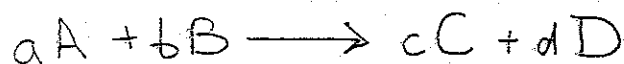
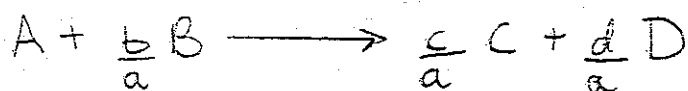


The Rate and Volume expressions and Stoichiometry

Stoichiometry:



Basis: use limiting reactant (arbitrarily choose A for example)



$$\underbrace{-\frac{r_A}{a} = -\frac{r_B}{b}}_{\substack{\text{negative} \\ \text{(consumed)}}} = \underbrace{\frac{r_C}{c} = \frac{r_D}{d}}_{\substack{\text{positive} \\ \text{(formed)}}$$

Stoichiometric table: (use to evaluate molar changes in species due to rxn.)

Species	Initially (mol)	Change (mol)	Remaining (mol)
A	N_{A0}	$-(N_{A0} X_A)$	$N_A = N_{A0} (1 - X_A)$
B	N_{B0}	$-\frac{b}{a} (N_{A0} X_A)$	$N_B = N_{B0} - \frac{b}{a} N_{A0} X_A$
C	N_{C0}	$+\frac{c}{a} (N_{A0} X_A)$	$N_C = N_{C0} + \frac{c}{a} N_{A0} X_A$
D	N_{D0}	$+\frac{d}{a} (N_{A0} X_A)$	$N_D = N_{D0} + \frac{d}{a} N_{A0} X_A$
I (inert)	N_{I0}	—	$N_I = N_{I0}$
	N_{T0}		$N_T = N_{T0} + \underbrace{\left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)}_{\delta} N_{A0} X_A$

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \leftarrow \text{Increase in total \# of moles per mol of A reacted}$$

Rate and Volume Expressions cont.

Volume change with Reaction:

Gas Phase

$$EoS - PV = Z N_T RT \quad \text{(ideal gas)}$$

$$V = V_0 \left(\frac{P_0}{P} \right) \frac{T}{T_0} \left(\frac{Z}{Z_0} \right) \frac{N_T}{N_{T0}}$$

no pressure drop

$$N_T = N_{T0} + \delta N_{A0} X$$

$$\frac{N_T}{N_{T0}} = 1 + \frac{N_{A0}}{N_{T0}} \delta X_A$$

y_{A0} or x_{A0} (gas or liquid ϕ)

$\epsilon = \frac{\text{change in total number of moles when reaction is completed}}{\text{total \# of moles fed to the reactor}}$

$$= Y_{A0} \delta$$

Rate Expression:

Ideal gas:

$$-r_A = k C_A \leftarrow \text{first order}$$

$$C_A = \frac{P_A}{RT} = \frac{y_A P}{RT}$$

$$\left. \begin{aligned} &= k C_A C_B \quad A + B \rightarrow C \\ &= k C_A^2 \quad 2A \rightarrow C \end{aligned} \right\} \text{second order}$$

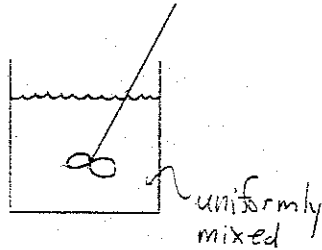
$$= k' C_A \sim \text{where } k' = k C_B \left\} \text{pseudo first order conc. of } B \gg \text{conc. of } A \text{ and remains essentially const.}$$

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

$$\text{Van Hoff's eqn.} \quad \frac{k_1}{k_2} = K_c \quad \frac{d \ln K_c}{dT} = \frac{\Delta H}{RT^2}$$

General Reactor Design

1) Batch Reactor



a) Composition changes with time, however, at any given instant the composition throughout the reactor is uniform

b) Generally used for liquid phase reactions

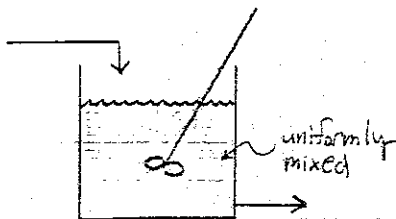
advantages

- simple, needs little supporting equipment
- Ideal for small scale laboratory studies on reaction kinetics
- for specialty chemicals, polymers, pharmaceuticals

Disadvantages

- low production capacities
- high labor costs per unit production

2) CSTR



a) Ideal feature is the assumption of complete uniformity of conc. and temp. throughout the reactor. — to approach this ideal mixing pattern it is necessary that the feed be intimately mixed with the contents of the reactor in a time interval that is very small compared to the mean residence time of the fluid flowing through the vessel

advantages

- Good when temp. control is a critical aspect
- good when catalyst must be kept in suspension
- for large scale operation when rate of reaction is fairly high to extremely high

Disadvantages

- conversion of reactant per volume reactor is smallest of the flow reactors (high capital costs)

3) PFR



Plug flow (fluid elements move with a uniform velocity along parallel stream lines / highly turbulent flow)

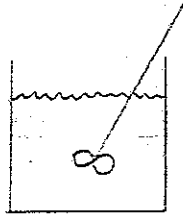
advantages

- easy to maintain
- usually produces highest conversion per reactor volume of any flow reactor

Disadvantages

- Difficult to control temperature (hot spots can occur when rxn is highly exothermic)

The Batch Reactor



material Balance

$$\left(\begin{array}{c} \text{rate of} \\ \text{reactant} \\ \text{flow into} \\ \text{element of} \\ \text{volume} \end{array} \right) = \left(\begin{array}{c} \text{rate of} \\ \text{reactant} \\ \text{flow out} \\ \text{of element} \\ \text{of volume} \end{array} \right) + \left(\begin{array}{c} \text{rate of reactant} \\ \text{loss due to} \\ \text{chemical reaction} \\ \text{within the element} \\ \text{of volume} \end{array} \right) + \left(\begin{array}{c} \text{rate of} \\ \text{accumulation} \\ \text{of reactant in} \\ \text{element of} \\ \text{volume} \end{array} \right)$$

$$F_{j0} = F_j + \int_V \overset{\text{negative (reactant loss)}}{r_j} dV + \frac{dN_j}{dt} \leftarrow \text{for species } j$$

Design Equation:

$$\frac{dN_A}{dt} = - \int_V r_A dV = - \bar{r}_A V$$

rate is not a function of V (well mixed)

Conversion:

$$X_A = \frac{N_{A0} - N_A}{N_{A0}}$$

$$N_A = N_{A0}(1 - X_A)$$

Differential form:

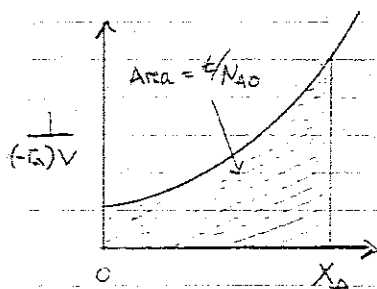
$$N_{A0} \frac{dX_A}{dt} = - \bar{r}_A V$$

Integral form:

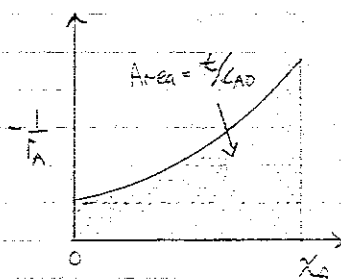
$$t = N_{A0} \int_0^X \frac{dX_A}{-\bar{r}_A V} \quad \text{and} \quad \underbrace{\int_0^t V(t) dt}_{\text{Semi-batch (V = V(t))}} = N_{A0} \int_0^X \frac{dX_A}{-\bar{r}_A}$$

note: These eqns. are completely general and apply to const./non-const. density (volume) and temp. reactions

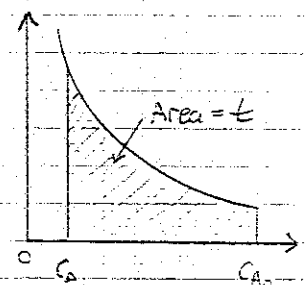
- Density (volume) changes occur due to the stoichiometry of the reaction
- Temp. changes occur due to external heating/cooling or energy generated by the rxn.



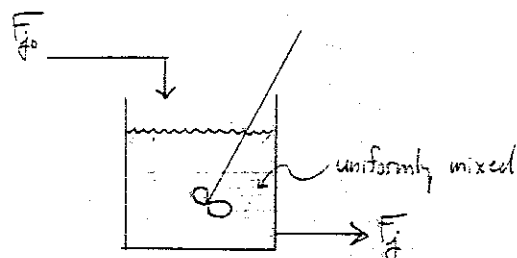
General Case



Constant-density Systems



CSTR



Material Balance:

Input = output + disappearance by reaction + accumulation

$$\underset{\text{(moles/time)}}{F_{j0}} = \underset{\text{(moles/time)}}{F_j} + (-r_j)V \left(\frac{\text{mole of species } j \text{ reacting}}{\text{(time) (volume of fluid)}} \right) \left(\text{volume of reactor} \right)$$

For $j = A$

$$F_{A0} = F_A - r_A V$$

$$F_A = F_{A0} (1 - X_A)$$

$$F_{A0} X_A = (-r_A) V ; \quad \tau = \frac{C_{A0} X_A}{-r_A}$$

Space time

$$\tau = \frac{1}{S} = \left(\frac{\text{time required to process one reactor volume of feed measured at specific conditions}}{\text{measured at specific conditions}} \right) = [\text{time}]$$

Space Velocity

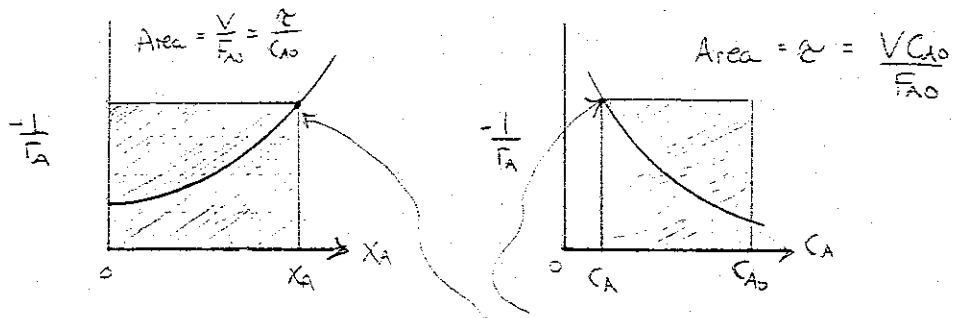
$$S = \frac{1}{\tau} = \left(\frac{\text{number of reactor volumes of feed at specified conditions which can be treated in unit time}}{\text{can be treated in unit time}} \right) = [\text{time}^{-1}]$$

$$\tau = \frac{1}{S} = \frac{C_{A0} V}{F_{A0}}$$

$$U_0 = \frac{F_{A0}}{C_{A0}} \left[\frac{\frac{\text{mol}}{\text{time}}}{\frac{\text{mol}}{\text{vol}}} \right] = \left[\frac{\text{vol}}{\text{time}} \right]$$

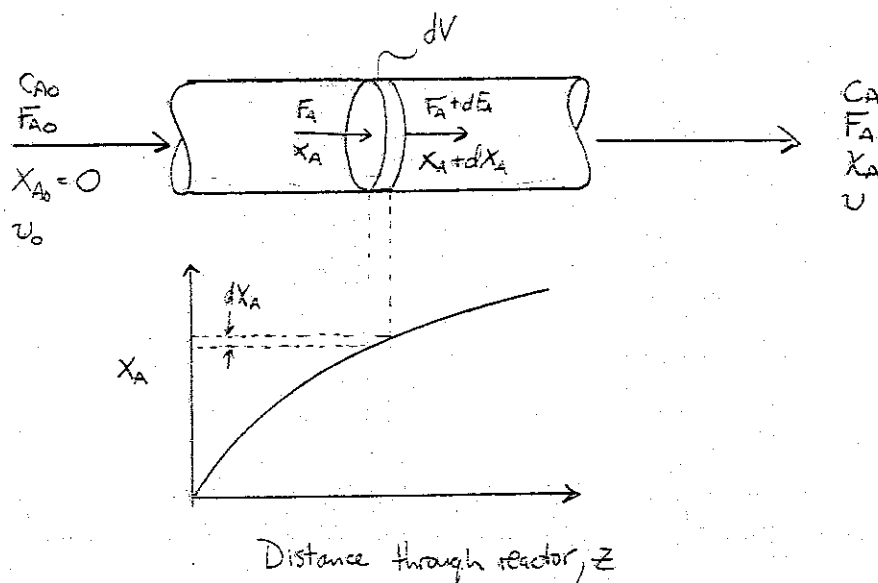
$$= \frac{V}{U_0}$$

General Case



conditions within reactor
and at the exit

PFR



Material Balance:

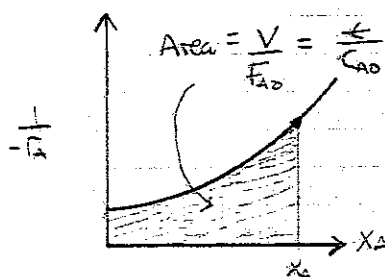
input = output + disappearance by reaction + accumulation

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

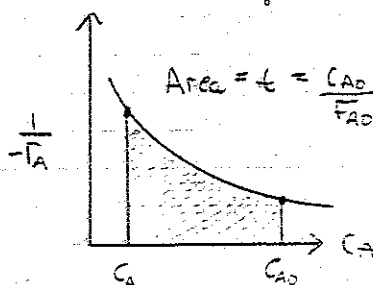
$$F_{A0} dX_A = (-r_A) dV$$

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A} \quad \Leftarrow \text{design eqn.}$$

General Case



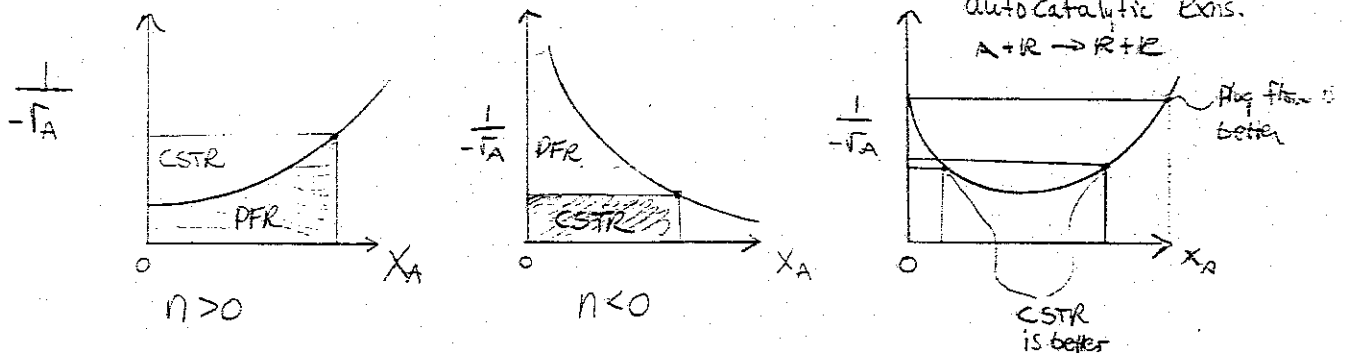
Const. density systems



Choosing The Right Kind of Reactor

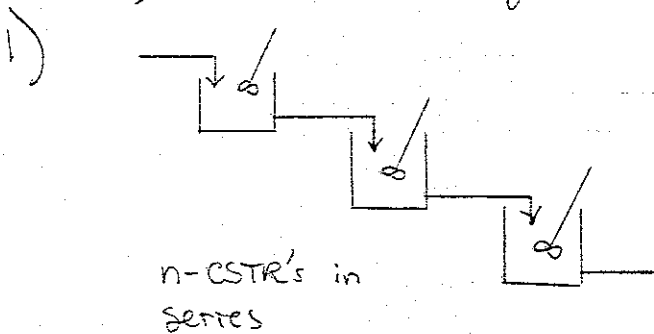
Rule 1. For single reactions

To minimize the reactor volume, keep the concentration as high as possible for a reactant whose order is $n > 1$. For components where $n < 1$ keep the concentration low.



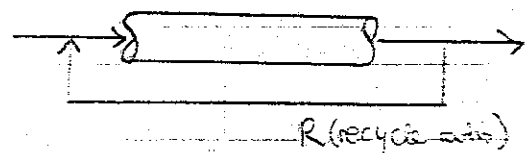
minimize area under curve ($\frac{1}{-r_A}$ vs. X_A); this also applies to multiple reactor configurations.

also, Two limiting cases



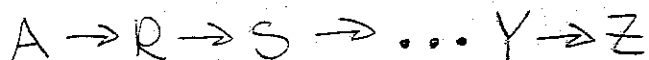
$n \rightarrow \infty$ this CSTR model reduces to that of a PFR.

2)

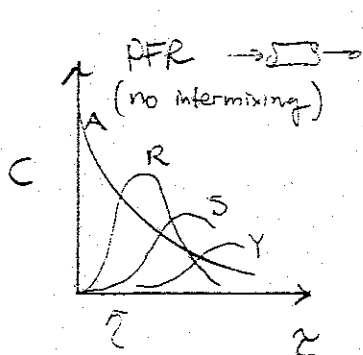


$R \rightarrow \infty$ the PFR reduces to an ideal CSTR

Rule 2: For reactions in series

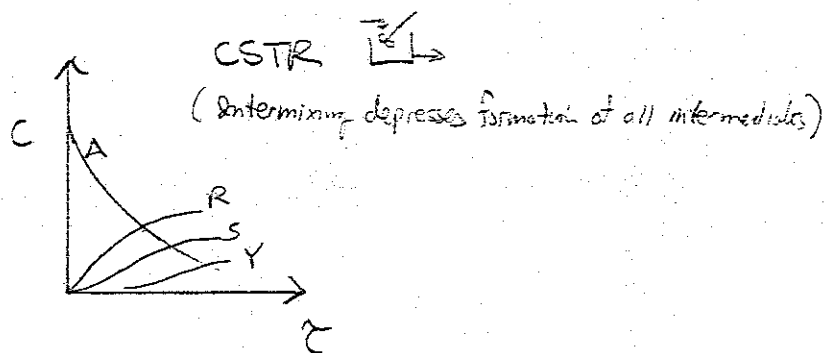


To maximize any intermediate, do not mix fluids that have different concentrations of the active ingredients - reactants or intermediates.

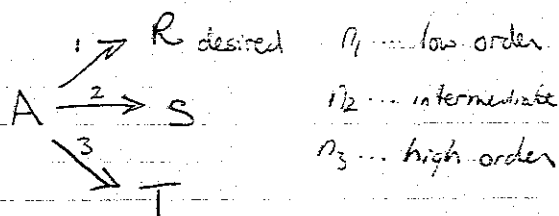


maximization
of intermediates

(keep intermediate conc. high)



Rule 3: For parallel reactions

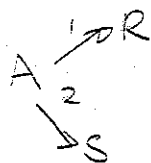
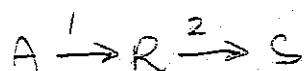


To get best product distribution:

- low C_A favors the reaction of lowest order
- high C_A favors the reaction of highest order
- If the desired reaction is of intermediate order then some intermediate C_A will give the best product distribution
- For reactions all of the same order the product distribution is not affected by the concentration level.

12

Rule 4: Effect of Temperature on Product Distribution



with

$$k_1 = k_{10} e^{-E_1/RT}$$

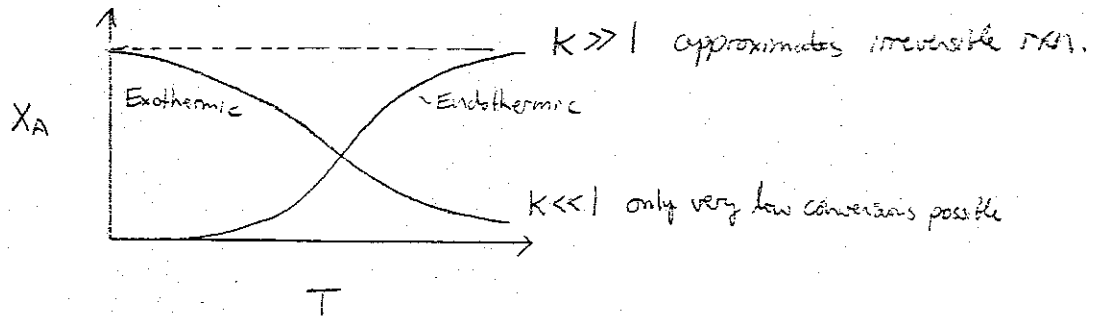
$$k_2 = k_{20} e^{-E_2/RT}$$

high T favors rxn. with larger E , while low T favors reaction with smaller E .

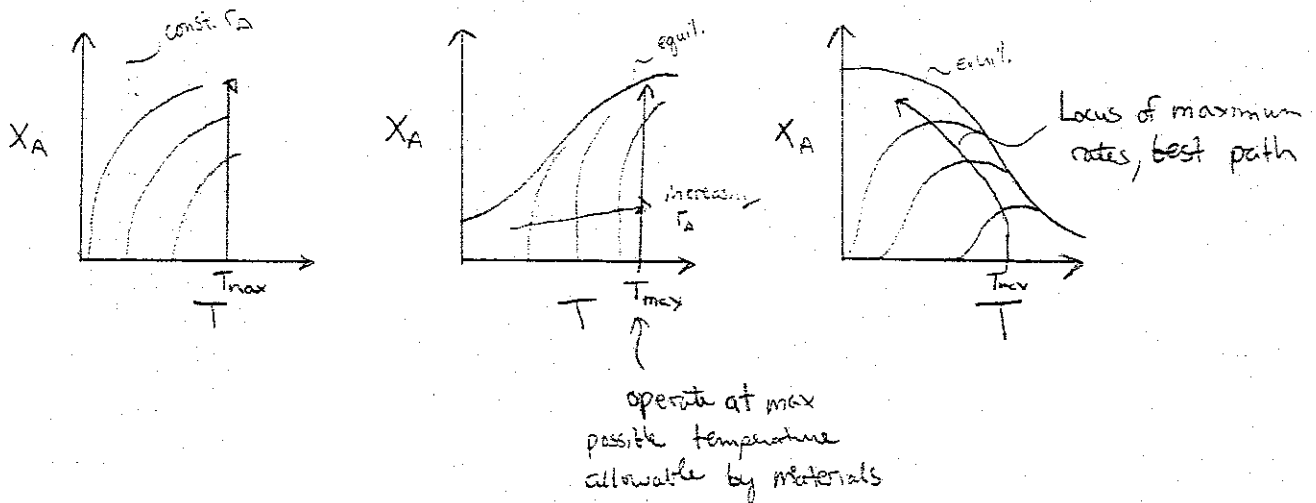
Non-Isothermal Reactors

For non-isothermal reactors, both mass and energy balances must be considered.

Effect of Temperature on equilibrium conversion



Consider general shape of conversion vs. Temp. Plots



For non-isothermal design mass and energy balances must be solved simultaneously

For a batch reactor:

$$\text{mass: } N_{A0} \frac{dX_A}{dt} = V r_A(X_A, T)$$

$$\text{Energy: } m C_p \frac{dT}{dt} = V(-\Delta H_{rxn}) r_A(X_A, T) + q A_k$$

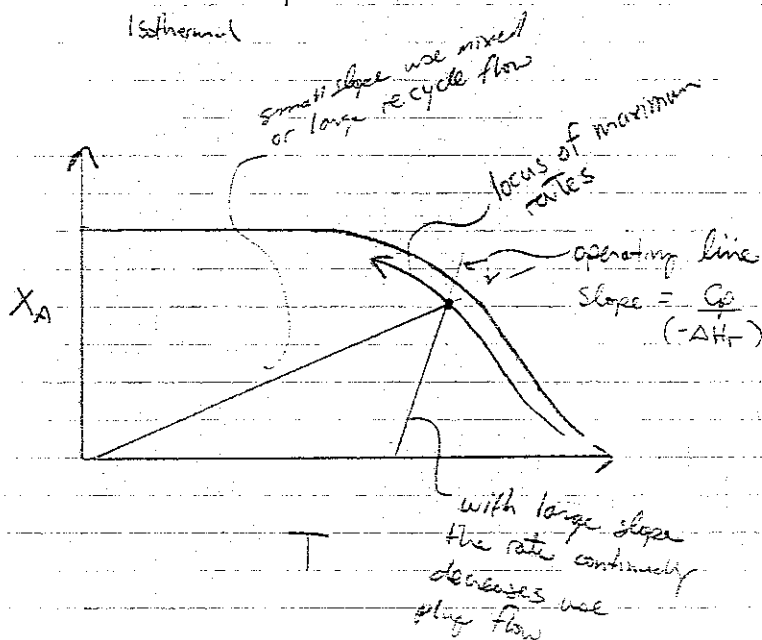
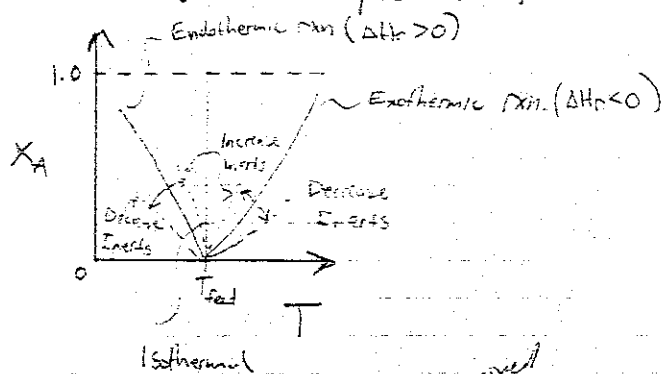
\uparrow generation \uparrow heat transferred
 \uparrow accumulation

$$q = U(T_f - T)$$

\uparrow temp. of heating medium

for adiabatic operation $q = 0$

Graphical representation of energy balance eqn. for adiabatic operation



CSTR:

Mass Balance:

$$\frac{dN_A}{dt} = F_{A0} - F_A + V(-r_A)$$

for steady-state operation

$$V = \frac{F_{A0} X_A}{-r_A}$$

Energy Balance:

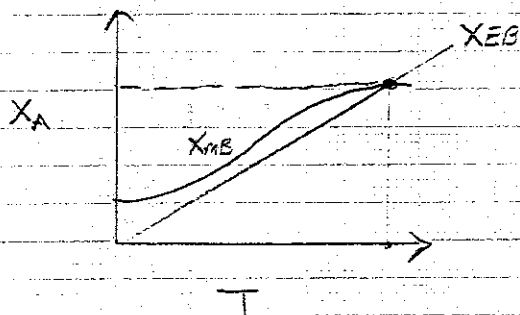
$$V \rho_f C_p \frac{dT}{dt} = F_{A0} \rho_f C_p (T_0 - T) + V(-\Delta H_r) r_A + A_k U (T_f - T)$$

for steady-state and adiabatic

$$F_{A0} \rho_f C_p (T_0 - T) = -V(\Delta H_r) r_A$$

Use mass balance to eliminate the rate term in the energy balance:

$$X_{EB} = \frac{\rho_f C_p}{-r_A} (T_0 - T)$$



* at steady-state the CSTR operates isothermally, which is a result of complete mixing. So, both the mass and energy balances can be considered independently (uncoupled)

Multiple steady-states in a CSTR (First-order Rxn)

Energy Balance : (Steady-state)

$$-F_{A0} X_A (\Delta H_r) = F_{A0} \rho_f C_p (T - T_0) + A_k U (T - T_r)$$

Mass Balance :

$$V = \frac{v_0 C_{A0} X_A}{k C_A}$$

$$X_A = \frac{\tau k}{1 + \tau k}$$

Substitute mass balance (X_A) into energy balance

$$F_{A0} (-\Delta H_r) \frac{\tau k}{1 + \tau k} = F_{A0} \rho_f C_p (T - T_0) + A_k U (T - T_r)$$

$$\text{Let } K = \frac{UA}{\rho_f C_p F_{A0}}$$

$$T_c = \frac{K T_r + T_0}{1 + K}$$

$$\underbrace{(-\Delta H_r) \frac{\tau k}{1 + \tau k}}_{G(T)} = \underbrace{\rho_f C_p (1 + K)(T - T_c)}_{R(T)}$$

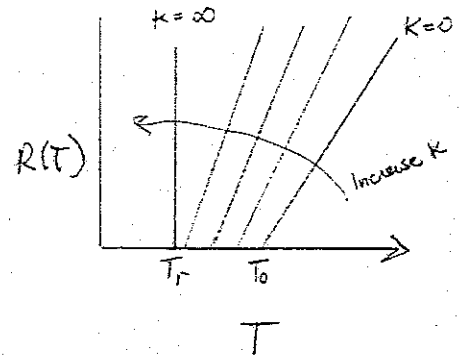
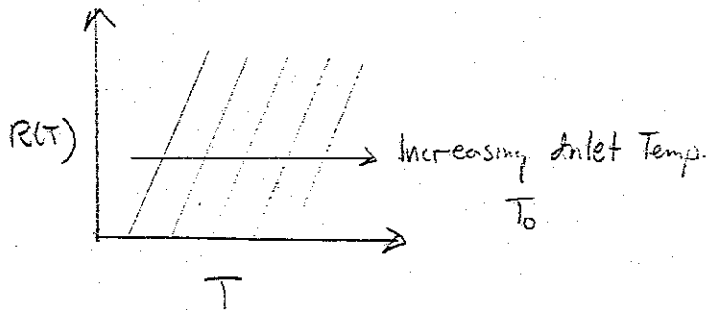
$G(T) \leftarrow$ heat generation term

$R(T) \leftarrow$ Heat removal term

$$G(T) = (-\Delta H_r) X_A = \frac{(-\Delta H_r) \tau k}{1 + \tau k}$$

$$R(T) = \rho_f C_p (1 + K)(T - T_c)$$

Heat removal $R(T)$



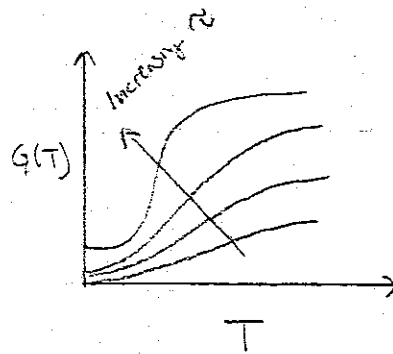
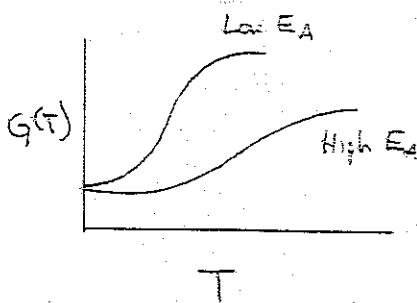
$$R(T) = \underbrace{\frac{P_0 Q}{1+k}}_{\text{Slope}} T - \underbrace{\frac{P_0 Q}{1+k} [kT_r + T_0]}_{\text{Intercept}}$$

$$\left. \begin{array}{l} K=0 \quad T_c = T_0 \\ K=\infty \quad T_c = T_r \end{array} \right\} T_r < T_0$$

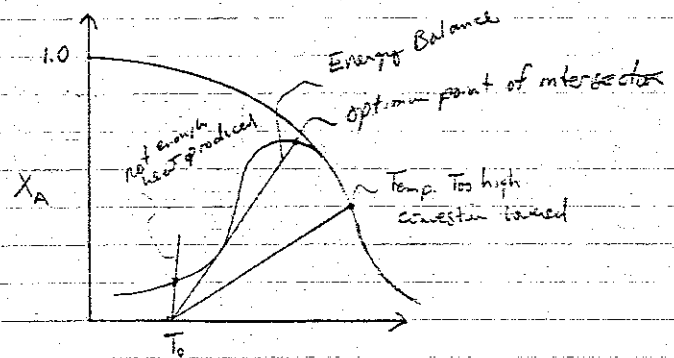
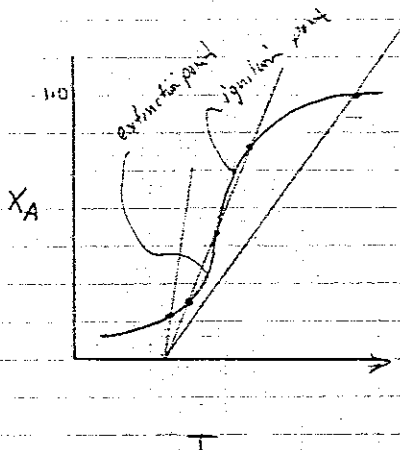
Slope increases & intercept moves to the left

For $T_r > T_0$ the intercept moves to the right

Heat Generation



Consider both mass and Energy Balances



Exothermic irreversible rxn.

Exothermic reversible rxn.

Non-Ideal Reactors

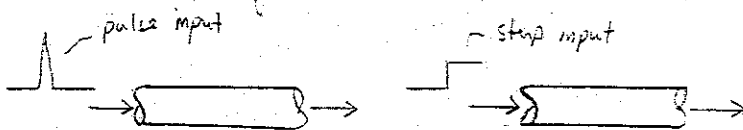
Factors to describe the contacting or flow pattern in a reactor :

1. RTD or residence time distribution of material that is flowing through the reactor
2. State of aggregation of the flowing material, its tendency to clump and for a group of molecules to move about together
3. Earliness and lateness of mixing of material in the vessel

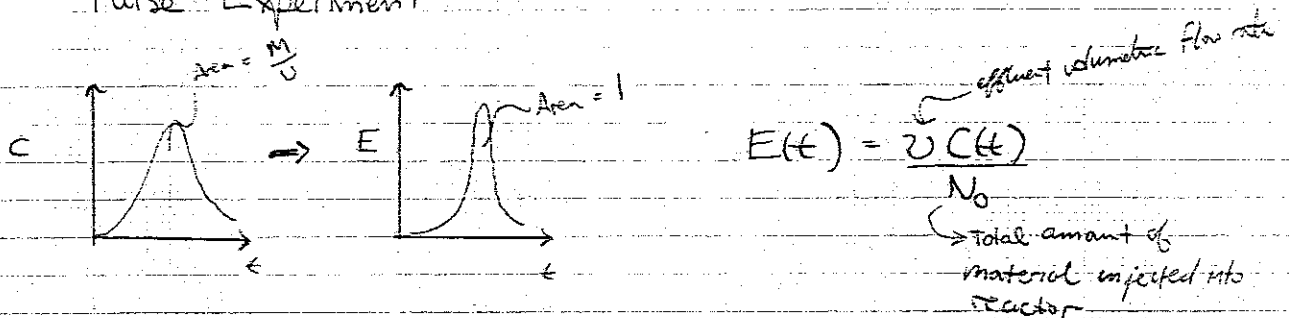
RTD : E = exit age distribution [fraction of material that has resided in the reactor between t and $t+dt$]

$$\int_0^{\infty} E dt = 1 \quad \text{dimensionless}$$

Determining E (Experimentally)

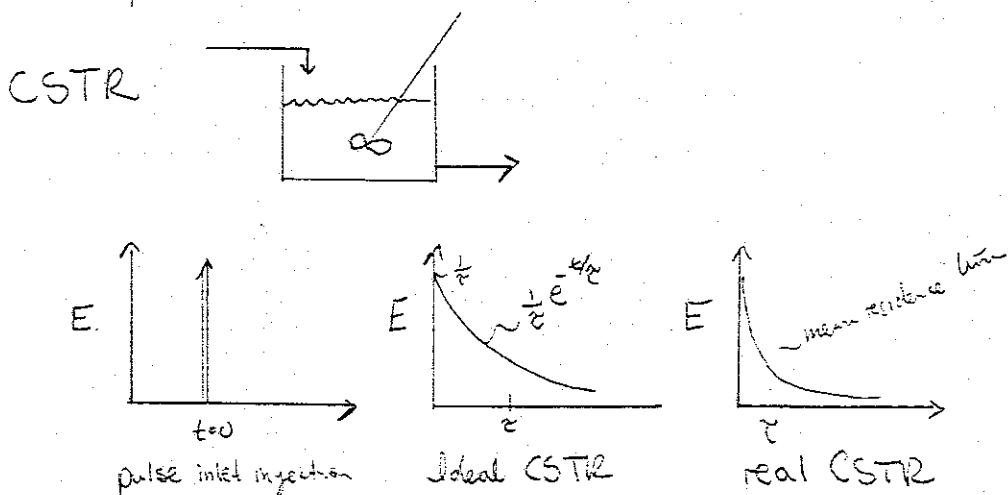
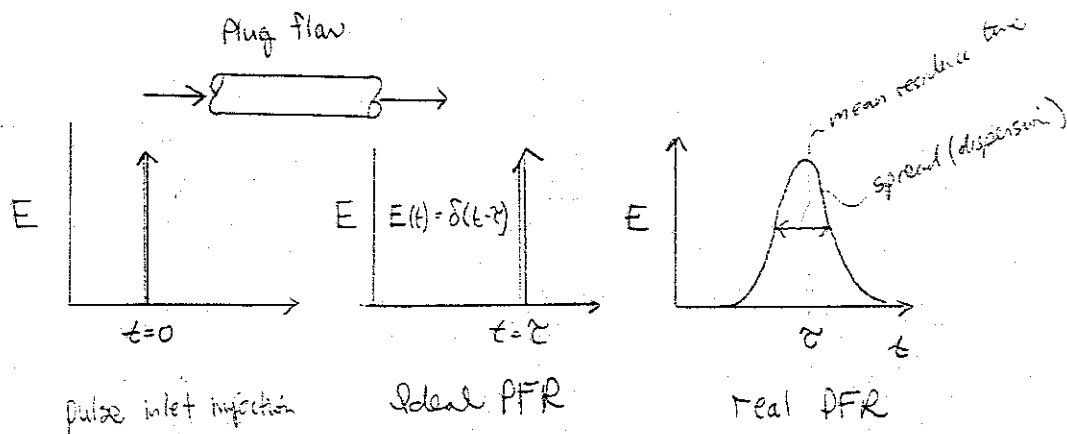


Pulse Experiment :



$$E(t) = \frac{C(t)}{\int_0^{\infty} C(t) dt}$$

Reactor response to a pulse injection:



Ideal RTD:

PFR - $E(t) = \delta(t - \tau)$

CSTR - $E(t) = \frac{1}{\tau} e^{-t/\tau}$

Mean Residence time is the Centroid of the RTD

$$\tau \equiv \int_0^{\infty} t E(t) dt = \frac{V}{F'_R} \quad \text{molar flow rate}$$

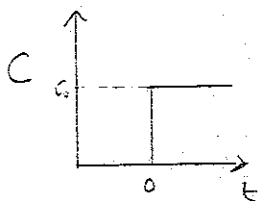
For CSTR the RTD is derived from a transient mass balance.

$$V \frac{dC}{dt} = \underbrace{M \delta(t)}_{\text{inlet}} - \underbrace{F'_R C}_{\text{outlet}} \quad \text{I.C. at } t=0 \quad C=0$$

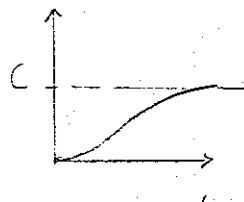
$$\frac{dC}{dt} + \frac{F}{V} C = \frac{M}{V} \delta(t)$$

Using integrating factor $\sim C = \frac{M}{V} e^{-t/\tau}$

Step experiment:



step injection



step response

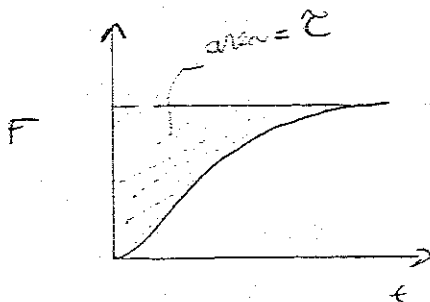
$$E(t) = \frac{d}{dt} \left[\frac{C(t)}{C_0} \right]$$

↑
step conc.

Other Distribution functions:

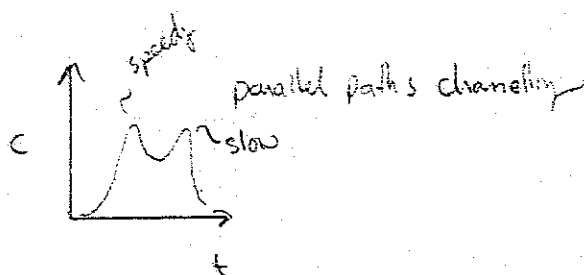
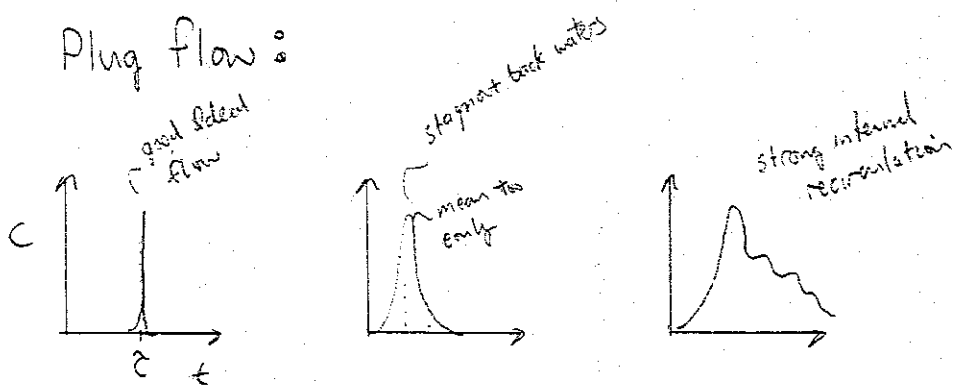
$$\int_0^t E(t) dt = \left[\begin{array}{l} \text{fraction of fluid that} \\ \text{has been in reactor} \\ \text{for less than time } t \end{array} \right] = F(t)$$

$$\int_t^\infty E(t) dt = \left[\begin{array}{l} \text{fraction of fluid that} \\ \text{has been in reactor} \\ \text{for longer than time } t \end{array} \right] = 1 - F(t)$$

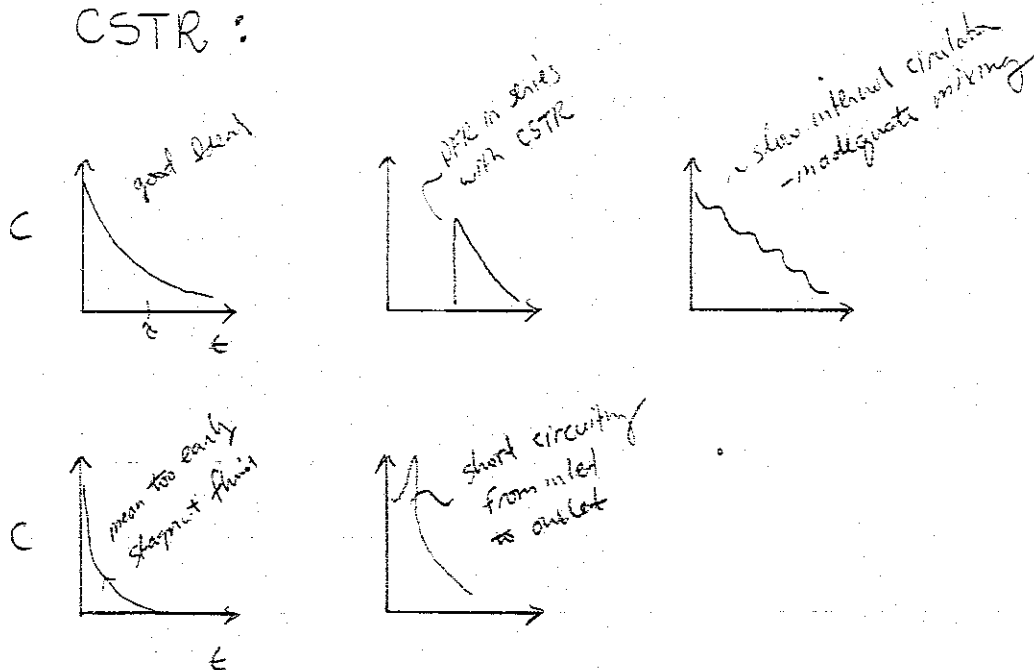


Interpretation of RTD:

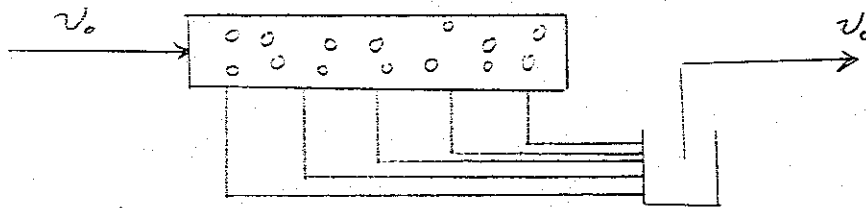
Plug flow:



CSTR:



Segregation and Maximum Mixedness



Segregation:

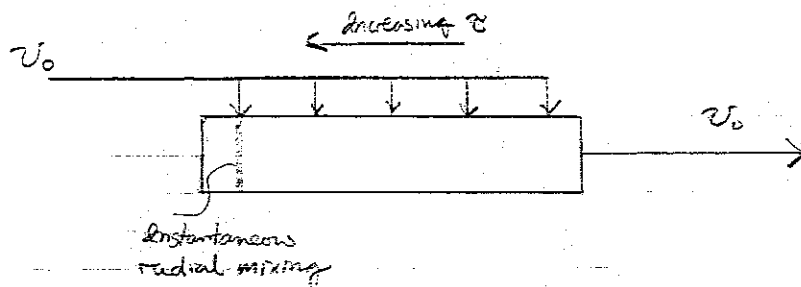
Batches of molecules are removed from the reactor at different locations along the reactor in such a manner to duplicate the RTD function $E(t)$. Lumping all of the molecules that have the same residence time in the reactor into the same globule.

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

$X(t) \sim$ determined for a batch reactor $\frac{dN_A}{dt} = (-r_A)V$

$E(t) \sim$ determined for specific reactor of interest

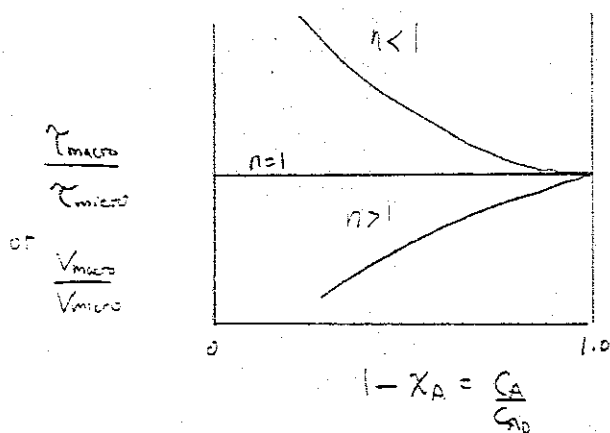
Maximum Mixedness:



$$\frac{d\bar{X}}{dt} = \frac{r_A}{C_{A0}} + \frac{E(t)}{1-F(t)} \bar{X}$$

For first order rxn. segregation and maximum mixedness are equivalent because conversion is independent of concentration, so mixing with surrounding molecules is unimportant.

For a given RTD and Reaction orders > 1 maximum mixedness model gives lower bound on conversion.



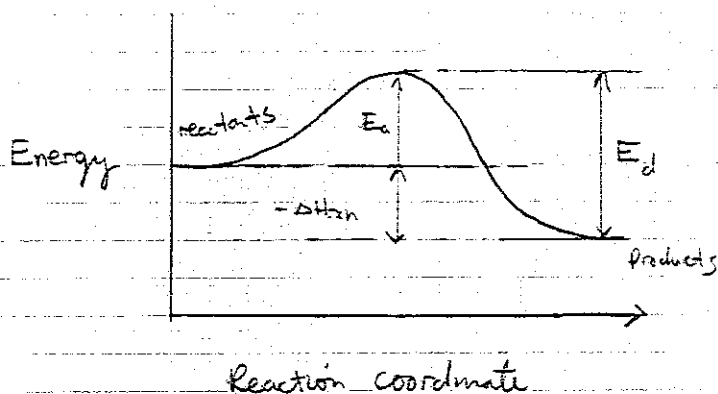
For $n > 1$ $X_{seg} > X_{max mix} \Leftarrow$ Keep conc. as high as possible

For $n < 1$ $X_{max mix} > X_{seg} \Leftarrow$ Keep conc. as low as possible

Transition State Theory

The reacting system is postulated to pass through a configuration of minimum potential energy as it goes from reactants to products, and the rate of passage through this configuration is the rate of reaction.

1. The # of activated complexes is determined by an equilibrium with reactant molecules
2. It is assumed that the generation of products by decomposition of the transition state complex doesn't affect this equilibrium



E_a = activation energy for forward rxn

$(E_a - \Delta H_{rxn}) = E_d$ = activation energy for reverse rxn



↖ transition state complex

Equilibrium Constant:

$$K_c^\ddagger = \frac{Q_\ddagger^\circ}{Q_{AB}^\circ Q_C^\circ} e^{-E/RT}$$

partition function for TS

reactant partition functions

Rate of reaction:

$$\Gamma = \nu_\ddagger C^\ddagger$$

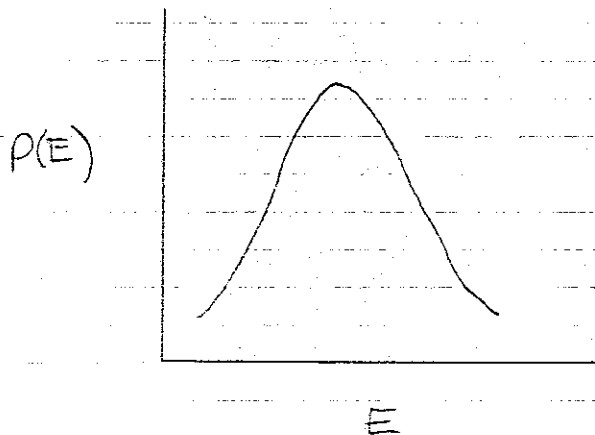
$$\Gamma = \nu_\ddagger \frac{Q_\ddagger^\circ}{Q_{AB}^\circ Q_C^\circ} e^{-E/RT} C_{AB} C_C$$

- assume one vibrational degree of freedom is fixed by the movement through the transition state

The exponential term \sim

The probability that a molecule will be in a particular energy state, E_i , is given by the Boltzmann law,

$$P(E_i) \propto g_i e^{-E_i/RT}$$



Features of TST :

- Predicts only first order behavior for the unimolecular rxn. This failure is due to the assumption of universal equilibrium between reactants and the transition state complex.

- At low pressures the collisional deactivation process becomes very slow, since collisions are infrequent, and the rate of decomposition becomes large compared to deactivation. In such an event, equilibrium cannot be established; nearly every molecule which is activated will decompose to product.


- Frequency Factor

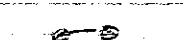
$$\frac{kT}{h} \sim 10^{13} \text{ sec}^{-1} \leftarrow \text{unimolecular rxn}$$

Range from 10^{-9} - 10^{-15}
 \uparrow \leftarrow two non-linear molecules
 two atoms non-linear complex

Why deviations from 10^{-13}

~ consider $(\Delta S^\ddagger)^\ddagger$ Large structural changes = large $(\Delta S^\ddagger)^\ddagger$

Case 1:  $\sim 10^{-12} - 10^{-11}$ sec. Configurational order)

Case 2: (resembles previous State more than Case 1)  non-linear $k \sim 10^{-11} - 10^{-10}$ sec. Configurational order)

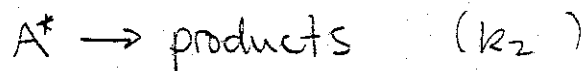
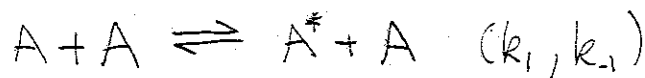
Case 1: $(\Delta S^\ddagger)^+$

$(\Delta S^\ddagger)^+$	k_0	Notes
2	1×10^{14}	less ordered, activation starts for less than 1000
0	6×10^3	unimolecular
-20	8×10^8	activation state has less entropy than the reactants (more ordered)
-40	1.3×10^4	

$(\Delta S^\ddagger)^+ > (\Delta S^\ddagger)^- \quad (\text{less ordered})$

Samples less configuration (more ordered) $(\Delta S^\circ)_1 \neq$ $(\Delta S^\circ)_1 > (\Delta S^\circ)_2$ $(\Delta S^\circ)_2 =$ Samples more configuration (less ordered)

Unimolecular Reactions



$$\frac{dC_A^*}{dt} = k_1 C_A^2 - k_{-1} C_A^* C_A - k_2 C_A^* \approx 0 \quad \text{PSSH}$$

$$C_A^* = \frac{k_1 C_A^2}{k_2 + k_{-1} C_A}$$

$$\text{rate} = k_2 C_A^* = \frac{k_1 k_2 C_A^2}{k_2 + k_{-1} C_A}$$

Two limits ~

at high concentrations $k_{-1} C_A \gg k_2$ (high pressure)

$$\text{rate} \approx \frac{k_1 k_2}{k_{-1}} C_A$$

at low concentrations $k_{-1} C_A \ll k_2$ (low pressure)

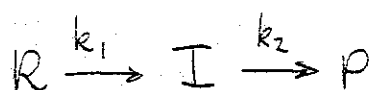
$$\text{rate} \approx k_1 C_A^2$$

PSSH II

Assume that the concentration of the intermediates is very low (i.e. the consumption of the intermediates is very rapid, hence, not changing with time)

$$\frac{dC_I}{dt} \approx 0$$

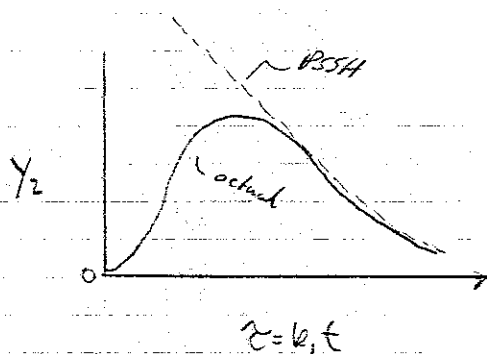
Consider:



$$\lambda = \frac{k_2}{k_1} \quad \hat{Y}_1 = \frac{[R]}{[R]_0} \quad \hat{Y}_2 = \frac{[I]}{[R]_0} \quad \tau = k_1 t$$

$$\textcircled{1} \quad \frac{d\hat{Y}_1}{d\tau} = -\hat{Y}_1$$

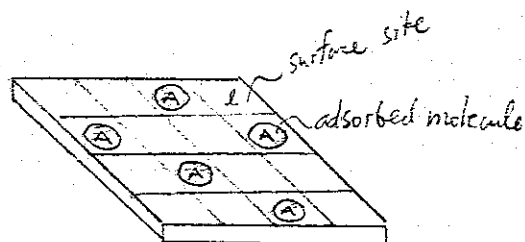
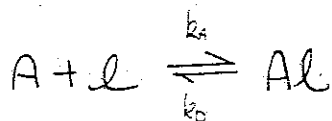
$$\textcircled{2} \quad \frac{1}{\lambda} \frac{d\hat{Y}_2}{d\tau} = \hat{Y}_1 - \hat{Y}_2 \quad \text{as } \lambda \rightarrow \infty \quad \frac{d\hat{Y}_2}{d\tau} \approx 0 \quad k_2 \gg k_1$$



PSSH, depends on λ and τ and can fall apart at both short and long times.

LHAW Kinetics

Adsorption Isotherms:



Langmuir:

- assumptions:
- Uniformly energetic adsorption sites
 - no interactions between adsorbed surface species
 - Mono layer coverage

at equilibrium $\Gamma_{\text{Adsorption}} = \Gamma_{\text{desorption}}$

$$\Gamma_A = k_A C_A C_e \quad \Gamma_D = k_D C_{AL}$$

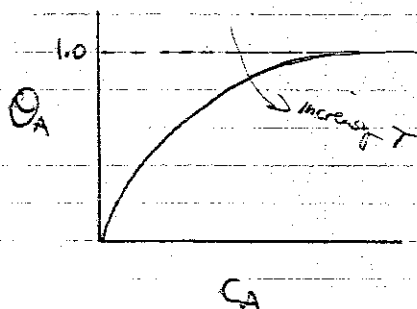
$$k_A C_A C_e = k_D C_{AL}$$

$$C_{AL} = \frac{k_A}{k_D} C_A C_e$$

$$K_A = \frac{k_A}{k_D} = \frac{A_a}{A_d} e^{-\frac{\Delta H_a}{RT}} \quad \text{heat of adsorption}$$

$$C_{AL} = \frac{C_e K_A C_A}{1 + K_A C_A}$$

$$\frac{C_{AL}}{C_e} = \theta_A = \frac{K_A C_A}{1 + K_A C_A}$$



good for intermediate surface coverages

Freundlich Isotherm

$$\Theta_A \equiv a C_A^m \quad m < 1$$

Templekin Isotherm ($Q = Q_0(1 - \alpha \Theta)$) ~ Heat of adsorption is linear with surface coverage

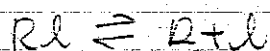
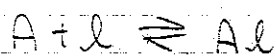
$$\Theta_A = \frac{RT}{Q_0 \alpha} \ln \left[k_A e^{-Q_0/2T} C_A \right]$$

Rate Expressions:

- ① Postulate a mechanism
- ② write molar balances on each species
- ③ Invoke PSSA for adsorbed intermediates
- ④ Eliminate concentrations of adsorbed species from rate expression

$$\text{rate} = \frac{(\text{kinetic factor})(\text{driving force group})}{(\text{adsorption group})^n} C_t$$

$n = \# \text{ of adjacent sites}$



$$\frac{d[A]}{dt} = k_A [C_A C_L - \frac{C_{AL}}{K_A}] \approx 0 \text{ PSSA}$$

$$\frac{d[AL]}{dt} = k_{sr} [C_{AL} - \frac{C_{RL}}{K_{sr}}]$$

$$\frac{d[RL]}{dt} = k_d \left[\frac{C_{RL}}{K_D} - C_R C_L \right] \approx 0 \text{ PSSA}$$

$$C_{AL} = K_A C_A C_L$$

$$C_{RL} = K_D C_R C_L$$

Site Balance: $C_t = C_L + C_{AL} + C_{RL}$

$$= C_L + K_A C_A C_L + K_D C_R C_L$$

$$C_L = \frac{C_t}{(1 + K_A C_A + K_D C_R)}$$

$$r_A = \frac{k_{sr} C_t \left[K_A C_A - \frac{K_D C_R}{K_{sr}} \right]}{(1 + K_A C_A + K_D C_R)}$$

Derivation of Van't Hoff's Law

$$K_{eq} = \frac{k_1}{k_{-1}}$$

$$k_1 = k_0 \exp\left(-\frac{E_1}{RT}\right)$$

$$\ln k_1 = -\frac{E_1}{RT} + \ln k_0$$

$$\ln k_{-1} = -\frac{E_2}{RT} + \ln k_0'$$

$$\ln \frac{k_1}{k_{-1}} = \frac{(E_2 - E_1)}{RT} + \ln \frac{k_0'}{k_0}$$

$$\frac{d \ln \frac{k_1}{k_{-1}}}{dT} = -\frac{(E_2 - E_1)}{RT^2} \Leftarrow \text{assuming preexponential factor is not a function of } T$$

$$\frac{d \ln K_{eq}}{dT} = \frac{\Delta H_{rxn}}{RT^2}$$

alternate Derivation

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT} dG - \frac{G}{RT^2} dT$$

$$dG = -SdT + VdP \quad G = H - TS$$

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT} dP - \frac{SdT}{RT} - \frac{HdT}{RT^2} + \frac{SdT}{RT}$$

at const. P

$$d\left(\frac{G}{RT}\right) = -\frac{HdT}{RT^2} \quad -\frac{\Delta G^\circ}{RT} = \ln K_{eq}$$

$$\frac{d \ln K_{eq}}{dT} = \frac{\Delta H^\circ}{RT^2}$$

