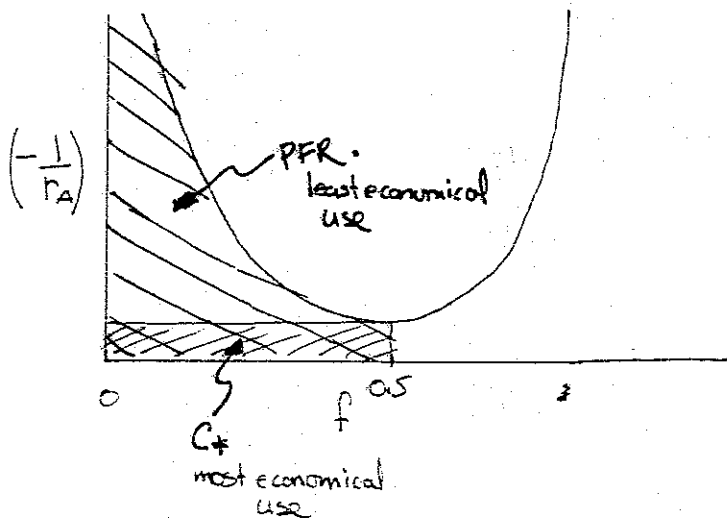
- in the design plots recall that CSTR is area in rectangle, PFR is area under curve
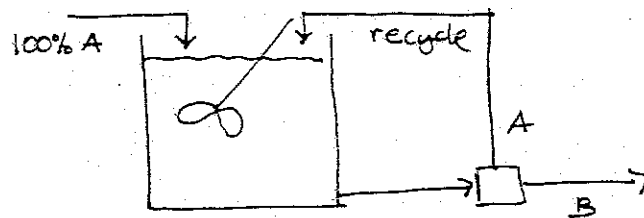
- for $f < \approx 0.5$ use CSTR
- for $f > f*$ use PFR
  there is a certain point $f*$ when PFR is better.
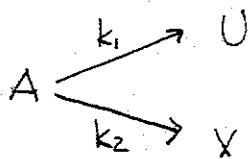
<u>design strategy</u>

1) Use CSTR for fractional conversion up to 0.5
Then use PFR after that

2) Use a recycle stream, if using one reactor

PARALLEL REACTIONS

$$(-r_A) = k_1 A + k_2 A$$

<u>design equation</u>
$$t_B = -\int_{A_0}^{A} \frac{dA}{(-r_A)} \qquad \text{constant density}$$

$$= -\int_{A_0}^{A} \frac{dA}{k_1 A + k_2 A}$$

$$\ln\left(\frac{A_0}{A}\right) = (k_1 + k_2) t_B$$

$$\boxed{A = A_0 \, e^{-(k_1 + k_2) t_B}}$$