

## Summary

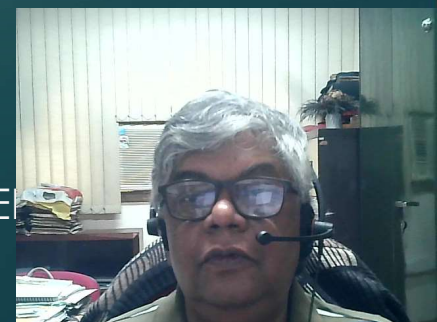
- Chemical industries involve at least one chemical reaction → chemical reactions take place in a REACTOR
- Mole/Species Balances in different reactors
- Basics of Reactor Design – design equation
- Definition of conversion for: (i) Batch and Flow systems, and (ii) single and multiple reactors
- Design equations in terms of conversion
- Levenspiel plots for single and multiple reactors

## Lecture # 4.1 CHE331A

For teaching purposes only



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# Reaction rates revisited

The rate is

- a function of temp, press, conc and type of catalyst (if used)
- an algebraic equation, e.g.,  $r_j = -k_i \cdot C_i C_j^2$ , this is called the rate law
  - Other forms of the equation are possible
- not a differential equation, e.g., rate is not  $\frac{dC_A}{dt}$ 
  - $\frac{dC_A}{dt} = -r_A$  used to calculate the rate for certain conditions
- Knowing the rate law is important in the design equation
  - The rate in terms of conversion,  $r = f(C) = g(X)$  can be used to size reactors



# Basic definitions in reactions and reaction rate laws

## ► Homogeneous reactions, $CH_3CHO (A) \rightarrow CH_4 + CO$

- Involves only one phase,  $-r_A = k_A \cdot C_A^{3/2}$

## ► Heterogeneous reactions, $Cumene(C) \rightarrow Benzene(B) + propene(P)$

- More than 1-phase, reaction often occurs at the interface,

$$-r_A = \frac{k \cdot C_C}{1 + K_B C_B + K_C C_C}$$

## ► Irreversible reactions, $A + B \rightarrow P$

- Occurs in one direction only till reactants are exhausted

## ► Reversible reactions, $A + B \rightleftharpoons P1 + P2$

- Proceeds in either direction depending on the conc of reactants and products relative to equilibrium conc



# Some more basics about reactions

## ► Molecularity of a reaction

- number of atoms, ions or molecules involved (colliding) in a reactions step
- Unimolecular, Bimolecular etc

## ► Reaction Order, $2A + B \rightarrow P$ , $-r_A = k_A \cdot C_A^\alpha \cdot C_B^\beta$ , order of A, B, & overall

- Refers to the power to which the conc are raised in the rate law

## ► Elementary reactions, $O^* + CH_3OH \rightarrow CH_3O^* + OH^*$

- Are those that involve a single step,  $-r_{O^*} = k \cdot C_{O^*} \cdot C_{CH_3OH}$

## ► Reactions following an elementary rate law, $2NO + O_2 \rightarrow 2NO_2$

- Reaction order agrees with the stoichio. coeff.,  $-r_A = k_A \cdot C_{NO}^2 \cdot C_{O_2}$





# Rate laws can be non-elementary

- ▶ For reaction:  $2A + B \rightarrow 3C$
- ▶ Reaction follows non-elementary rate law:  $-r_A = k_A \cdot C_A^2$ 
  - 2<sup>nd</sup> order in A
  - Zero order in B
  - Overall order 2
- ▶ Also,  $-r_B = k_B \cdot C_A^2$  and  $r_C = k_C \cdot C_A^2$
- ▶ The relationship between  $k_A, k_B$  and  $k_C$  is obtained from
$$\frac{r_A}{-2} = \frac{r_B}{-1} = \frac{r_C}{3}$$
- ▶ Thus,  $k_A = 2 \cdot k_B = \frac{2}{3} k_C$



# Reaction rate for each species is related by stoichiometry

- ▶ For a reaction, where A reacts with B with a stoichiometric of



- ▶ The rates of disappearance and formation of species is given by

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d} \quad \text{also} \quad \frac{\Delta n_A}{-a} = \frac{\Delta n_B}{-b} = \frac{\Delta n_C}{c} = \frac{\Delta n_D}{d} = d\epsilon$$

- ▶ For a rate law such as  $-r_A = k_A \cdot C_A^a \cdot C_B^b$

- Temperature effect of the reaction rate is given by  $k_A$  (rate constant)
- Temperature and concentration terms can be separated

- ▶ For a rate law such as  $-r_A = \frac{k_A \cdot C_A}{1 + K_B C_B + K_C C_C}$

- Temperature effects given by  $k_A$  and  $K_B$  or  $K_C$  (equilibrium constant)
- Temperature and concentration terms cannot be separated



**For gas-solid catalyzed reactions the rate is often given in terms of partial pressures**

► For example,  $C_6H_5CH_3(T) + H_2 \xrightarrow{\text{Catalyst}} C_6H_6(B) + CH_4$

► The rate of toluene disappearance is given by 
$$-r'_T = \frac{kP_{H_2}P_T}{1+K_BP_B+K_TP_T}$$

► Where,  $k$  is the rate constant having units of  $\frac{\text{moles of toluene}}{(\text{kg-cat}).(\text{s}).(\text{kPa})^2}$  and

►  $K_B$  and  $K_T$  are equilibrium (adsorption) constants, with units of  $(\text{kPa})^{-1}$



# For reversible reactions, rate eq<sup>n</sup> must include backward/reverse rate

- ▶ At equilibrium the rate of reaction is equal to zero for all species
- ▶ For  $aA + bB \rightleftharpoons cC + dD$  at equilibrium the conc. of the species are related by the equilibrium constant 
$$K_C = \frac{C_{Ce}^c C_{De}^d}{C_{Ae}^a C_{Be}^b}$$
- ▶ To write the rate law for a reversible elementary reaction consider  $A + 2B \rightleftharpoons 3C$  having: forward rate constant of  $k_A$  and backward rate constant of  $k_{-A}$
- ▶ Net rate of disappearance of A is given by  $-r_A = k_A \cdot C_A C_B^2 - k_{-A} C_C^3$





# Rate eq<sup>n</sup> must reduce to equilibrium relations

- ▶ Net rate of disappearance of A for  $A + 2B \rightleftharpoons 3C$  is given by

$$-r_A = k_A \cdot C_A C_B^2 - k_{-A} C_C^3 = k_A \cdot \left[ C_A C_B^2 - \frac{C_C^3}{k_A/k_{-A}} \right]$$

$$-r_A = k_A \left[ C_A C_B^2 - \frac{C_C^3}{K_e} \right]$$

- ▶  $K_e = k_A/k_{-A}$  and at equilibrium  $C_A = C_{Ae}$ ;  $C_B = C_{Be}$ ;  $C_C = C_{Ce}$

- ▶ Furthermore,  $r_A = 0$  and so are  $r_B$  and  $r_C$

- Thus,  $K_e = \frac{C_{Ce}^3}{C_{Ae} C_{Be}^2} \rightarrow$  equilibrium constant in terms of concentration for  
reaction  $A + 2B \rightleftharpoons 3C$  Relationship between  $k_A$  &  $k_B$ ?

