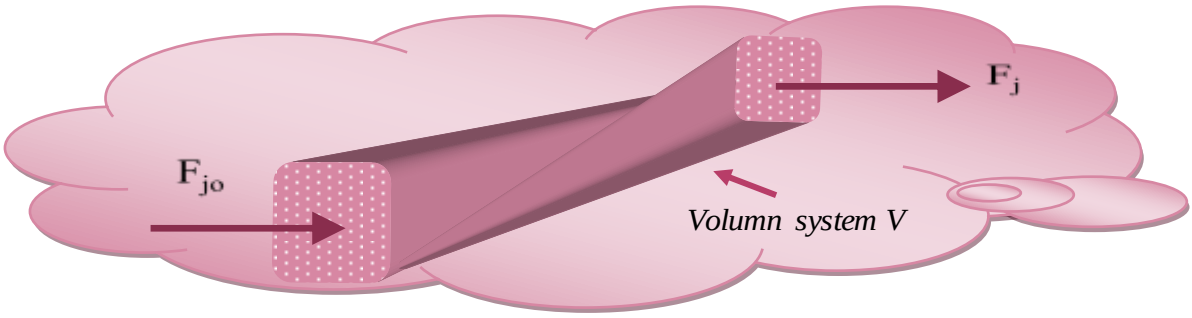
Lecture (10)

Reactor Sizing and Design

1. General Mole Balance Equation

Mole balance on species j at any instance in time t ;

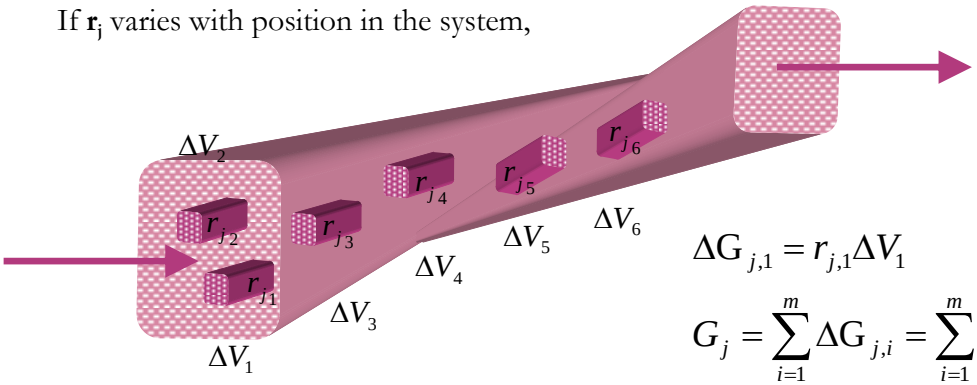


$$\begin{bmatrix}\text{rate of flow}\\ \text{of j into system}\end{bmatrix}+\begin{bmatrix}\text{rate of generation}\\ \text{of j in system by rxn}\end{bmatrix}-\begin{bmatrix}\text{rate of flow}\\ \text{of j out of system}\end{bmatrix}=\begin{bmatrix}\text{rate of accumulation}\\ \text{of j within system}\end{bmatrix}$$

$$F_{jo}+G_j-F_j=\frac{dN_j}{dt} \qquad \text{.....4.1}$$

F_{j0} = Entering molar flow rate of species j (mol/time)
F_j = Exiting molar flow rate of species j (mol/time)
G_j = Rate(total rate) of generation(formation) of species j (mol/time)=r_j .V
V = Volume (e.g. m^3)
r_j = rate of generation(formation) of species j (mole/time.vol)
N_j = number of moles of species j inside the system Volume V (mole)

If $\mathbf{r_j}$ varies with position in the system,



$$\Delta G_{j,1}=r_{j,1}\Delta V_1$$

$$G_j=\sum_{i=1}^{m}\Delta G_{j,i}=\sum_{i=1}^{m}r_{j,i}\Delta V_i$$

$$Let\ \ m\to\infty,\ \ \Delta V\to 0$$

$$G_j=\int^{V} r_j dV$$

Then general mole balance:-

$$F_{jo} + \int^{V} r_j dV - F_j = \frac{dN_j}{dt} \qquad \text{.....4.2}$$

From this general mole balance equation **we** can develop the design equations for the various types of industrial reactors: batch, semi-batch. and continuous-flow reactors.

REACTOR SIZING AND DESIGN

PART ONE

Batch Reactor

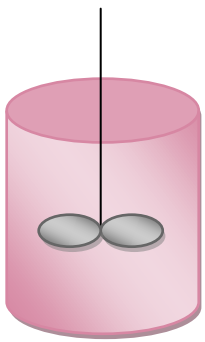
Isothermal Operation

- **Operate under unsteady state**
- **Neither inflow nor outflow of reactants or products**
  If the reaction mixture **is perfectly mixed *so:***
- **Constant rate of reaction throughout** the **reactor volume**
- **Composition $\neq f$(Position)**
- **Composition $= f$(time)**
- **Temperature $\neq f$(Position)**
- **Temperature $\neq f$(time)**

} **ideal restrictions**

Mole Balance

$$F_{j,o} = F_j = 0$$



$$\cancel{F_{jo}} + \int^{V} r_j dV - \cancel{F_j} = \frac{dN_j}{dt}$$

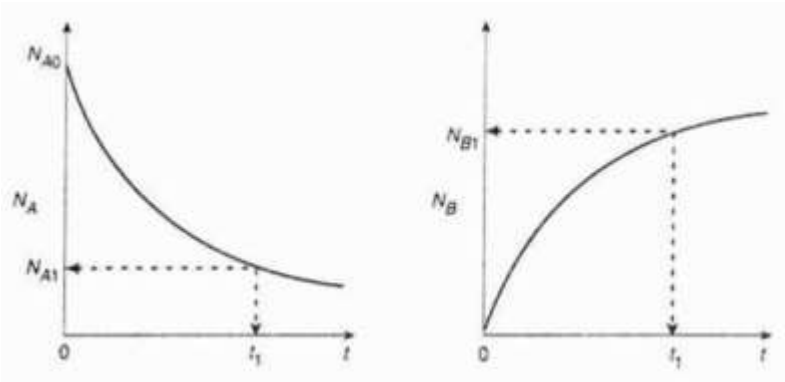
$$\int^{V} r_j dV = \frac{dN_j}{dt} \quad \text{.....4.3}$$

$$\boxed{r_j V = \frac{dN_j}{dt}} \quad \text{.....4.4}$$

Let's consider the isomerization **of** species **A in** a batch reactor

$$A \rightarrow B$$

As the reaction proceeds. the number **of moles of A decreases and the number of** moles **of B increases, as** shown **in Figure below**



The time t necessary to reduce the initial number of **moles** N_{Ao} **to** a final number of mole N_A **can be estimated as :**
from equation 4.4

$$\boxed{r_A V = \frac{dN_A}{dt}} \quad \text{.....4.4}$$

$$dt = \frac{dN_A}{r_A V}$$

integrating with limits that at :
$t = 0 \quad N_A = N_{A0} \leftarrow$ stat of reaction and at
$t = t \quad N_A = N_A$ reaction time (end of reaction) we obtain

$$t = \int_{N_A}^{N_{A0}} \frac{dN_A}{r_A V} \quad \text{.....4.5}$$

$$\begin{bmatrix} \text{moles of A} \\ \text{reacted or consumed} \end{bmatrix} = \begin{bmatrix} \textit{moles} \text{ of A} \\ \text{initially fed} \\ \text{at t = 0} \end{bmatrix} \bullet \begin{bmatrix} \dfrac{\textit{moles} \text{ of A } \textit{reacted}}{\textit{moles} \text{ of A } \textit{fed}} \end{bmatrix}$$

$$\begin{bmatrix} \text{moles of A} \end{bmatrix}$$

number of mole N_A remain un-reacted after time **t** ,

$$\begin{bmatrix} \text{moles of A} \\ \text{in reacter (remain) at} \\ \text{time t} \end{bmatrix} = \begin{bmatrix} \textit{moles} \text{ of A} \\ \text{initially fed to} \\ \text{the reactor at t} = 0 \end{bmatrix} - \begin{bmatrix} \text{moles of A} \\ \text{reacted or consumed} \\ \end{bmatrix}$$

$$[N_A] = [N_{A0}] - [N_{A0}] \bullet [X]$$

$$\boxed{N_A = N_{Ao}(1 - X)}$$ Sub in equation 4.5 and 4.4

$$\boxed{X = \frac{N_{Ao} - N_A}{N_{Ao}}}$$

$$\frac{dN_A}{dt} = r_A V \qquad \boxed{N_A = N_{Ao}(1 - X)} \qquad t = \int_{N_A}^{N_{A0}} \frac{dN_A}{r_A V}$$

$$\boxed{N_{Ao} \frac{dX}{dt} = -r_A V}$$ …….4.6

$$\boxed{t = N_{Ao} \int_0^{X(t)} \frac{dX}{-r_A V}}$$ …4.7

Differential form
Batch Reactor Design Equation
m

Integral form
Used in the Interpretation of
Lab Rate Data

Space time or Mean Residence Time= **is the time necessary to process one reactor volume of fluid based on entrance conditions.**

$t_B = t + t_D$

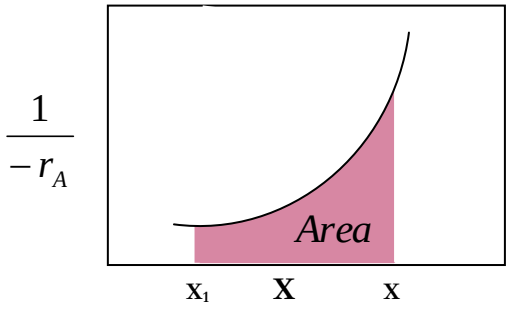
- **At constant volume batch reactor**
  i.e constant density reaction mixture.
  $\mathbf{N_{Ao} = C_{Ao} * V}$ → then; equations 4.4 and 4.5 become ($C_i = \frac{N_i}{V}$) :

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

$$\boxed{t = \int_{C_{Ao}}^{C_A} \frac{dC_A}{-r_A}}$$ ……4.8….(Reaction Time)

Evaluation of Reaction Time Graphically:

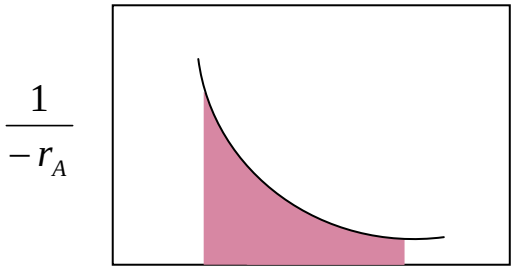
From equation 4.7 plot $\frac{1}{-r_A}$ **vs. X and evaluate the area under the curve to estimate reaction time**



$$\boxed{t = N_{Ao} \int_0^{X(t)} \frac{dX}{-r_A V}}$$

$$\boxed{t = \frac{N_{Ao}}{V} * Area}$$

Or
From equation 4.7 plot $\frac{1}{-r_A}$ **vs.** $\mathbf{C_A}$ **and evaluate the area under the curve to estimate reaction time**



$$\boxed{t = \int_{C_{Ao}}^{C_A} \frac{dC_A}{-r_A}}$$

$$\boxed{t = Area}$$

$$Area$$

CA **CA** **CA_o**

Example

Evaluation of Reaction Time Numerically:

Need $-r_A = f(C_A)$ **to size reactors or calculate reaction time**

- For the reactions in which the rate depends only on the concentration of one species then $-r_A = f(CA)$

First order and Irreversible :-

$$A \rightarrow B \quad , \qquad -r_A = kC_A$$

$$t = \int_{C_{Ao}}^{C_A} \frac{dC_A}{-kC_A} = -\frac{1}{k}\int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A}$$

$$t = -\frac{1}{k}.\ln\left(\frac{C_A}{C_{Ao}}\right)$$

$$C_A = C_{Ao}e^{-kt}$$

Second order and Irreversible :-

$$A \rightarrow B \quad , \qquad -r_A = kC_A^2$$

$$t = \int_{C_{Ao}}^{C_A} \frac{dC_A}{-kC_A^2} = -\frac{1}{k}\int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A^2}$$

$$t = -\frac{1}{k}\left(\frac{1}{C_A} - \frac{1}{C_{Ao}}\right) \quad , \quad C_A = \frac{C_{Ao}}{1 + C_{Ao}kt}$$

nth order and Irreversible :-

$$A \rightarrow B \quad , \qquad -r_A = kC_A^n$$

$$-kt = \frac{1}{-n+1}\left(C_A^{-n+1} - C_{Ao}^{-n+1}\right)$$

$$C_A = C_{Ao}\left[1+(n-1)kC_{Ao}^{-n+1}t\right]^{\frac{1}{1-n}}$$

Example

Bimolecular Reactions

- when the rate law depends on more than one species , we must relate the concentrations of the different species to eac2h other **"as a function of conversion** $-r_A = f(X)$ **"**. This relationship is most easily established with the aid of a Stoichiometric table.

In formulating our stoichiornetsic table, **we** shall take species **A component** as our basis of calculation (i.e.. limiting reactant) and then divide through by the stoichiometric coefficient of A , in order to put everything on **a** basis of "pet mole of **A "**.

Stoichiornetsic table presents the following information

- **Column I: the particular species**
- **Column 2: the number of moles of each species initially present**
- **Column 3: the change in the number of moles brought about by reaction**
- **Column 4: the number of moles remaining in the system at time t**
- **Column 5: concentrations as a function of conversion of each species**

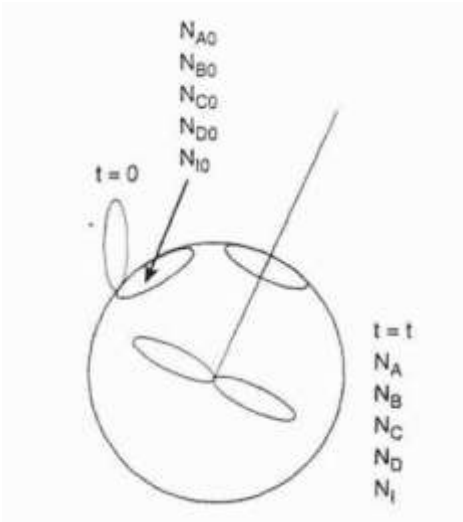
- Consider the general reaction;

Stoichiometry set up of equations with A as basis

$$A + \left(\frac{b}{a}\right)B \Leftrightarrow \left(\frac{c}{a}\right)C + \left(\frac{d}{a}\right)D$$

The rate law is :

$$-r_A = k_A\left(C_A^a C_B^b - \frac{C_C^c C_D^d}{K_C}\right)$$



- Constant Volume (Constant Density) $V = V_0$

liquid-phase and some of gas phase reaction system fall into this category.

Stoichiometric Table Batch System

Specie	Initial	Change	Remaining	Concentration
A	N_{Ao}	$-N_{Ao}X$	$N_A = N_{Ao}(1 - X)$	$C_A = C_{A0}(1-X)$
B	$N_{Bo} = N_{Ao}\Theta_B$	$-(b/a)N_{Ao}X$	$N_B = N_{Ao}[\Theta_B - (b/a)X]$	$C_B = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$
C	$N_{Co} = N_{Ao}\Theta_C$	$+(c/a)N_{Ao}X$	$N_C = N_{Ao}[\Theta_C + (c/a)X]$	$C_C = C_{A0}\left(\Theta_C + \frac{c}{a}X\right)$
D	$N_{Do} = N_{Ao}\Theta_D$	$+(d/a)N_{Ao}X$	$N_D = N_{Ao}[\Theta_D + (d/a)X]$	$C_D = C_{A0}\left(\Theta_D + \frac{d}{a}X\right)$
I	$N_I = N_{Ao}\Theta$		$N_I = N_{Ao}\Theta_I$	C_{Io}
	$N_{To} = \Sigma N_{Ao}\Theta_i$		$N_T = N_{To} + \delta N_{Ao}X$	

Where

$$\Theta_i = N_{io}/N_{Ao} = C_{io}/C_{Ao} = y_{io}/y_{Ao}$$

$$\delta = (d/a) + (c/a) - (b/a) - 1$$

- Express table in terms of concentrations
  - Concentration (batch): $C_i = \frac{N_i}{V}$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X)$$

$$C_B = \frac{N_B}{V} = \frac{N_{A0}}{V_0}\left(\Theta_B - \frac{b}{a}X\right) = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

$$C_C = \frac{N_D}{V} = \frac{N_{A0}}{V_0}\left(\Theta_C + \frac{c}{a}X\right) = C_{A0}\left(\Theta_C + \frac{c}{a}X\right)$$

$$C_D = \frac{N_D}{V} = \frac{N_{A0}}{V_0}\left(\Theta_D + \frac{d}{a}X\right) = C_{A0}\left(\Theta_D + \frac{d}{a}X\right)$$

Mole balance equation and the rate law are coupled and then solved

Example

- **Variable Volume (Variable Density, but with Constant T and P)**

Individual concentration can be determined by expressing the volume for batch system as a function of conversion using the equation of state:

$PV = ZN_TRT$……..at any time in the reaction

$P_oV_o = Z_oN_{To}RT_o$……at any time =0;when reaction is initiated

Then,

$$V = V_0\left(\frac{N_T}{N_{T0}}\right)\left(\frac{T}{T_0}\right)\left(\frac{P_0}{P}\right)\left(\frac{Z}{Z_0}\right) \text{.....4.9}$$

Change in the total **number** *of* **moles** during reaction in gas phase reaction system, but with constant temperature and pressure, and the compressibility factor will not change significantly du**ring** the course of the reaction ,

$$V = V_0\left(\frac{N_T}{N_{T0}}\right)$$

Where $N_T = N_{To} + \delta N_{Ao}X$

$\delta = (d/a) + (c/a) - (b/a) - 1$

= (change in total number of mole) / (mole of A reacted)

$$\frac{N_T}{N_{T0}} = 1 + \frac{N_{Ao}}{N_{T0}}\delta X$$

$$y_{Ao} = \frac{N_{Ao}}{N_{T0}}$$

$$\varepsilon = \frac{N_{Ao}}{N_{T0}}\delta = y_{Ao}\delta \quad \text{.....4.10a.}$$

Then

$$\frac{N_T}{N_{T0}} = 1 + \varepsilon\ X$$

$$\varepsilon = \frac{N_T - N_{To}}{N_{T0}X} \quad \text{.....4.10b}$$

At complete conversion i.e X=1 , $N_T = N_{Tf}$; therefore ,

$$\varepsilon = \frac{N_{Tf} - N_{To}}{N_{T0}} \quad \text{.....4.11}$$

= (change in total number of mole for complete conversion) / (total moles fed)

Then the volume as a function of conversion :

$$V = V_0\left(1 + \varepsilon\ X\right) \quad \text{.....4.12}$$

Concentration at variable volume or density

Specie			
$C_A = \left(\frac{N_A}{V}\right)$	$= \frac{N_{A0}(1-X)}{V}$	$= \frac{N_{A0}(1-X)}{V_o(1+\varepsilon X)}$	$= \frac{C_{A0}(1-X)}{(1+\varepsilon X)}$
$C_B = \left(\frac{N_B}{V}\right)$	$= \frac{N_{B0}(\Theta_B - (b/a)X)}{V}$	$= \frac{N_{B0}(\Theta_B - (b/a)X)}{V_o(1+\varepsilon X)}$	$= \frac{C_{B0}(\Theta_B - (b/a)X)}{(1+\varepsilon X)}$
$C_C = \left(\frac{N_C}{V}\right)$	$= \frac{N_{Co}(\Theta_C + (c/a)X)}{V}$	$= \frac{N_{Co}(\Theta_C + (c/a)X)}{V_o(1+\varepsilon X)}$	$= \frac{C_{Co}(\Theta_C + (c/a)X)}{(1+\varepsilon X)}$
$C_D = \left(\frac{N_D}{V}\right)$	$= \frac{N_{D0}(\Theta_D - (d/a)X)}{V}$	$= \frac{N_{D0}(\Theta_D - (d/a)X)}{V_o(1+\varepsilon X)}$	$= \frac{C_{D0}(\Theta_D - (d/a)X)}{(1+\varepsilon X)}$

$C_I = \left(\frac{N_I}{V}\right)$	$= \frac{N_{Ao}\Theta_I}{V}$	$= \frac{N_{Ao}\Theta_I}{V_o(1+\varepsilon X)}$	$= \frac{C_{Ao}\Theta_I}{(1+\varepsilon X)}$

Example

Non-Isothermal Operation

Chemical reactors can liberate or absorb very large amounts of energy , and the handling of this energy is a major concern in reaction engineering. It is important to estimate the temperature increase or decrease in an adiabatic reactor in which no heat is add or removed, and exothermic reactor and also the composition of the reaction mixture at any time.

- Energy Balance

Heat Generated by Reaction + **Heat Addition and Removal by wall** = **Heat Accumulated by Reaction**

$$-\Delta H_r(T)\cdot(-r_A V) \qquad \dot{Q} = UA(T_a - T) \qquad V\sum\left(C_{p,i}C_i\frac{dT}{dt}\right)$$

T = reaction temperature K
T_a= wall temperature K
T_R= reference temperature K
A = heat transfer area m^2
Cp_i = specific heat KJ/Kmol
U = overall heat transfer KJ/s.m^2.K

ΔH_r =enthalpy change in the reaction per mole of Areacting

The number of moles of species i at any X is $= N_i = N_{A0}(\Theta_i + \upsilon_i X)$
Then energy balance is :

$$-\Delta H_r(T)\cdot(-r_A V) + UA(T_a - T) = \sum\left(C_{p,i} N_i \frac{dT}{dt}\right)$$

$$-\Delta H_r(T)\cdot(-r_A V) + UA(T_a - T) = N_{A0}\left(\sum \Theta_i C_{p,i} + \Delta CpX\right)\frac{dT}{dt}$$

…….4.13

Energy and mole balance equations with the rate law are coupled and then solved

Mole balance equation $N_{Ao}\dfrac{dX}{dt} = -r_A V$

ΔH_r **is calculated as**

$$\Delta H_r(T) = \Delta H_r^o(T_R) + \int_{T_R}^{T} \Delta C_p dT$$

The rate law is required as a function of temperature and composition

- **Variable Volume (Variable Density ,T and/or P)**

"Variable T in non-isothermal"

The volume for batch system as a function of conversion as :-

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

$$V = V_0(1+\varepsilon X)\left(\frac{T}{T_0}\right)\left(\frac{P_0}{P}\right)\left(\frac{Z}{Z_0}\right)$$

If the compressibility factor will not change significantly during the course of the reaction Z_o=Z $\quad V = V_0(1+\varepsilon X)\left(\frac{T}{T_0}\right)\left(\frac{P_0}{P}\right)$

Concentration at variable volume (density , T and/or P)

Specie

$C_A = \left(\frac{N_A}{V}\right)$	$\frac{N_{A0}(1-X)}{V}$	$\frac{N_{A0}(1-X)}{V_o(1+\varepsilon X)}\left(\frac{T_o}{T}\right)\left(\frac{P}{P_o}\right)$	$\frac{C_{A0}(1-X)}{(1+\varepsilon X)}\left(\frac{T_o}{T}\right)\left(\frac{P}{P_o}\right)$
$C_B = \left(\frac{N_B}{V}\right)$	$\frac{N_{B0}(\Theta_B - (b/a)X)}{V}$	$\frac{N_{B0}(\Theta_B - (b/a)X)}{V_o(1+\varepsilon X)}\left(\frac{T_o}{T}\right)\left(\frac{P}{P_o}\right)$	$\frac{C_{B0}(\Theta_B - (b/a)X)}{(1+\varepsilon X)}\left(\frac{T_o}{T}\right)\left(\frac{P}{P_o}\right)$
$C_C = \left(\frac{N_C}{V}\right)$	$\frac{N_{Co}(\Theta_C + (c/a)X)}{V}$	$\frac{N_{Co}(\Theta_C + (c/a)X)}{V_o(1+\varepsilon X)}\left(\frac{T_o}{T}\right)\left(\frac{P}{P_o}\right)$	$\frac{C_{Co}(\Theta_C + (c/a)X)}{(1+\varepsilon X)}\left(\frac{T_o}{T}\right)\left(\frac{P}{P_o}\right)$
$C_D = \left(\frac{N_D}{V}\right)$	$\frac{N_{D0}(\Theta_D - (d/a)X)}{V}$	$\frac{N_{D0}(\Theta_D - (d/a)X)}{V_o(1+\varepsilon X)}\left(\frac{T_o}{T}\right)\left(\frac{P}{P_o}\right)$	$\frac{C_{D0}(\Theta_D - (d/a)X)}{(1+\varepsilon X)}\left(\frac{T_o}{T}\right)\left(\frac{P}{P_o}\right)$
$C_I = \left(\frac{N_I}{V}\right)$	$\frac{N_{Ao}\Theta_I}{V}$	$\frac{N_{Ao}\Theta_I}{V_o(1+\varepsilon X)}\left(\frac{T_o}{T}\right)\left(\frac{P}{P_o}\right)$	$\frac{C_{Ao}\Theta_I}{(1+\varepsilon X)}\left(\frac{T_o}{T}\right)\left(\frac{P}{P_o}\right)$

Example

Adiabatic Operation of a Batch Reactor

A batch reactor is usually well mixed, so that may neglect the special variation in temperature and species concentration .

Batch reactors operated adiabatically are often used to determine the reaction orders, activation energies, and specific reaction rates of exothermic reactions by monitoring the temperature-time trajectories for different initial conditions.

In adiabatic operation of a batch reactor $\dot{Q} = 0$

$$-\Delta H_r(T)\cdot(-r_A V) = \sum\left(C_{p,i}N_i\right)\frac{dT}{dt}$$

$$-\Delta H_r(T)\cdot(-r_A V) = N_{A0}\left(\sum\Theta_i C_{p,i} + \Delta CpX\right)\frac{dT}{dt}$$

…….4.14

Energy and mole balance equations with the rate law are coupled and then solved:

$$X = \frac{\sum \Theta_i C_{p,i}(T - T_o)}{-\Delta H_r(T)}$$

$$T = T_o + \frac{-\Delta H_r(T)X}{\sum \Theta_i C_{p,i} + \Delta CpX}$$

;Where T_o = initial temperature

Example

Equilibrium Conversion

The highest conversion that can be **achieved** in reversible **reactions is** the **equilibrium** conversion X_{EB}. For endothermic reactions, the **equilibrium conversion** increases **with increasing temperature up** to a **maximum** of 1.0. For exothermic reactions, the **equilibrium** conversion decreases with increasing **temperature**

Figure ( ) show the variation of the concentration equilibrium constant as a function of temperature for an exothermic reaction the corresponding equilibrium conversion X_{EB} as a function of temperature.

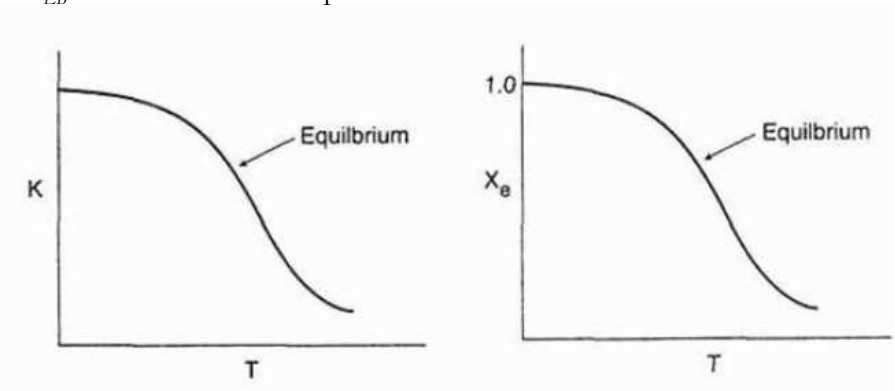
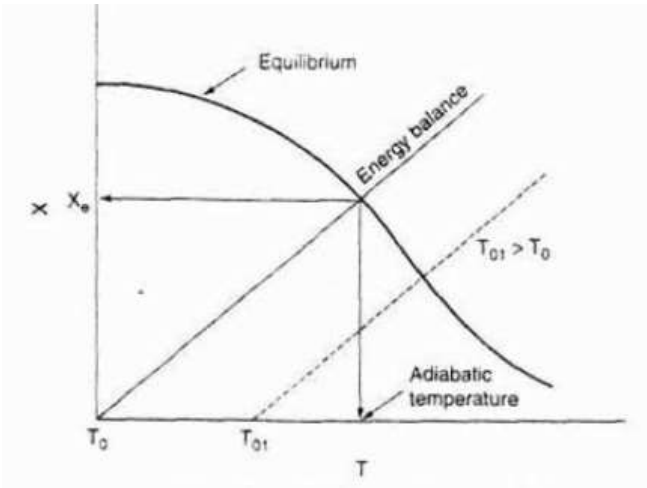


Figure ( ) show the variation of the concentration equilibrium constant and equilibrium conversion as a function of temperature for an exothermic reaction.

To determine the maximum conversion that can be achieved in an exothermic reaction carried out adiabatically, we find the intersection of the equilibrium conversion as a function of temperature ,with temperature –conversion relationships from the energy balance

$$X_{EB} = \frac{\sum \Theta_i C_{p,i}(T - T_o)}{-\Delta H_r(T)} \quad \text{……..4.15}$$



Graphical solution of equilibriurn and energy balance equations to obtain the adiabatic temperature

and the adiabatic equilibriurn

conversion X_{EB}.

Example