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KINETICS

Prelim Review Notes: Kinetics and Chemical Fundamentals — Reaction Rates and Equilibrium

Note: Numbers in parentheses refer to questions from the "Thermodynamic, Kinetics and Chemical Fundamentals Prelim Questions" review sheet.

Basic Definitions

- homogeneous reaction - a reaction that involves only one phase
- heterogeneous reaction - a reaction that involves more than one phase; reaction usually occurs at or very near the interface between the phases
- irreversible reaction - a reaction that proceeds in only one direction and continues in that direction until the reactants are exhausted.
- reversible reaction - a reaction that can proceed in either direction, depending on the concentrations of reactants and products relative to the corresponding equilibrium concentrations.

Reaction Rate

The reaction rate gives the rate of appearance of products or disappearance of reactants, as a function of one or more reaction rate constants and the concentrations of species involved in the reaction.

$$-r_A = f[k(T), C_A, C_B, \dots]$$

The reaction rate constant is not truly constant, but is independent of concentrations of the species involved in the reaction. It is almost always strongly dependent on temperature, usually expressed by the Arrhenius equation:

$$k = A e^{-E/RT}$$

where A = pre-exponential factor or frequency factor (74)

E = activation energy [=] J/mol, cal/mol

R = gas constant (8.314 J/mol.K, 1.987 cal/mol.K)

T = absolute temperature, K (7)

The activation energy E has been equated with a minimum energy required by reacting molecules before the reaction will occur. It is determined experimentally by measuring the reaction rate constant at several different temperatures.

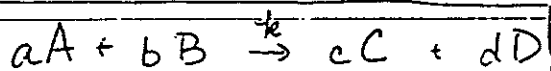
$$\ln k = \ln A - \frac{E}{R} \left(\frac{1}{T} \right)$$

According to the above equation, a plot of $\ln k$ vs. $1/T$ should yield a straight line whose slope is proportional to the activation energy.

Reaction Order and Rate Laws

The dependence of the reaction rate on the concentrations of the species present is almost without exception determined by experimental observation. One of the most common general forms of this dependence is the product of concentrations of the individual reacting species, each of which is raised to a power. The order of a reaction refers to the powers to which the concentrations are raised in the kinetic rate law.

An elementary reaction is one in which the reaction order of each species is identical with the stoichiometric coefficient of that species in the reaction as written. Consider the following reaction:



The reaction rate for this elementary reaction can be expressed

$$r_A = \frac{dA}{dt} = -kA^aB^b$$

For the case of a reversible reaction, let k_f represent the reaction rate constant of the forward reaction and k_b the reaction rate constant of the backward reaction. Then the rate law can be expressed:

$$r_A = -k_f A^a B^b + k_b C^c D^d$$

At equilibrium, the forward reaction rate equals the backward reaction rate and $\frac{dA}{dt} = \frac{dB}{dt} = \frac{dC}{dt} = \frac{dD}{dt} = 0$. The following is true:

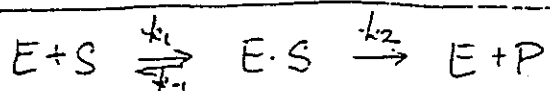
$$K_{eq} = \frac{C^c D^d}{A^a B^b} = \frac{k_f}{k_b}$$

where K_{eq} is an equilibrium constant. (4B)

Examples of Reaction Rate Expressions

Michaelis-Menten Kinetics (62)

Michaelis-Menten kinetics are often used to describe enzymatically catalyzed reactions. Consider the following reaction mechanism for the enzymatic conversion of a substrate (S) to product (P):



Consider each step in the mechanism to be an elementary reaction. Then we can write the following expressions:

$$\frac{dS}{dt} = k_1(E \cdot S) - k_1(E)(S) \quad \text{Eq. 1}$$

$$\frac{dE}{dt} = (k_1 + k_2)(E \cdot S) - k_1(E)(S) \quad \text{Eq. 2}$$

$$\frac{dE \cdot S}{dt} = k_1(E)(S) - (k_1 + k_2)(E \cdot S) \quad \text{Eq. 3}$$

$$\frac{dP}{dt} = k_2(E \cdot S) \quad \text{Eq. 4}$$

The total concentration of enzyme remains constant at $E_t = E_0 = E + E \cdot S$. We can then express the free enzyme concentration $E = E_0 - E \cdot S$.

The pseudo-steady-state assumption (PSSA) is used to set Eq. 3 equal to zero. This assumption is a good approximation when the active intermediate (in this case $E \cdot S$) has a very short lifetime because of its high reactivity (i.e. large specific reaction rates), and the catalyst/enzyme is present in low concentrations ($E_0 \ll S_0$). Then we can make the approximation that the rate of formation of the active intermediate is equal to its rate of disappearance ($\frac{dE \cdot S}{dt} = 0$).

So, from Eq. 3 we get: $k_1(E)(S) = (k_1 + k_2)(E \cdot S) = k_1(S)(E_0 - E \cdot S)$

$$E \cdot S = \frac{k_1(S)(E_0)}{k_1(S) + (k_1 + k_2)} = \frac{(E_0)(S)}{(S) + \left(\frac{k_1 + k_2}{k_1}\right)}$$

$$\text{and } \frac{dP}{dt} = v = \frac{V_{\max}(S)}{K_m + (S)}$$

$$\text{where } V_{\max} = k_2(E_0) \\ K_m = \frac{k_1 + k_2}{k_1}$$

Langmuir - Hinshelwood Kinetics (15, 42) - Catalysis

The following are steps in a catalytic reaction:

1. Mass transfer (diffusion) of the reactant(s) from the bulk fluid to the external surface of the catalyst pellet.
2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface.
3. Adsorption of reactant onto the catalyst surface.
4. Reaction on the surface of the catalyst.
5. Desorption of the products from the surface.
6. Diffusion of the products from the interior of the pellet to the pore mouth at the external surface.
7. Mass transfer of the products from the external pellet surface to the bulk fluid.

The overall rate of reaction is equal to the rate of the slowest step in the mechanism. In systems where diffusion from the bulk gas or liquid to the catalyst surface or to the mouths of catalyst pores affects the rate, changing the flow conditions past the catalyst should change the overall reaction rate.

- Adsorption

Consider the adsorption of species A on vacant site S on the catalyst surface

$$A(g) + S \xrightleftharpoons[k_{-A}]{k_A} A \cdot S$$

Assuming an elementary reaction, we can then write the adsorption rate as the rate of attachment minus the rate of detachment:

$$r_{AD} = k_A P_A C_v - k_{-A} C_{A \cdot S}$$

where P_A is the partial pressure of species A and C_v is the concentration

Defining the adsorption equilibrium constant $K_A = \frac{k_f}{k_d}$, we can write

$$r_{AD} = k_A \left[P_A C_v - \frac{C_{A \cdot S}}{K_A} \right]$$

A site balance gives the total concentration of active surface sites as the sum of vacant sites and adsorbed species. For this case

$$C_t = C_v + C_{A \cdot S}$$

At equilibrium, the rate of attachment equals the rate of detachment, a $r_{AD} = 0$. Substituting $C_v = C_t - C_{A \cdot S}$ into the boxed relationship above

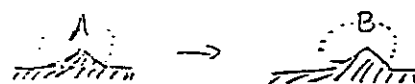
$$C_{A \cdot S} = \frac{K_A P_A C_t}{1 + K_A P_A}$$

This is known as a Langmuir isotherm for adsorption. More complicated expressions for Langmuir isotherms can be developed for reactions involving more than one adsorbed molecule and vacant site.

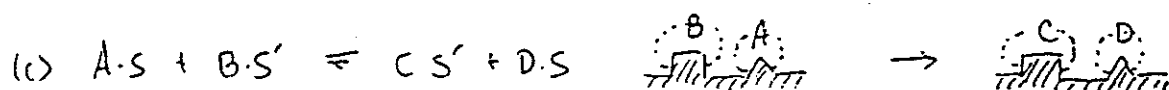
- Surface Reaction

Once a reactant has been adsorbed onto the surface, it is capable of reacting in a number of ways to form the reaction product:

1. Single-site mechanism is which only the site on which the reactant is adsorbed is involved in the reaction.

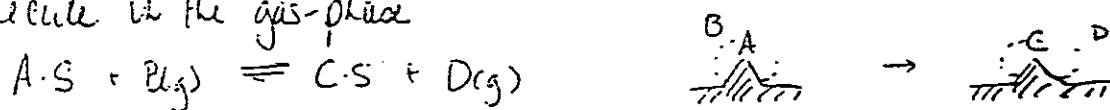


2. Dual-site mechanism in which the adsorbed reactant interacts with another site to form the product



Reactions involving either single- or dual-site mechanisms described above are sometimes referred to as following Langmuir-Hinshelwood kinetics

3. Eley-Rideal mechanism - reaction between an adsorbed molecule and a molecule in the gas-phase



The surface reaction rate, r_s , is determined by assuming that the appropriate reaction mechanism is an elementary step.

- Desorption

The rate of desorption of a species, r_d , is written just as the rate of adsorption but with opposite sign

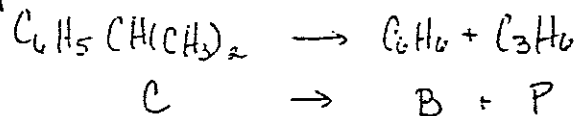
- Rate-Limiting Step

At steady-state, the rates of adsorption, reaction, and desorption are all equal to one another. However, one particular step in the series is usually found to be rate-limiting.

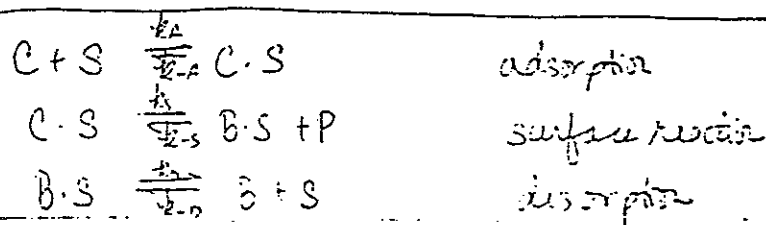
The Langmuir-Hinshelwood approach in determining catalytic and heterogeneous mechanisms is as follows:

- assume a sequence of steps in the reaction, choosing molecular or atom adsorption, single- or dual-site reaction.
- write rate laws for the individual steps, assuming all steps are reversible.
- postulate a rate-limiting step. Steps that are not rate-limiting are used to eliminate all coverage-dependent terms

- Example



Mechanism:



$$K_A = k_1/k_{-1}$$

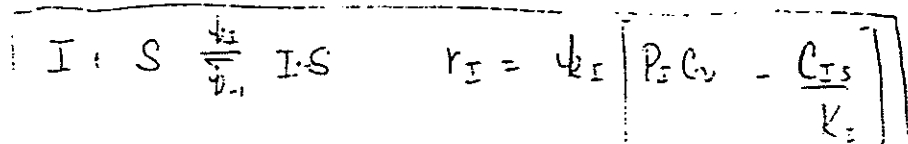
$$K_S = k_2/k_{-2}$$

$$K_D = k_3/k_{-3}$$

Rate Expressions:

Adsorption	$r_{AD} = k_A \left[P_C C_0 - \frac{C_{C \cdot S}}{K_A} \right]$
Surface reaction	$r_S = k_S \left[C_{C \cdot S} - \frac{P_P C_{B \cdot S}}{K_S} \right]$
Desorption	$r_D = k_D \left[C_{B \cdot S} - \frac{P_B C_0}{K_D} \right]$

Also consider the presence of an inhibitor, I, that does not participate in the reaction but does occupy active sites on the surface



To determine which step is rate-limiting, assume a rate-limiting step, derive the corresponding rate law, and then check to see if it is consistent with experimental observation

A. Adsorption is Rate-Limiting

For adsorption-limited reactions, k_A is small and k_s and k_o are large. Therefore, $r_s/k_s \approx 0$ and $r_o/k_o \approx 0$ while r_{AO}/k_A is relatively large.

$$\frac{r_s}{k_s} = C_{A,s} - \frac{P_P C_{O,s}}{K_S} \approx 0 \Rightarrow C_{A,s} = \frac{P_P C_{O,s}}{K_S} \quad (A.1)$$

$$\frac{r_o}{k_o} = C_{B,s} - \frac{P_B C_v}{K_O} \approx 0 \Rightarrow C_{B,s} = \frac{P_B C_v}{K_O} \quad (A.2)$$

Substituting the result from (A.2) into (A.1) gives

$$C_{A,s} = \frac{P_B P_P}{K_O K_S} C_v \quad (A.3)$$

A site balance gives $C_t = C_v + C_{A,s} + C_{B,s} + C_{I,s}$

$$\Rightarrow C_t = C_v + \frac{P_B P_P C_v}{K_O K_S} + \frac{P_B C_v}{K_O} + P_I K_I C_v$$

$$C_v = \frac{C_t}{P_B P_P / K_O K_S + P_B / K_O + P_I K_I + 1} \quad (A.4)$$

Substitute (A.3) and (A.4) into the adsorption rate law to get

$$-r'_C = r_{AO} = \frac{C_t k_A (P_C - P_P P_B / K_E)}{1 + P_B P_P / K_S K_O + P_B / K_O + K_I P_I}$$

where $K_E = K_A K_S K_O$ is the overall equilibrium constant

B. Surface Reaction is Rate-Limiting

For surface reaction-limited reaction mechanisms, the following is true:

$$\frac{r_{A0}}{k_A} = P_C C_v - \frac{C_{C,s}}{K_A} = 0 \Rightarrow C_{C,s} = K_A P_C C_v \quad (B.1)$$

$$\frac{r_D}{k_D} = C_{B,s} - \frac{P_B C_v}{K_D} = 0 \Rightarrow C_{B,s} = \frac{P_B C_v}{K_D} \quad (B.2)$$

The site balance using (B.1) and (B.2) and $C_{I,s} = K_I P_I C_v$ gives

$$C_v = \frac{C_t}{1 + P_B/K_D + K_A P_C + P_I K_I} \quad (B.3)$$

Substitute (B.1), (B.2) and (B.3) into the surface reaction rate law to get

$$-r_c' = r_s = \frac{k_s C_t K_A (P_C - P_I P_B / K_e)}{1 + P_B/K_D + K_A P_C + P_I K_I} \quad \text{where } K_D = \frac{1}{k_D}$$

C. Desorption is Rate-Limiting

For desorption-limited reactions, the following is true: $r_{A0}/k_A = r_s/k_s = 0$

Using (A.1), $C_{B,s} = \frac{K_s}{P_P} C_{C,s}$ and from (B.1), $C_{C,s} = K_A P_C C_v$

Then a site balance gives

$$C_v = \frac{C_t}{1 + K_A K_s P_C / P_P + K_A P_C + K_I P_I}$$

and

$$-r_c' = r_D = \frac{k_D C_t K_s K_A (P_C - P_B P_I / K_e)}{P_P + P_C K_A K_s + K_A P_C P_C + K_I P_I P_P}$$

Note: More than 75% of all heterogeneous reactions that are not diffusion-limited are surface-reaction-limited. Thus, the best guess is to assume surface-reaction-limitation in developing the rate law.

Extent of Reaction and Equilibrium Constants

The extent of reaction, or conversion, is defined with respect to some reactant species, i , as follows:

$$X_i = \frac{\text{moles of 'i' reacted}}{\text{moles of 'i' fed}}$$

The extent of reaction will equal the equilibrium conversion if a reversible reaction is allowed to reach equilibrium. (38)

The equilibrium constant, K_p , was defined on page ⑤ as a function of concentration, K_c . For gas-phase reactions, the equilibrium constant is written in terms of partial pressures (K_p).

Consider the general reaction $aA + bB \rightleftharpoons cC + dD$.

Then for ideal gases $K_p = K_c (RT)^\delta$
 where $\delta = \frac{c}{a} + \frac{d}{a} - \frac{b}{a} - 1$

The equilibrium constant is a function of temperature only, and the temperature dependence of K_p is given by van't Hoff's equation (20).

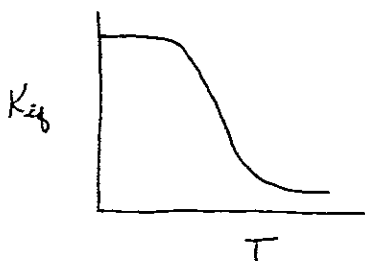
$$\ln K_{p1} = \frac{\Delta H_{rxn}(T)}{RT} = \frac{\Delta H_{rxn}(T_R)}{RT_R} + \frac{\Delta C_p}{R} \ln \left(\frac{T}{T_R} \right)$$

If $\Delta G^\circ = 0$, integration of the previous boxed equation gives

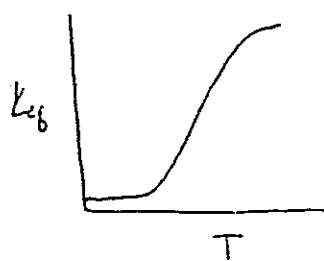
$$\ln \frac{K_{eq}}{K_{eq,1}} = \frac{\Delta H_{rxn}^\circ(T_R)}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Thus the slope of a $\ln K_{eq}$ vs. $1/T$ curve is $-\Delta H_{rxn}^\circ(T_R)/R$ (23).

For exothermic reactions, by Le Chatelier's principle the equilibrium shifts to the left as the temperature increases.



Exothermic Rxn

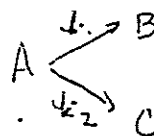


Endothermic Rxn

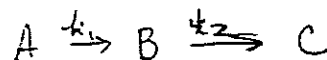
Likewise, the extent of reaction will decrease as temperature increases for an exothermic reaction. However, the rate constant will increase with increasing temperature regardless of whether the reaction is exo- or endotherm

Multiple Reactions

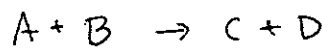
Definitions: (a) parallel (competing) reactions



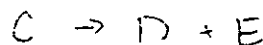
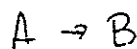
(b) series (consecutive) reactions



(c) combination



(d) independent reactions



A. Parallel Reactions

Consider the following competing reactions for the production of a desired (D) and undesired (U) product from a single reactant A:



Then define the selectivity parameter,
$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$$

Case #1: $\alpha_1 > \alpha_2$ and $\alpha_1 - \alpha_2 = a \Rightarrow S_{DU} = k_D/k_U C_A^a$

To make S_{DU} as large as possible, keep the concentration of A as high as possible during the reaction:

- in the gas phase, run without inerts
- in the liquid phase, minimize diluents
- use batch or plug-flow reactor

Case #2: $\alpha_2 > \alpha_1$ and $a = \alpha_2 - \alpha_1 \Rightarrow S_{DU} = k_D/k_U C_A^a$

To maximize S_{DU} , minimize the concentration of A:

- dilute the feed with inerts
- use CSTR

Determine the optimal temperature by examining the ratio of reaction rates.
Assuming an Arrhenius dependence:

$$\frac{k_D}{k_U} = \frac{A_D}{A_U} \exp \left[-\frac{(E_D - E_U)}{RT} \right]$$

Case #3: $E_D > E_U$

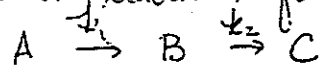
k_D increases more rapidly with increasing temperature than $k_U \Rightarrow$ operate at highest possible temperature to maximize S_{DU} .

Case #4: $E_D < E_U$

Reaction should be carried out at low temperature to maximize S_{DU} , but not so low that the desired reaction does not proceed to any significant extent.

B. Series Reactions

Consider the following reaction sequence where B is the desired product:



For series reactions, the most important variable is time (space-time for a flow reactor and real-time for a batch reactor).

1. Mole balance on A: $\frac{dF_A}{dW} = r_A'$

Rate law: $-r_A' = k_1 C_A$

Stoichiometry: $F_A = C_A v_0$

$$\Rightarrow v_0 \frac{dC_A}{dW} = -k_1 C_A \Rightarrow C_A = C_{A0} \exp[-k_1 \tau']$$

where $\tau' = W/v_0$

2. Mole balance on B: $\frac{dF_B}{dW} = r_B'$

Rate law: $r_B' = k_1 C_A - k_2 C_B$

Stoichiometry: $F_B = v_0 C_B$

$$\Rightarrow v_0 \frac{dC_B}{dW} = k_1 C_A - k_2 C_B$$

$$\frac{dC_B}{d\tau'} - k_2 C_B = k_1 C_{A0} \exp[-k_1 \tau']$$

$$\Rightarrow C_B = k_1 C_{A0} \left[\frac{e^{-k_1 \tau'} - e^{-k_2 \tau'}}{k_2 - k_1} \right]$$

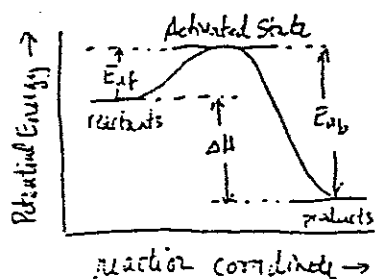
3. Optimum yield: $\frac{dC_B}{d\tau'} = 0 \Rightarrow \tau'_{opt} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$

Corresponding conversion: $X_{opt} = 1 - \left(\frac{k_2}{k_1} \right)^{k_1/(k_1 - k_2)}$

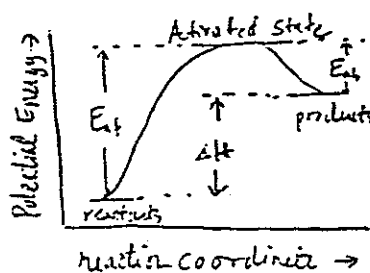
Temperature Dependence: For the rate constants k_1 and k_2 , if $E_1 > E_2$ (assuming an Arrhenius dependence), then k_1 will increase more rapidly with increasing temperature than k_2 . In this case, operating at higher temperatures will optimize production of B. Similarly, if $E_2 > E_1$, then one should operate at lower temperature to optimize production of B. (19)

Reaction Coordinate

The reaction coordinate is a measure of the extent to which the reaction has proceeded toward completion along the reaction pathway. (33)



Exothermic Rxn



Endothermic Rxn

Unit 11: Equilibrium Constant

Recall that $\Delta G_{\text{rxn}} = -RT \ln K_{\text{eq}}$

Thus $\Delta G_{\text{rxn}} = 0$ when $K_{\text{eq}} = 1$. (24)

(Note: Use of the Gibbs-Helmholtz Equation leads to the van't Hoff equation discussed on page (11).)

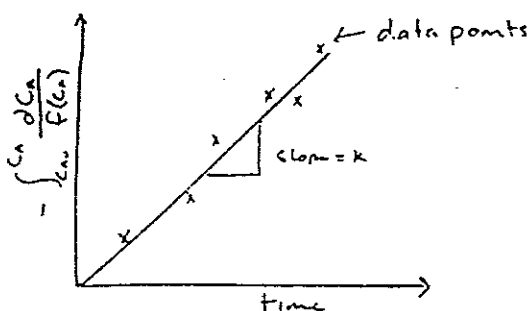
Reaction Mechanism Testing

1. Integral Method (constant volume)

In general, $-r_A = -\frac{dC_A}{dt} = k f(C_A)$

this can be rearranged to give $kt = -\int_{C_{A0}}^{C_A} \frac{dC_A}{f(C_A)}$

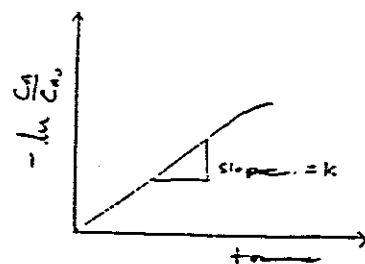
a plot of this integral vs. time will yield a straight line with slope = k if the proposed rate expression $f(C_A)$ is correct.



Example: First order reaction $A \rightarrow \text{products}$

$$-\frac{dC_A}{dt} = kC_A$$

$$kt = -\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = -\ln \frac{C_A}{C_{A0}}$$



2. Integral Method (variable volume)

$X_A \equiv$ fractional conversion

For variable volume, $C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X_A)}{V_0(1+\epsilon_A X_A)} = C_{A0} \frac{1-X_A}{1+\epsilon_A X_A}$

therefore, $-r_A = -\frac{dC_A}{dt} = \frac{C_{A0}}{1+\epsilon_A X_A} \frac{dX_A}{dt}$

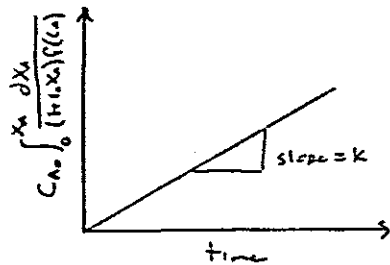
so, $kt = C_{A0} \int_0^{X_A} \frac{dX_A}{(1+\epsilon_A X_A) f(C_A)}$

Aside
 $\epsilon_A = \frac{V_{\infty} - V_{A0}}{V_{A0}}$

Thus for $A \rightarrow 4R$

$$\epsilon_A = \frac{4-1}{1} = 3$$

Again, a plot of this integral vs. time will yield a straight line if the proposed rate expression $f(C_A)$ is correct.

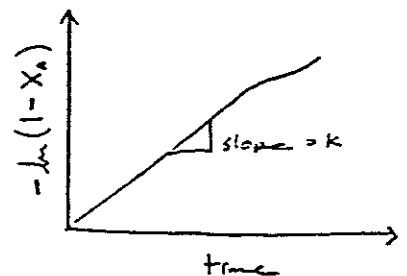


Example: First order reaction $A \rightarrow \text{products}$

$$-r_A = k f(C_A) \quad f(C_A) = C_A = C_{A0} \frac{1-x_A}{1+\epsilon_A x_A}$$

$$kt = C_{A0} \int_0^{x_A} \frac{dx_A}{(1+\epsilon_A x_A) \left[C_{A0} \frac{1-x_A}{1+\epsilon_A x_A} \right]}$$

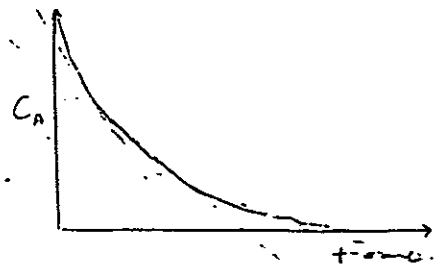
$$kt = \int_0^{x_A} \frac{dx_A}{1-x_A} = -\ln(1-x_A)$$



3. Differential Method

$$(-r_A) = k C_A^m \quad \text{or} \quad \log(-r_A) = \log k + m \log C_A$$

- Plot C_A vs time and differentiate to obtain $(-r_A)$ vs. time.
- Then plot $\log(-r_A)$ vs $\log C_A$ to obtain the reaction order m .
- Then plot $(-r_A)$ vs C_A^m to obtain the rate constant k .

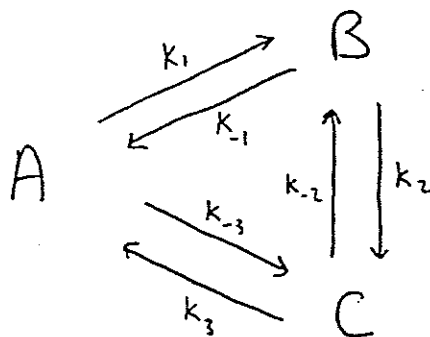


Chemical Equilibrium

The Principle of Microscopic Reversibility states that, at equilibrium the rate of direct conversion from a state A to another state must exactly equal the direct conversion rate from state B to A.

The thermodynamic definition of equilibrium states that the net global rate of reaction of all species is equal to zero.

Both of these statements are slightly different as will be demonstrated for the reaction below.



The thermodynamic definition of equilibrium requires

$$r_{A \text{ net}} = 0 \quad r_{B \text{ net}} = 0 \quad r_{C \text{ net}} = 0$$

$$\begin{aligned} \text{thus, } (k_1 + k_{-3}) [A]_e &= k_3 [C]_e + k_{-1} [B]_e \\ (k_2 + k_{-1}) [B]_e &= k_{-2} [C]_e + k_1 [A]_e \\ (k_3 + k_{-2}) [C]_e &= k_{-3} [A]_e + k_2 [B]_e \end{aligned}$$

Combining these 3 equations we get

$$\frac{[A]_e}{[B]_e} = \frac{k_3 k_2 + k_3 k_{-1} + k_{-1} k_{-2}}{k_{-3} k_{-2} + k_3 k_1 + k_1 k_{-2}}$$

$$\frac{[B]_e}{[C]_e} = \frac{k_1 k_3 + k_1 k_{-2} + k_{-2} k_3}{k_{-1} k_{-3} + k_{-1} k_2 + k_2 k_3}$$

$$\frac{[C]_e}{[A]_e} = \frac{k_2 k_1 + k_2 k_{-3} + k_{-3} k_{-1}}{k_{-2} k_1 + k_{-2} k_3 + k_3 k_1}$$

The Principle of Microscopic Reversibility however, requires that

$$\Gamma_{A \rightarrow B} = \Gamma_{B \rightarrow A}$$

$$\Gamma_{B \rightarrow C} = \Gamma_{C \rightarrow B}$$

$$\Gamma_{A \rightarrow C} = \Gamma_{C \rightarrow A}$$

Thus, it must also be true that,

$$\frac{[A]_e}{[B]_e} = \frac{k_{-1}}{k_1}$$

$$\frac{[B]_e}{[C]_e} = \frac{k_{-2}}{k_2}$$

$$\frac{[C]_e}{[A]_e} = \frac{k_{-3}}{k_3}$$

Thermodynamic Restrictions on the form of the Kinetic Rate Equation

Consider the reaction $aA + bB \rightleftharpoons cC$

Using power-law kinetics, the most general way we can express the net rate of formation of product C is given by,

$$(+r_c)_{\text{net}} = k_f [A]^{\alpha} [B]^{\beta} [C]^{\gamma} - k_r [A]^{\alpha'} [B]^{\beta'} [C]^{\gamma'}$$

Thermodynamics requires that at equilibrium $(+r_c)_{\text{net}} = 0$

$$\text{Thus } \frac{k_f}{k_r} = [A]^{(\alpha' - \alpha)} [B]^{(\beta' - \beta)} [C]^{(\gamma' - \gamma)}$$

Also from thermodynamics, we know that the equilibrium constant (K_{eq}) is given by,

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

K_{eq} is related to the ratio k_f/k_r by,

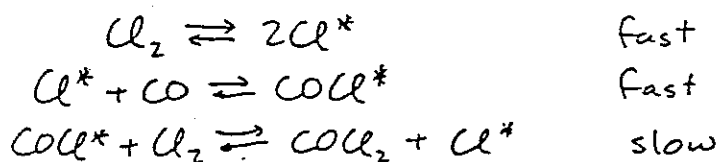
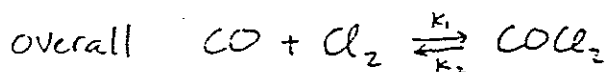
$$K_{eq} = \left(\frac{k_f}{k_r} \right)^s$$

where s is the stoichiometric number of the rate limiting step.

$$\text{Thus, } \boxed{\frac{(\alpha' - \alpha)}{-a} = \frac{(\beta' - \beta)}{-b} = \frac{(\gamma' - \gamma)}{c} = \frac{1}{s}}$$

Consequently, if α, β , and γ are determined for the forward reaction, then α', β' , and γ' for the reverse reaction can be determined from the above equation.

Example: The formation and decomposition of phosgene proceeds by the following mechanism



Given that $(+r_{\text{COCl}_2}) = k_1 [\text{Cl}_2]^{3/2} [\text{CO}]$ find an expression for $(-r_{\text{COCl}_2})$.

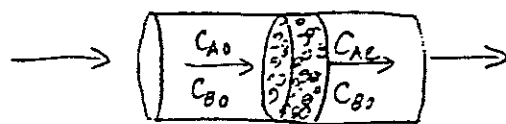
Solution: $a=1 \quad b=1 \quad c=1 \quad \alpha=1 \quad \beta=3/2 \quad \gamma=0 \quad s=1$

$$\frac{(\alpha' - 1)}{-1} = \frac{(\beta' - 3/2)}{-1} = \frac{(\gamma' - 0)}{1} = \frac{1}{1}$$

$$\alpha' = 0 \quad \beta' = \frac{1}{2} \quad \gamma' = 1$$

$$\boxed{(-r_{\text{COCl}_2}) = k_2 [\text{Cl}_2]^{1/2} [\text{COCl}_2]}$$

For the heterogeneous, non-elementary rxn $A + B \rightleftharpoons C$, what experiments should be run and how should the data be analyzed to obtain the correct form of the rate expression?



catalyst of mass W

$$0 = v_0 C_{A0} - v_0 C_{AE} + r'_A W$$

$$\text{where } r'_A = k' C_A^n C_B^m$$

Now if we let B be present in excess,

$$r'_A \approx k' C_{B0}^m C_A^n = K C_A^n$$

\uparrow
 conc. doesn't change

Since it's a differential reactor, $C_{A0} \approx C_{AE}$ and we'll approximate C_A as $\frac{C_{A0} + C_{AE}}{2}$.

$$\therefore r'_A = \frac{v_0}{W} (C_{AE} - C_{A0})$$

\uparrow
 this can be measured

Now, for various feed inlets C_{A0} 's, we measure r'_A .

$$r'_A = K C_A^n = K \left[\frac{C_{A0} + C_{AE}}{2} \right]^n$$

$$\ln r'_A = \ln K + n \ln \left(\frac{C_{A0} + C_{AE}}{2} \right)$$

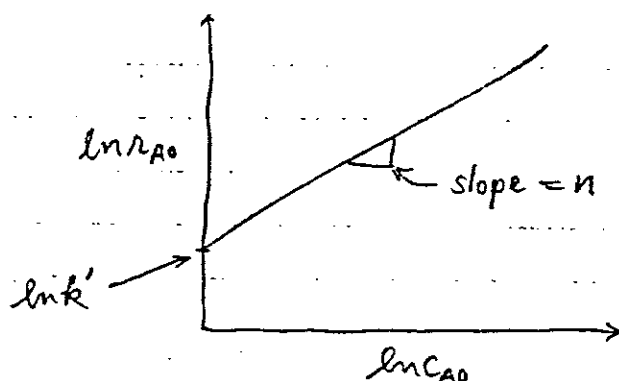
Now, we have C_{A0} vs. r_{A0} data.

$$\text{Since, } r_{A0} = -k C_{B0}^m C_{A0}^n$$

$$r_{A0} = k' C_{A0}^n$$

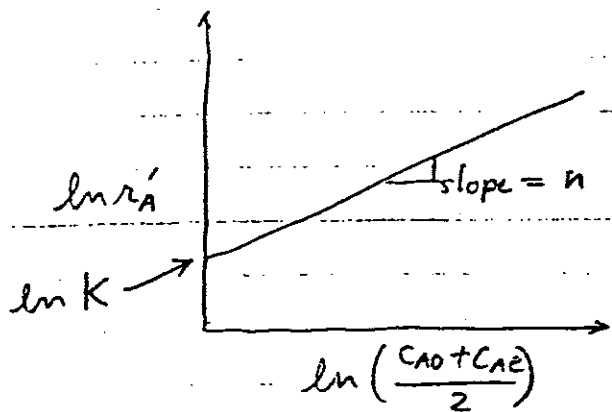
$$\ln r_{A0} = n \ln C_{A0} + \ln k'$$

Plot $\ln r_{A0}$ vs. $C_{A0} \Rightarrow$ will get straight line =



Do the same for B (let A be in excess) and find n !! Then can find k .

Plot $\ln r_A'$ vs. $\ln\left(\frac{C_{AO} + C_{AE}}{2}\right)$ for the various C_{AO} 's.



$$K = k' C_{BO}^m$$

Do the same for B (let A be in excess) and find m !!
Then can find k .

For the non-elementary, liquid phase rxn $A + B \rightleftharpoons C$, what experiments would you run, and how would you analyze the data to determine the rate expression for the rxn?

Run batch reactions:



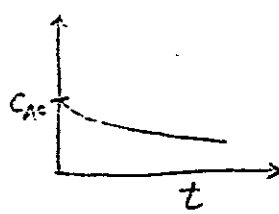
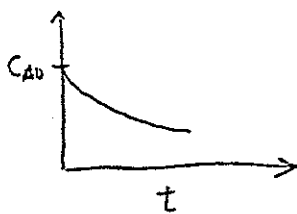
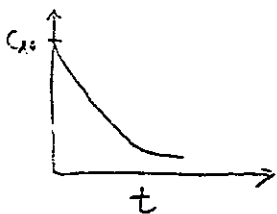
$$r_A = -k C_A^n C_B^m$$

For batch reactor, $\frac{dC_A}{dt} = -k C_A^n C_B^m$

But since the rxn is reversible, we want to use initial rates experiment. If we also have B in excess, then $C_B \approx \text{const.} \approx C_{B0}$.

$$r_A = -k C_{B0}^m C_A^n$$

For different values of C_{A0} , plot C_A vs. t :



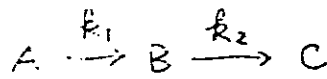
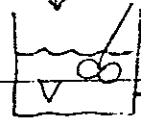
We can get $r_{A0} = -k C_{B0}^m C_{A0}^n$ for each experiment because:

$$r_{A0} = \left. \frac{dC_A}{dt} \right|_{t=0} \Leftarrow \text{So measure slope of each curve above.}$$

Reactors

CSTR

$\dot{V} C_{A0}$



$$\frac{\partial(V C_A)}{\partial t} = \dot{V} C_{A0} - \dot{V} C_A + r_A V$$

mol. bal. for A

$$\frac{\partial V C_B}{\partial t} = r_B V - \dot{V} C_B$$

$$\text{where } r_B = k_1 C_A - k_2 C_B$$

$$\frac{\partial V C_B}{\partial t} = (k_1 C_A - k_2 C_B) V - \dot{V} C_B$$

mol. bal. for B

Solve for C_A first: at S.S.

$$0 = \dot{V} C_{A0} - \dot{V} C_A + (-k_1 C_A) V$$

$$0 = C_{A0} - C_A - \tau k_1 C_A = C_{A0} - C_A (1 + \tau k_1)$$

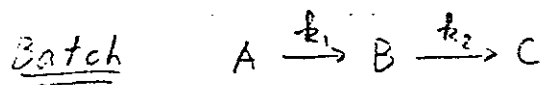
$$C_A = \frac{C_{A0}}{1 + \tau k_1}$$

Now for C_B :

$$0 = k_1 \frac{C_{A0}}{1 + \tau k_1} V - k_2 C_B V - \dot{V} C_B$$

$$0 = \frac{k_1 C_{A0} \tau}{1 + \tau k_1} - k_2 C_B \tau - C_B = \frac{k_1 C_{A0} \tau}{1 + \tau k_1} - C_B (\tau k_2 + 1)$$

$$C_B = \frac{k_1 \tau C_{A0}}{(1 + k_1 \tau)(1 + k_2 \tau)}$$



$$V \frac{d}{dt} C_A = r_A V = -k_1 C_A V$$

Need to consider transient,

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^t -k_1 dt$$

$$\ln \frac{C_A}{C_{A0}} = -k_1 t$$

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

$$C_A = C_{A0} \exp(-k_1 t)$$

$$V \frac{d}{dt} C_B = r_B V = (k_1 C_A - k_2 C_B) V$$

$$\frac{dC_B}{dt} = k_1 C_{A0} \exp(-k_1 t) - k_2 C_B$$

1st order linear DE

$$\text{let } C_B = u(t)v(t)$$

$$\frac{dC_B}{dt} = u \frac{dv}{dt} + v \frac{du}{dt} = k_1 C_{A0} \exp(-k_1 t) - k_2 uv$$

$$\text{let } u \frac{dv}{dt} = -k_2 uv$$

$$\int \frac{dv}{v} = \int -k_2 dt$$

$$\ln v = -k_2 t$$

$$v = e^{-k_2 t}$$

Find $u(t)$:

$$v \frac{du}{dt} = k_1 C_{A0} \exp(-k_1 t)$$

$$\exp(-k_2 t) \frac{du}{dt} = k_1 C_{A0} \exp(-k_1 t)$$

$$\frac{du}{dt} = k_1 C_{A0} \exp(k_2 t - k_1 t)$$

$$\int du = \int k_1 C_{A0} \exp[(k_2 - k_1)t] dt + C_1$$

$$u = k_1 C_{A0} \frac{1}{k_2 - k_1} \exp[(k_2 - k_1)t] + C_1$$

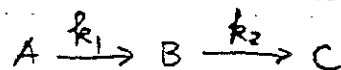
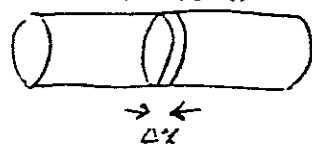
$$\text{BC } t=0, C_B=0 \Rightarrow u=0 \text{ since } v \neq 0$$

$$C_1 = \frac{-k_1 C_{A0}}{k_2 - k_1}$$

$$u = \frac{k_1 C_{A0}}{k_2 - k_1} \left[e^{(k_2 - k_1)t} - 1 \right]$$

$$\therefore C_B = \frac{k_1 C_{A0}}{k_2 - k_1} \left[e^{-k_1 t} - e^{-k_2 t} \right]$$

PFR



$$\Delta x A \frac{dC_A}{dt} = \dot{V} C_A \Big|_x - \dot{V} C_A \Big|_{x+\Delta x} + r_A A \Delta x$$

$$0 = -\dot{V} \frac{dC_A}{dx} + r_A A$$

$$\dot{V} \frac{dC_A}{dx} = r_A A$$

$$\dot{V} \frac{dC_A}{dV} = r_A = -k_1 C_A$$

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^V -\frac{k_1}{\dot{V}} dV$$

$$\ln \frac{C_A}{C_{A0}} = -\frac{k_1}{\dot{V}} V$$

$$C_A = C_{A0} \exp(-k_1 \tau)$$

$$\dot{V} \frac{dC_B}{dV} = r_B = k_1 C_A - k_2 C_B$$

$$= k_1 C_{A0} \exp(-k_1 \tau) - k_2 C_B$$

$$\frac{dC_B}{dV} = \frac{k_1 C_{A0}}{\dot{V}} \exp(-k_1 \tau) - \frac{k_2}{\dot{V}} C_B$$

$$\frac{dC_B}{d\tau} = k_1 C_{A0} \exp(-k_1 \tau) - k_2 C_B$$

$$\text{let } C_B = u(\tau) v(\tau)$$

$$u \frac{dv}{d\tau} + v \frac{du}{d\tau} = k_1 C_{A0} e^{-k_1 \tau} - k_2 u v$$

$$\text{let } v \frac{dv}{d\tau} = -k_2 u v$$

$$\int \frac{dv}{v} = \int -k_2 d\tau$$

$$\ln v = -k_2 \tau$$

$$v = e^{-k_2 \tau}$$

$$e^{-k_2 \tau} \frac{du}{d\tau} = k_1 C_{A0} e^{-k_1 \tau}$$

$$\frac{du}{d\tau} = k_1 C_{A0} e^{(k_2 - k_1) \tau}$$

$$\int du = \int k_1 C_{A0} e^{(k_2 - k_1) \tau} d\tau$$

$$u = \frac{k_1 C_{A0}}{k_2 - k_1} e^{(k_2 - k_1) \tau} + C_1$$

$$\text{BC: } \tau=0, C_B=0 \Rightarrow u=0 \text{ since } v \neq 0 \text{ at } \tau=0$$

$$\therefore C_1 = - \frac{k_1 C_{A0}}{k_2 - k_1}$$

$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1} \left[e^{-k_1 \tau} - e^{-k_2 \tau} \right]$$

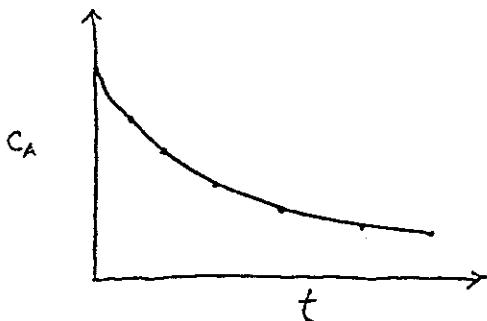
What is the integral method of analysis? When is it used?

The integral method of analysis is used when we want to analyze data from a irreversible reaction.



In a batch reactor, $\frac{dC_A}{dt} = r_A$

For a given C_{A0} , measure C_A at intervals of time after the beginning of the reaction:



Propose a reaction mechanism: $r_A = -k C_A$

$$\frac{dC_A}{dt} = -k C_A$$
$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^t -k dt$$

$$\ln \frac{C_A}{C_{A0}} = -kt$$

Plot $\ln \frac{C_A}{C_{A0}}$ vs. $t \Rightarrow$ should be straight line w/ slope $= -k$

DESIGN EQUATIONS

BATCH REACTOR $\frac{dN_i}{dt} = r_i V \xrightarrow{CV} \frac{dC_A}{dt} = r_A \begin{cases} N_{A0} \frac{dx}{dt} = -r_A V \\ t = N_{A0} \int_0^x \frac{dx}{-r_A V} \end{cases}$

CSTR $V = \frac{F_{j0} - F_j}{-r_j} \rightarrow V = \frac{F_{A0}(X_{out} - X_{in})}{(-r_A)_{out}}$

PFR $\frac{dF_j}{dV} = r_j \begin{cases} F_{A0} \frac{dx}{dV} = -r_A \\ V = F_{A0} \int_{X_{in}}^{X_{out}} \frac{dx}{-r_A} \end{cases}$

Space time: $\tau \equiv \frac{V}{v_0}$; $v_0 \equiv$ vol flow rate entering reactor

STOICHIOMETRIC TABLES: FOGLER PP. 78, 79, 82.

$$C_j = \frac{C_{A0}(\theta_j - \alpha_j / \alpha_A X_A)}{(1 + \epsilon X_A)} \quad \epsilon = Y_{A0} \delta; \quad \delta = - \sum_j \frac{\alpha_j}{\alpha_A}$$

COLLISION THEORY

$$Z_{AB} = \frac{\text{\# collisions}}{\text{time} \times \text{vol}}$$

COLLISION RADIUS: $\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$ SO, $Z_{AB} = \eta_B \left(\frac{\#}{\text{vol}} \right) C_A \cdot \eta_A$

FOR A, B MOVING: $Z_{AB} = \eta_A \eta_B \left(\frac{8k_B T}{\pi \mu_{AB}} \right)^{1/2} (\pi \sigma_{AB}^2); \mu_{AB} = \frac{M_A M_B}{M_A + M_B}$

FOR A, SURFACE B

$$Z_{AB} = \frac{1}{4} \eta_A \left(\frac{8k_B T}{\pi M_A} \right)^{1/2}$$

NOW, WHICH COLLISIONS \rightarrow REACTIONS

$$Z_T(AB) = (\pi \sigma_{AB}^2) \left(\frac{8k_B T}{\pi \mu_{AB}} \right)^{1/2} \eta_A \eta_B e^{-\eta^*/k_B T}; \quad \text{RCT IF } E_r = \frac{1}{2} \mu_{AB} v_r^2 > \eta^*$$

$$\therefore K_{AB} = (\pi \sigma_{AB}^2) \left(\frac{8k_B T}{\pi \mu_{AB}} \right)^{1/2} e^{-\eta^*/RT}$$

ABOVE GIVES NO INFORMATION ABOUT $E = \eta^*$.

TURN TO TRANSITION STATE THEORY

TRANSITION STATE THEORY

- ASSUMPTIONS
- REACTANTS IN EQUIL. W/ ACTIVATED COMPLEX
 - COMPLEX FORMS PRODUCTS VERY QUICKLY.
 - ACTIVATION BARRIER PASSED ONCE IN $R \rightarrow P$.

REACTION RATE GIVEN BY

$$r = \nu_i C^\ddagger ; \nu_i \equiv \text{VIBRATION ALONG RETN AXIS.}$$

$$C^\ddagger = K_c^\ddagger C_{AB} C_C \text{ FOR } AB + C \rightleftharpoons (A-B-C)^\ddagger \rightarrow A + BC$$

$$\therefore r = \nu_i K_c^\ddagger C_{AB} C_C \rightarrow \text{CORRECT MASS ACTION.}$$

FROM STAT MECH

$$K_c^\ddagger = \frac{Q^\ddagger}{Q_{AB} Q_C} e^{-E/RT} ; Q = Q_T Q_R Q_V Q_C$$

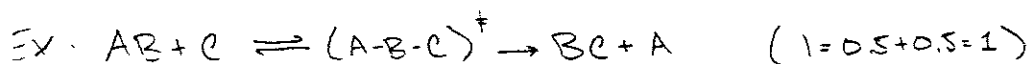
1D SE POTENTIAL - BEBO CONSERVATION

$$\text{ENERGY WELL} \rightarrow U(r) = D_c (1 - e^{-(r-r_0)/\alpha x})^2$$

• BEBO CONS

$$n = \text{BOND ORDER} = e^{-(r-r_0)/\alpha x} \Rightarrow \sum_i n_i = 1$$

$\Rightarrow n = 1 \quad r = r_0$



TO ESTIMATE:

$$E_{ABC} = D_{AB} (2n_{AB} - n_{AB}^2) + D_{BC} (2n_{BC} - n_{BC}^2)$$

$$\text{WHERE } n_{AB} + n_{BC} = 1$$

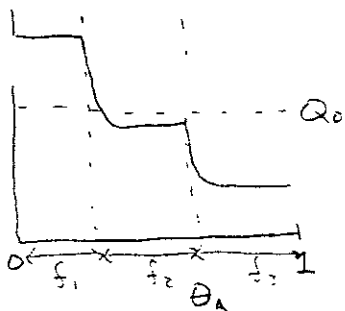
$$\text{TRANSITION STATE} \Rightarrow \frac{\partial E_{ABC}}{\partial n_{AB}} = 0 \Rightarrow n_{AB} = \frac{D_{AB}}{D_{AB} + D_{BC}}$$

$$\Rightarrow \Delta E_{ABC} = E_{ABC} - D_{AB} = \frac{D_{BC}^2}{D_{AB} + D_{BC}} = n_{BC}^2 \cdot D_{BC}$$

PAULING CORRELATIONS

$$D_{AB} = (D_{AA} D_{BB})^{1/2} + c (\chi_A - \chi_B)^2 ; c \approx 30 \frac{\text{kcal}}{\text{mol}} \quad \chi_i = \text{ELECTRONEGATIVITY}$$

NON-UNIFORM SURFACES / INTERACTING MOLECULES (REPULSIVE/ATTRACTIVE INTERACTIONS) (MORE APPARENT @ HIGH COVERAGES).



• DIFFERENT FRACTIONS OF SITES HAVE DIFFERENT THERMODYNAMIC PROPERTIES

• UNIFORM TREATMENT IS OKAY USUALLY BC OF SABATIER PRINCIPLE - HIGH PROB OF FORMING A BOND AND ALSO BREAKING TO FORM P IN INTERMEDIATE RANGE.

DIVIDE SURFACE INTO INDEPENDENT, LANGMUIRIAN PARTS.

$$\theta_A = \sum_i f_i \theta_{Ai} ; \theta_{Ai} = \frac{K_{Ai}[A]}{1 + K_{Ai}[A]} ; K_{Ai} = \text{function of } Q_{Ai}$$

DESCRIBE NONUNIFORMITY \rightarrow CONT. DISTRIBUTION OF ΔH_A . (HEAT OF ADSORPTION)

$df \equiv$ fraction of sites with $(Q, Q+dQ) = g(Q)dQ$.

$$\text{SO } Q_A = \int \theta df = \int \theta g(Q) dQ. \Rightarrow \text{LIMITS } 0-\infty, \text{ OKAY BC GUES TO ZERO AT EACH} \\ \Rightarrow \text{NEED DISTRIBUTION FN.}$$

FREUNDLICH ISOTHERM.

$$g(Q) = \frac{1}{Q_m} e^{-Q/Q_m} ; Q_m \equiv \text{NORMALIZATION CONSTANT}$$

$$\Rightarrow \theta_A = \int_0^\infty \left(\frac{K_A e^{Q/RT} [A]}{1 + K_A e^{Q/RT} [A]} \right) e^{-Q/Q_m} dQ ; Q_m \gg RT \text{ so } \theta_A = a[A]^m ; m \approx \frac{RT}{Q_m} \ll 1 \\ \Rightarrow \text{POWER LAW KINETICS.}$$

LANGMUIR ISOTHERM

$$g(Q) = \delta(Q - Q_0) \Rightarrow \text{BACK TO LANGMUIR IN ABOVE.}$$

TEMKIN ISOTHERM

$$\text{AS ABOVE (F) BUT } Q/Q_m \approx 1, K_A [A] \gg 1 \Rightarrow \theta_A = \frac{RT}{Q_0 \alpha} \ln \left\{ K_A e^{-Q_0/RT} [A] \right\}$$

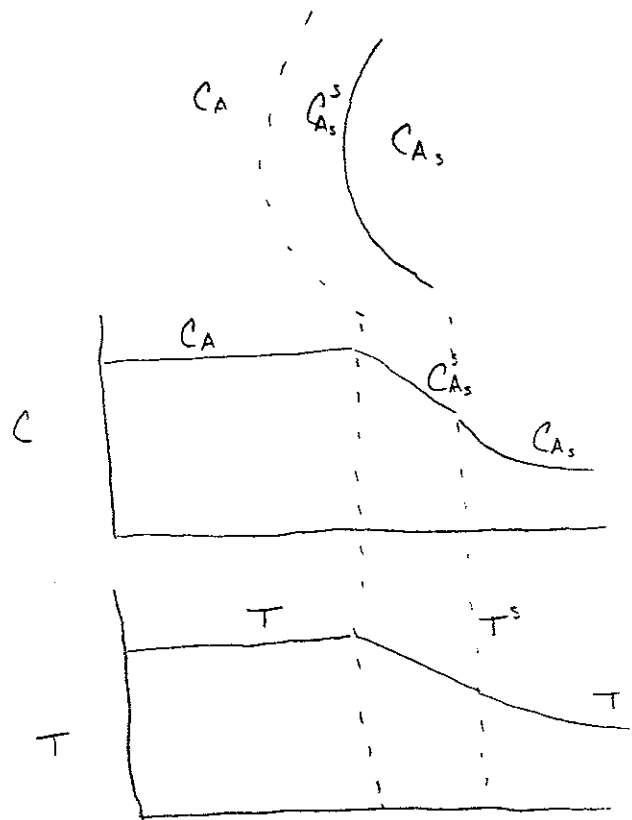
$$\text{SO } Q = Q_0(1 - \alpha)$$

TRANSPORT LIMITATIONS

CAUSES RATE OF RXN TO BE LOWER AND η TO BE LESS THAN 1.

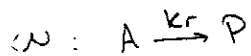
GRADIENTS PICTURED OCCUR.

- TRANSFER RATE CANNOT SUPPORT KINETIC LOAD.
- IN AND OUTSIDE PELLETS
- CHANGE REACTION CONDITIONS: C_A, T .



INTERNAL LIMITATIONS

$C_s = C_{A_s} = \text{CONSTANT}$ \Leftarrow NO INTERNAL LIMITATIONS



$$-r' = k_r C_{A_s}^n$$

$$T = k_g (C_A - C_{A_s}) \cdot A_{ext}$$

$$\text{SOLVE FOR } C_{A_s} \Rightarrow k_g (C_A - C_{A_s}) \cdot A_{ext} = k_r C_{A_s}^n \cdot A_{int}$$

$$\eta = 1 \Rightarrow C_{A_s} = \frac{C_A}{1+\delta}; \quad \delta = \frac{k_r S_v}{k_g a_v} \Rightarrow \eta = \frac{k_r C_A}{1+\delta}$$

0 FIRST ORDER CONSERVED BUT $\frac{1}{k_{app}} = \frac{1}{k_r} (1+\delta)$.

$$n=2 \Rightarrow C_{A_s} = \frac{C_A}{2\delta} \left\{ \sqrt{1+4\delta} - 1 \right\}; \quad \delta = \frac{k_r S_v C_A}{k_g a_v}$$

$$\Rightarrow -r_A = \frac{k_r C_A^2}{4\delta^2} \left(\sqrt{1+4\delta} - 1 \right)^2$$

$$\delta \gg 1 \Rightarrow (-r_A') = k_g \left(\frac{a_v}{S_v} \right) C_A$$

$$\delta \ll 1 \Rightarrow (-r_A') = k_r C_A^2$$

SEE HANDOUT TO ESTIMATE k_g :

MEARS CRITERIA

$\left(\frac{\text{reaction rate/pellet}}{\text{max trans rate/pellet}} \right) \ll 1$ TO ENSURE KINETIC CONTROL.

$$\frac{(-r_A') \left(\rho_p \frac{4}{3} \pi r_p^3 \right)}{k_g C_A (4 \pi r_p^2)} = \frac{(-r_A') \rho_p r_p}{3 k_g C_A} \ll 1 \Rightarrow \frac{(-r_A') \rho_p r_p}{3 k_g C_A} \ll 0.15$$

1st ORDER ONLY

DIFFUSION IN POROUS MEDIA

$$J = -D_{eA} \frac{dC_A}{dx} ; D_{eA} \equiv \text{EFFECTIVE DIFFUSIVITY} \Rightarrow D_{eA} = \bar{D}_A \frac{\epsilon}{\tau}$$

$= f(D_A, r_p, \phi, \tau, \dots)$
↳ VOID FRACTION.

DIFFUSIVITY IN AVERAGE PORE.

BULK DIFFUSION

$$D_A = D_{AB} = \frac{\lambda g \nu}{3} \sim \frac{T^{3/2}}{P} \quad \text{INDEP OF PORE SIZE}$$

KNUDSON DIFFUSION

$$D_{KA} = \frac{(\lambda r) \nu}{3} \sim T^{1/2} r^{1.0} \neq f(P)$$

$$\rightarrow D_{KA} = \frac{4}{3} r \left(\frac{2 RT}{\pi M_A} \right)^{1/2} \quad \text{F+B PP 142.}$$

TRANSITION DIFFUSION

$$\frac{1}{D_{eA}} = \frac{1}{D_{AB}} + \frac{1}{D_{KA}}$$

$$\frac{1}{\bar{D}_A} = \frac{1}{D_{AB}} + \frac{1}{D_{KA}(F_P)} ; \bar{r}_P \approx \frac{2\epsilon_0}{\rho_s S_g} = \frac{2\epsilon_s}{S_v}$$

RANDOM PORE MODEL

$$D_{eA} = \epsilon_s^2 \bar{D}_A$$

BETHE LATTICE + RANDOM SPHERES

FIND τ FROM ϵ_s ON PLOTS THEN

$$\text{USE IN } D_{eA} = \frac{\epsilon}{\tau} \bar{D}_A$$

Thiele Modulus + Internal Effectiveness Factor

Perform Shell Balance for Geometry $\begin{cases} \text{Sphere} \rightarrow \text{Fog 610} \\ \text{Slab} \rightarrow \text{F+B 157} \\ \text{Cylinder} \rightarrow \text{HW} \end{cases}$

$$(IN) - (OUT) = (GEN)$$

$$(W_{Ar} \times A|_r) - (W_{Ar} \times A|_{r+\Delta r}) = \left(r'' \times A_i \times V(\Delta r) \right) \quad ; \quad W_{Ar} = -D_e \frac{dC_A}{dr}$$

NONDIMENSIONALIZE + SOLVE TO GET COEFFICIENT OF CONCENTRATION, THIS IS ϕ^2 ; ϕ = Thiele Modulus.

$$\text{FIRST ORDER SLAB } \phi = L \sqrt{\frac{k_p C_s}{D_e}}$$

$$\text{FIRST ORDER ANY } \phi = f \sqrt{\frac{k_p C_s}{D_e}} \quad ; \quad f \equiv \text{SHAPE FACTOR (SPHERE} \Rightarrow f = \frac{R}{3}) = \frac{V}{S}$$

$$\text{ANY ORDER, ANY SHAPE } \phi = f \sqrt{\left(\frac{n+1}{2}\right) \frac{k_p C_s^{n-1}}{D_e}}$$

INTERNAL EFFECTIVENESS FACTOR

$$\eta = \frac{\text{OVERALL RATE OF RXN}}{\text{RATE IF SURFACE ALL AT } C_s} = \frac{A \times W_{Ar}}{(-r_A'') \cdot A} \quad \begin{matrix} \sim \text{RATE OF DIFFUSION INTO PELLET/PORE} \\ \sim \text{RATE EVALUATED AT } C_s \end{matrix}$$

$$\text{FOR 3 EX ABOVE } \eta = \frac{\tanh \phi}{\phi}$$

\therefore ACTUAL RATE = $\eta \times \text{rate at } C_s$ \Leftarrow USEFUL APPROXIMATION.

$$\text{FOR SPHERICAL PELLET } \eta \approx \frac{3}{\phi} = \frac{3}{R} \sqrt{\frac{D_e}{k_p C_s}}$$

SIMPLIFIED KINETICS

AT DIFF LIMITED RXNS EXHIBIT: $\eta_{app} = \frac{n+1}{2}$ $k_{app} = \sqrt{k}$

IP CRITERIA FOR INTERNAL DIFFUSION

$$\Phi = \frac{\text{RATE RXN/PELLET}}{\text{RATE DIFF/PELLET}} = \frac{(-r_A'')_{obs} \rho_s (A \cdot L)}{D_e C_s (A) / L} = \frac{(-r_A'')_{obs} \rho_s L^2}{D_e C_s} \ll 1 \quad \begin{matrix} \text{TO BE SAFELY AWAY} \\ \text{FROM RESTRICTED} \\ \text{REGIME (} \eta = 1 \text{)} \end{matrix}$$

WHERE $L = \frac{V}{S}$

COMBINING INTERNAL / EXTERNAL DIFFUSION LIMITATIONS.

MATCHING RATE AND DIFFUSION AGAIN

F+B PP 171

$$\eta(-r_A'')|_{C_{A_s}} \cdot \rho_s \cdot A \cdot L = k_g(C - C_s^s)A$$

FOR 1st ORDER RXN : $k_g(C - C_s^s) = \eta k C_s^s \rho_s L = \eta \phi^2 \left(\frac{D_e A C_s^s}{L} \right)$

$$\Rightarrow C_s = \frac{C}{1 + \eta \phi^2 \left(\frac{D_e A}{k_g L} \right)}$$

DEFINE $\eta_G = \frac{(-r_A'')_{obs}}{(-r_A'')_c} = \frac{\eta k C_s^s}{k C} = \frac{\eta}{1 + \eta \phi^2 \left(\frac{D_e A}{k_g L} \right)}$

$$\therefore \frac{1}{\eta_G} = \frac{1}{\eta} + \frac{\phi^2}{(k_g L / D_e A)} ; B_{in} = \frac{\text{ext rate MT}}{\text{int rate MT}} = \frac{k_g}{D_e A / L}$$

FOR SPHERICAL PELLETS : $B_{in} = \frac{k_g f}{D_e A} = \frac{k_g R}{3 D_e A} \sqrt{k_g \sim \frac{D_{AB}}{R_0} \text{ c low } Re} = \frac{D_{AB}}{3 D_e A} = \frac{\tau}{3 \epsilon_s} \sim 2 \text{ or } 3$

SO USUALLY INTERNAL MASS TRANSFER IS LIMITING.

MATERIAL / ENERGY BALANCES.

PFR • CONVECTIVE FLOW \gg DISPERSIVE FLOW • $\rho_j u_z \frac{dx_j}{dz} = - \left(\frac{\rho_j}{C_j} \right) R_j$ • $\frac{d}{dz} (\rho_j u_z) = 0$
 • STEADY STATE

$$\therefore F_0' \frac{dx_j}{dV} = - \frac{1}{C_{j0}} R_j(x_j) \quad ; \quad F_0' \equiv \text{Vol flow rate} = u_0 \Omega$$

$$\Rightarrow u_0 \frac{dx_j}{dz} = - \frac{1}{C_{j0}} R_j(x_j)$$

$$\frac{V}{F_0'} = - \int_{x_0}^{x_j} \frac{dx_j}{R_j(x_j)}$$

BATCH REACTOR • WELL MIXED • $\frac{d(P_j V)}{dt} = 0 \Rightarrow N_{j0} \frac{dx_j}{dt} = - R_j \cdot V$ OR $t = - N_{j0} \int_{x_0}^{x_j} \frac{dx_j}{R_j \cdot V}$

CSTR • STEADY STATE • NO DISPERSION / DIFFUSION

$$C_{j0} u_0 \frac{dx_j}{dz} = \frac{F_{j0}}{\Omega} \frac{dx_j}{dz} = F_{j0} \frac{dx_j}{dV} = - R_j \Rightarrow F_{j0} (x_{jf} - x_{j0}) = R_j V \Rightarrow \frac{x_{jf} - x_{j0}}{R_j} = \frac{V}{F_{j0}} = \frac{V}{F_0' C_{j0}} = \frac{\tau}{C_{j0}}$$

ENERGY BALANCES.

PFR • SS • NO AX COND / DISP

$$\sum_j \dot{m}_j C_{pj} \frac{dT}{dz} - \frac{\pi d_f^2}{4} \sum_i (-\Delta H_i) r_i - \pi d_f U (T_r - T) = 0 \quad \begin{matrix} \dot{m}_j \equiv \text{mass flow rate } j \\ U \rightarrow 0 \equiv \text{adiabatic reactor} \end{matrix}$$

STIRRED REACTORS • $C_j, x_j, T \neq f(z)$

$$\sum_j m_j C_{pj} \frac{dT}{dt} - \sum_j F_{j0} (H_{j0} - H_j) = V \sum_i (-\Delta H_i) r_i + A_k U (T_r - T) \quad ; \quad \sum_j m_j C_{pj} = \overset{\text{total mass}}{m_t \bar{C}_p}$$

• BATCH STR. • $F_j = F_{j0} = 0$

$$m_t \bar{C}_p \frac{dT}{dt} = V \sum_i (-\Delta H_i) r_i + A_k U (T_r - T)$$

• CSTR • SS

$$0 = \sum_j F_{j0} (H_{j0} - H_j) + V \sum_i (-\Delta H_i) r_i + A_k U (T_r - T)$$

$$\begin{aligned} \Delta H_i(T) &= \Delta H_i^\circ(T_r) + \int_{T_r}^T \Delta C_p dT = \Delta H_i^\circ(T_r) + \Delta \hat{C}_p (T - T_r) \\ F_{j0} (H_{j0} - H_j) &= m_{j0} C_{pj} (T_0 - T) \\ &= m_j C_{pj} (T_0 - T) + \text{PHASE TRANS?} \end{aligned}$$

APPLICATIONS

• ISOTHERMAL BATCH • $N_{j0} \frac{dx_j}{dt} = R_j V = V \sum_i \alpha_{ij} r_i \Rightarrow t = N_{j0} \int_{x_0}^{x_{jf}} \frac{dx_j}{V \sum_i \alpha_{ij} r_i}$

NONISOTHERMAL BATCH • ① $\frac{dx_A}{dt} = \frac{V}{N_{A0}} r_A(x_A, T)$ ② $m_t \bar{C}_p \frac{dT}{dt} = V(-\Delta H) r_A(x_A, T) + A_k U (T_r - T)$

• MULT ① BY $(-\Delta H \cdot N_{A0})$ AND ADD TO 2: $m_t \bar{C}_p (T - T_0) + N_{A0} (-\Delta H) (x_A - x_{A0}) = \int_0^\theta A_k U (T_r - T) d\theta$

• ADIABATIC $\Rightarrow T - T_0 = \frac{(-\Delta H) N_{A0}}{m_t \bar{C}_p} (x_A - x_{A0}) \Rightarrow \Delta T_{Ad} = T_{Ad} - T_0 = \frac{(-\Delta H) N_{A0}}{m_t \bar{C}_p} ; \quad \frac{T - T_0}{\Delta T_{Ad}} = x_A$

PACKED BED REACTORS.

- ID MODELS • RADIAL UNIFORMITY $\langle U \rangle, \langle C_A \rangle, \langle T \rangle$. • VOID FRACTION CONTROLS FLOW $U_s \equiv \epsilon_B U_z$ $\rightarrow F/\Omega$
- MOLE B $\frac{d(U_s C_A)}{dz} = r_A \rho_B$; $\rho_B = \rho_P(1 - \epsilon_B)$ • BED DENSITY
- ENERGY B $U_s \rho_P C_p \frac{dT}{dz} = (-\Delta H)(-r_A) \rho_B - \frac{4U}{d_t}(T - T_R)$ • MOM B $-\frac{dP}{dz} = f \frac{\rho_P U_s^2}{d_p}$ f = FRICTION FACTOR.
 SUPERFICIAL C_{ACT}
- BC: $z=0: C_A = C_{A0}, T = T_0, P = P_0$
- SOLVE BY FORWARD INTEGRATION.
- IG: $\frac{U_s}{U_{s0}} = U_{s0}(1 + \epsilon_X) \left(\frac{T}{T_0} \right) \left(\frac{P_0}{P} \right)$

HOT SPOTS / THERMAL RUNAWAY

PREDICTING / RUNAWAY PLOTS.

- BALANCES • $U_s \frac{dC_A}{dz} = r_A \rho_B$ ① $U_s \rho_P C_p \frac{dT}{dz} = \rho_B r_A \Delta H - \frac{4U}{d_t}(T - T_0)$ ②

- NONDIMENSIONALIZE, EXPAND AROUND T_0 ; DIVIDE ② BY ①

$$\frac{1}{S} \frac{d\theta}{dx_A} = 1 - \frac{N\theta e^{-\theta}}{S(1-x_A)}; S = \beta \cdot X = \left(\frac{(-\Delta H) C_{A0}}{\rho_P C_p T_0} \right) \cdot \frac{E}{RT_0} = \left(\frac{T_{A0} - T_0}{T_0} \right) \frac{E}{RT_0} = \text{VALUE OF } \theta \text{ WHEN FEED } (T_0) \text{ TOTALLY REACTS IN ADIA.}$$

$$\frac{N}{S} = \frac{\left(\frac{4U}{d_t} \right) \left(\frac{RT_0^2}{E} \right)}{\rho_B k(T_0) C_{A0} (-\Delta H)} \leftarrow \text{RATE OF WALL HEAT TRANSFER.}$$

$$\rho_B k(T_0) C_{A0} (-\Delta H) \leftarrow \text{RATE OF HEAT GEN @ INLET.}$$

- AT RUNAWAY $\theta = f(x_A)$ LOSES MAX. AND $\frac{1}{S} \frac{d\theta}{dx_A} = 1 - \frac{N\theta e^{-\theta}}{S(1-x_A)} \neq 0$
- APPLY RUNAWAY PLOT.

INTERSTAGE COOLING.

$$\frac{(-r_A)}{C_{A0}} = A_1 e^{-E_1/RT}(1-x_A) - A_2 e^{-E_2/RT}(1-x_A)$$

$$\frac{x_A - x_{A0}}{T - T_0} = \lambda = \frac{\dot{m}_1 \bar{C}_p}{F_{A0} (-\Delta H)} = \frac{\rho_P C_p}{C_{A0} (-\Delta H)}$$

- PLOT CONTOURS OF $(-r_A)$ VALUES IN x_A VS. T DIAGRAM
- PLOT ADIABATIC COOLING LINES
- USE $\frac{\Delta x_A}{\Delta T}$ IN HEAT EXCHANGER

AUTOTHERMAL REACTORS • ΔH_{exo} USED TO PREHEAT FEED TO T_0 TO ACHIEVE X_A

NUMERICAL

- RCTR MOLE B ON A ① $\frac{dX_A}{dz} = \frac{\pi d_L^2}{4 F_{A0}} P_B (-r_A)$; $X_{A0} = X_{AL}$
- RCTR ENERGY B ② $\frac{dT}{dz} = \frac{\pi d_L^2}{4} \frac{P_B (-r_A) (-\Delta H)}{\dot{m} C_p}$; $T(0) = T_i(L')$ EXIT HEAT EXCHANGER
- HEAT EXCHANGER EB (FRESH SIDE) ③ $\frac{dT_i}{dz'} = \frac{U \pi d_L'}{(\dot{m} C_p)_i} (T_2 - T_i)$
 \hookrightarrow fresh feed; $T_i(0) = T_i$ INITIAL FEED.
- TOTAL EXCHANGER EB ④ $(\dot{m} C_p)_i dT_i = (\dot{m} C_p)_2 dT_2$; $T_i(0) = T_i$
 $T_2(0) = T_e \leftarrow \text{UNKNOWN}$
- GUESS T_0 UNTIL $T(L) = T_2(L')$

GRAPHICAL APPROACH

①/② $\Rightarrow \Delta X_A = X_A - X_{Ai} = \lambda (T(z) - T(0))$; $\lambda = \frac{\dot{m} C_p}{F_{A0} (-\Delta H)}$

$\therefore T(z) = T(0) + \frac{\Delta X_A}{\lambda}$ ⑤

• SUB ABOVE INTO ① TO GET CONVERSION VS. T (CALL IT ⑥)
 (USE $(-r_A)$ AS BEFORE)

• SO WE CAN NOW GET $T(0)$ REQD FOR GIVEN CONVERSION

USE ③, ④ TO RELATE T_i TO $T(0)$ (RCTR INLET)

• ASSUME $(\dot{m} C_p)_i = (\dot{m} C_p)_2$ SO $dT_i = dT_2 \Rightarrow \Delta T = T_2 - T_i = \text{CONSTANT}$

$\therefore \frac{dT_i}{dz} = \frac{U \pi d_L'}{(\dot{m} C_p)_i} \Delta T = \chi \Delta T$

• INTEGRATING $\Rightarrow T_i(L') - T_i(0) = T(0) - T_i = \chi \Delta T L'$

• ADD/SUB $T(L)$ $(T(L) - T_i) - (T(L) - T(0)) = \chi \Delta T L'$
 $(T(L) - T_i) = \Delta T = \chi \Delta T L'$

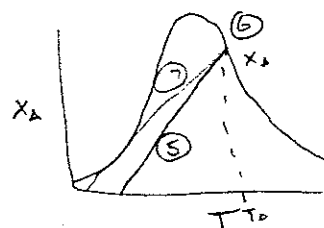
• NOW WE RELATED $T(L)$ TO T_i (KNOWN) $\Rightarrow T(L) - T_i = (1 + \chi L') \frac{\Delta X_A}{\lambda}$

REARRANGE TO PLOT: $X_A(L) - X_A(0) = - \frac{\lambda (T(L) - T_i)}{1 + \chi L'}$ \therefore INT T_i SLOPE $\frac{\lambda}{1 + \chi L'}$

SO CAN FIND FOR GIVEN X_A , $T(0)$, T_i (AND SINCE KNOW ΔT , ALL FREE)

GOOD EXCEPT • MSS

• $\frac{dr_A}{dz} \neq 0$



PSEUDOHOMOGENEOUS 1D MODELS

DISPERSED FLOW REACTOR.
 ACCOUNTS AX DISP
 ACCOUNTS RAD DISP $\rightarrow J_z = -E_B D_{EA} \frac{dC_A}{dz}$

MOLE BALANCE $E D_{EA} \frac{d^2 C_A}{dz^2} - u_s \frac{dC_A}{dz} - (-r_A) \rho_B = 0$

ENERGY BALANCE $\lambda_{EA} \frac{d^2 T}{dz^2} - \rho_B u_s \bar{C}_p \frac{dT}{dz} + (-\Delta H)(-r_A) \rho_B - \frac{4U}{d_t} (T - T_c) = 0$
 \uparrow AX TH CONDUCTIVITY

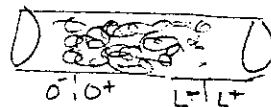
BCS: DIFF B/C DISPERSION COEFF CHANGES QUICKLY AT BOUNDARIES.

DANCKWERTZ "CLOSED" CONDITIONS.

$u_s (C_A(0^-) - C_A(0^+)) = -E_B D_{EA} \frac{dC_A}{dz} \Big|_{z=0}$
 $\uparrow C_{A0}$

$\rho_B u_s (T(0^-) - T(0^+)) = -\lambda_{EA} \frac{dT}{dz} \Big|_{z=0}$
 $\uparrow T_0$

$\frac{dC_A}{dz} \Big|_L = \frac{dT}{dz} \Big|_L = 0$



REQ T+E FI OR FINITE ELEMENT METHODS. (2 PT BVP)

REDUCING USING DIMENSIONAL ANALYSIS.

$Pe_{ma} = \frac{u_s d_p}{E D_{EA}} = \frac{u_s d_p}{D_{EA}}$ $Pe_{ha} = \frac{\rho_B u_s \bar{C}_p d_p}{\lambda_{EA}}$

CRITERIA FOR NEGLECTING

MAX AT 0 $\rightarrow -D_{EA} \frac{dC_A}{dz} \Big|_0 \ll u_s$; $-\lambda_{EA} \frac{dT}{dz} \Big|_0 \ll u_s$

MAX AT $\theta \rightarrow \max \left| \frac{dx_A}{d(z/d_p)} \right| \ll Pe_{ma}$

$\max \left| \frac{d\theta}{d(z/d_p)} \right| \ll Pe_{ha}$; $\theta = \frac{T}{T_0 - T_w}$

2D PSEUDOHOMOGENEOUS MODELS $(C_A, T = f(z, r))$

HEAT BALANCE IN ANNULAR VOLUME

SOLUTION METHOD

FINITE ELEMENT

USE CHARTS: Pe_{mr} vs. Re

λ_{er} vs. Re

Nu vs. Re

ASYMPTOTIC REDUCTION OF ABOVE

NONDIMENSIONALIZE ABOVE USING $\bar{r} = \frac{r}{R_t}$, $X = \frac{C_0 - C}{C_0}$, $S(x, \tau) = \frac{(-r_A(x, \tau))}{(-r_A(z=0, \bar{r}))}$, $\bar{z} = \frac{z}{\frac{U_0 C_0}{\rho_B (-r_A)_{ref}}}$

$$MB: \frac{\partial X}{\partial \bar{z}} = \frac{1}{\eta Le} \left(\frac{\partial^2 X}{\partial \bar{r}^2} + \frac{1}{\bar{r}} \frac{\partial X}{\partial \bar{r}} \right) + S(x, \tau); \quad \frac{\partial X}{\partial \bar{r}} \Big|_{\bar{r}=1} = 0 \quad X=0 \Big|_{\bar{z}=0}$$

$$\eta = \frac{\rho_B C_p U_0^2}{\lambda_{er}} \cdot \frac{(-r_A)_{ref} \rho_r}{C_0}; \quad Le = \frac{\lambda_{er}}{\rho_B C_p D_{er}} \sim 1-z; \quad \eta Le = \frac{r_{ref} \rho_r}{r_{add} \rho_{ref}}$$

$$EB: \eta \frac{\partial T}{\partial \bar{z}} = \left(\frac{\partial^2 T}{\partial \bar{r}^2} + \frac{1}{\bar{r}} \frac{\partial T}{\partial \bar{r}} \right) + QS(x, \tau); \quad T=T_0 \Big|_{\bar{z}=0} \quad \frac{\partial T}{\partial \bar{r}} = 0 \Big|_{\bar{r}=1} \quad -\frac{\partial T}{\partial \bar{r}} \Big|_{\bar{r}=1} = \gamma (T-T_0); \quad \gamma = \frac{E_i}{\lambda_{er} R_t}$$

$$Q = \frac{(-\Delta H)(-r_A)_{ref} R_t^2 \rho_r}{\lambda_{er}} \sim T/K \sim \Delta T_{rad}; \quad Q/\eta = \frac{C_0(-\Delta H)}{\rho_B C_p} = \Delta T_{Ad}$$

$$\frac{\Delta T_{rad}}{\Delta T_{Ad}} \ll 1 \sim \frac{Q}{Q_{th}} \sim \eta \ll 1$$

$$MB: \therefore \left(\frac{\partial^2 X}{\partial \bar{r}^2} + \frac{1}{\bar{r}} \frac{\partial X}{\partial \bar{r}} \right) \ll \frac{\partial X}{\partial \bar{z}} \Rightarrow \frac{\partial X}{\partial \bar{z}} = \langle S(x, \tau) \rangle = 2 \int_0^1 \bar{r} S(x(\bar{r}, \bar{z}), T(\bar{r}, \bar{z})) d\bar{r}$$

So $X(\bar{r})$ changes predominantly in \bar{z} scale.

$$EB: 0 = \frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} \left(\bar{r} \frac{\partial T}{\partial \bar{r}} \right) + QS(x, \tau) \quad \text{SAME B.C. AS ABOVE}$$

LOCAL SOLUTION PROVIDES GROUNDWORK IN \bar{z} SCALE WITH $S(x, \tau)$ (CUE OF $X(\bar{r})$).

ASYMPTOTIC SOLUTION

$$S(x, \tau) = a(x) e^{-E|\tau|} = a(x) e^{-E|\tau|} (e^{\theta} = e^{\theta^2 + \dots}) = S(x, \bar{r}) (e^{\theta} = e^{\theta^2 + \dots}) \quad \theta = \frac{E(T-T_0)}{RT^2}$$

$$\text{SO } S(x, \tau) = S(x, \bar{r}) e^{A(\tau-\bar{r})}; \quad A = \frac{E}{RT^2} \cdot \frac{1}{\bar{r}}$$

$$\therefore 0 = \frac{1}{\bar{r}} \left(\frac{\partial}{\partial \bar{r}} \left(\bar{r} \frac{\partial T}{\partial \bar{r}} \right) \right) + QS(x, \bar{r}) e^{A(\tau-\bar{r})}$$

$$\text{EXACT SOLN: } T(\bar{r}, \alpha) = T_r + \frac{1}{A} \left(\frac{4\alpha}{\gamma} - 2 \log(1 - \alpha + \alpha \bar{r}^2) \right); \quad \alpha \text{ SATISFIES } \rightarrow 8\alpha(1-\alpha) e^{-4\alpha/\gamma} = A Q \cdot S(x, T_0) e^{-A(\bar{r}-T_r)}$$

JACKET TEMP

SO NEED TO RETURN TO $S(x, T) \Rightarrow \frac{dx}{dz} = \int_0^1 2F S(x, T(F)) dF$

AVAILABILITY OF $T(F)$ ALLOWS RIGOROUS AVERAGING OF $S(x, T)$.

RIGOROUS CSA

$\bar{T}(z) \equiv$ reaction averaged temperature $\quad e^{-E/RT(z)} = \int_0^1 F e^{-E/RT(F, z)} dF$

NOW AVE MOLE FRACTIONAL WITHIN CS USING SOLUTION $T(F, z)$

$\frac{d\langle x \rangle}{dz} = S(\langle x \rangle, \langle T \rangle) \xrightarrow{\quad} \bar{T}(z) \quad \int_0^1 2F \frac{d}{dF} (F \frac{dT}{dF}) dF = -\frac{8\sigma}{A}$

$\eta \frac{dT}{dz} = \langle \frac{1}{F} \frac{d}{dF} (F \frac{dT}{dF}) \rangle + Q S(\langle x \rangle, \langle T \rangle)$

AND $\frac{dx}{dz} = \frac{8x(x, F)}{A \cdot Q} \Rightarrow \eta \frac{dT}{dz} = -\frac{8x}{A} + Q S(x, \bar{T})$
 $= -\frac{8\sigma}{A} + Q S(x, T_r) e^{-A(T - T_r)}$

RIGOROUSLY EQUIVALENT TO 1D MODEL

EXCEPT α IS FN BY $8\alpha(1-\alpha)e^{-\gamma L/8} = A Q S(x, T_0) e^{-A(T - T_r)}$

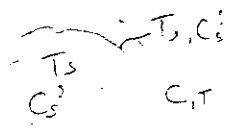
WHICH Varies WITH z

HETEROGENEOUS REACTOR MODELS

INTERFACIAL GRADIENTS

- MDE/ENERGY BAL BOTH PHASES
- FLUX MATCHING @ INTERFACE

EX. PACKED BED w/ EXT MT RESIST



$$① -u_s \frac{dC}{dz} = k_g a_v (C - C_s^s)$$

$$② u_s \rho_p C_p \frac{dT}{dz} = h a_v (T_s - T) - \frac{4U}{d} (T - T_r)$$

$$③ -r_A|_{C_s^s, T_s} = k_g a_v (C - C_s^s)$$

$$④ (-\Delta H) \rho_p (-r_A|_{C_s^s, T_s}) = h a_v (T_s - T)$$

$$\left. \begin{matrix} C = C_0 \\ T = T_0 \end{matrix} \right\} z = 0 \quad \left. \vphantom{\begin{matrix} C = C_0 \\ T = T_0 \end{matrix}} \right\} \text{FLUID}$$

$$\left. \vphantom{\begin{matrix} C = C_0 \\ T = T_0 \end{matrix}} \right\} \text{PARTICLE}$$

• USUALLY CANNOT SOLVE 3, 4 ANALYTICALLY SO USE NUMERICAL SOLUTION OF ①-④

INTERFACIAL GRADIENTS.

① ② SAME AS BEFORE, BUT ③ ④ CHANGE CUZ CONCL CHANGE INSIDE PARTICLE

$$③' \frac{De}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_s}{dr} \right) - \rho_s (-r_A) = 0$$

$$\frac{dC_s}{dr} = \frac{dT_s}{dr} = 0 \quad | \quad r=0$$

$$④' \frac{\lambda_e}{r^2} \frac{d}{dr} \left(r^2 \frac{dT_s}{dr} \right) - \rho_s (-\Delta H_A) (-r_A) = 0$$

$$-De \frac{dC_s}{dr} \Big|_{r_p} = k_g (C_s - C)$$

$$-\lambda_e \frac{dT_s}{dr} \Big|_{r_p} = h_f (T_s - T)$$

Es on ① ②: Matching fluxes at surface (Kobayashi)

AXIAL DISPERSION - USU NOT IMP

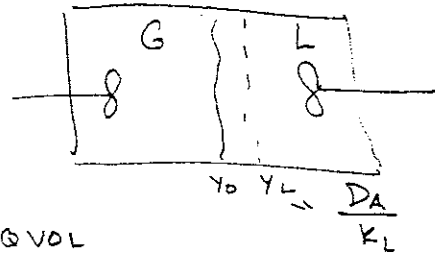
RAD DISPERSION - USU IMP - ESP IN ADIABATIC

FLUID-CAT HEAT TRANS - USU CONST T IN PARTICLE BUT DIFF FROM FLUID - BL

FLUID-CAT MASS TRANS - OPPOSITE ABOVE

MULTIPHASE REACTORS

MODEL 2 PHASE AS WELL MIXED G/L PHASES →



IE BALANCES: G

$$\textcircled{1} F_{A0}X_{A0} - F_A X_A \approx F[Y_{A0} - Y_A] \quad \text{LIQ VOL}$$

$$= \frac{F}{P_T} (P_{A0} - P_A) = N_A|_{y=0} \cdot A_v \cdot V \cdot (1 - E_G)$$

L (-FILM)

FRACTION OUTSIDE FILM

$$\textcircled{2} N_A|_{y=L} \cdot A_v \cdot (1 - E_G) \cdot V = -r_A Y (1 - E_G) (1 - A_v Y_L)$$

OVERALL ($aA(g) + bB(l) \rightarrow$)

$$\textcircled{3} \frac{F}{P_T} (P_{A0} - P_A) = \frac{a}{b} L (C_{B0} - C_B)$$

LIMITING CASES: . FAST RXN COMPLETED IN FILM $C_{Ab} \approx C_{Ab,out} \approx 0 \Rightarrow \textcircled{1}, \textcircled{3}$
 . SLOW RXN - FILM NEGLIGIBLE $\Rightarrow \textcircled{1}, \textcircled{2}$ ^{stirrer}

SOLUTION NEEDS i) $(-r_A)$

ii) $N_A|_{y=0}, N_A|_{y=y_L}$

iii) $E_G = f(V_L, P_L, U_{ST}, d_{ST}, d_r)$

iv) $A_v = f(E_G, d_b) \approx \frac{6}{d_p} \frac{E_G}{1 - E_G} \frac{d_b(P_L - P_0)g}{\sigma_L} =$

ii) FILM MODEL RESULTS

$$\textcircled{4} N_A|_{y=0} = \frac{k_L \delta}{\sinh \delta} (C_{Ai} \cosh \delta - C_{Ab}) \quad \text{interface}$$

$$\textcircled{5} N_A|_{y=y_L} = \frac{k_L \delta}{\sinh \delta} (C_{Ai} - C_{Ab} \cosh \delta)$$

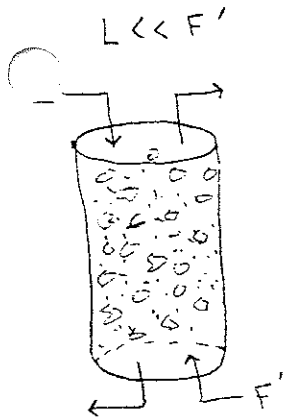
$$\textcircled{6} C_{Ai} = \frac{P_{Ab}}{H}; \quad \delta = y_L \sqrt{\frac{k}{D_A}}$$

AFTER ALGEBRA ZEROS IN C_{Ab}, P_{Ab}

$$\frac{F}{P_T} [P_{A0} - P_{Ab}] = \frac{k_L \delta}{\sinh \delta} \left(\frac{P_{Ab}}{H} \cosh \delta - C_{Ab} \right) A_v (1 - E_G) V$$

$$\frac{k_L \delta}{\sinh \delta} \left(\frac{P_{Ab}}{H} - C_{Ab} \cosh \delta \right) = (1 - A_v Y_L) V (1 - E_G) k C_{Ab} + L C_{Ab}$$

BUBBLE COLUMN REACTOR



GAS \rightarrow PFR

LIQUID \rightarrow CSTR OR AXIAL DISPERSION REACTOR (D_{eff})

BALANCES

GAS $-\frac{F}{P_T} \frac{dP_{Ab}}{dV} = N_A|_{y=0} \cdot a'_v$; $a'_v = \frac{G-L \text{ INTERFACE AREA}}{\text{VOLUME OF LIQUID}}$

LIQUID $\int_0^V N_A|_{y=y_L} a'_v dV = (1 - a'_v y_L) V (1 - \epsilon_G) (-r_A) + L C_{Ab}$

OVERALL $\frac{F}{P_T} [P_{Ab_0} - P_{Ab}] = \frac{a}{b} L [C_{Ab_0} - C_{Ab}] + L C_{Ab}$