University of Anbar

College of Engineering

Chemical and Petrochemical Engineering Department

Chemical Reacior Design

Third Year

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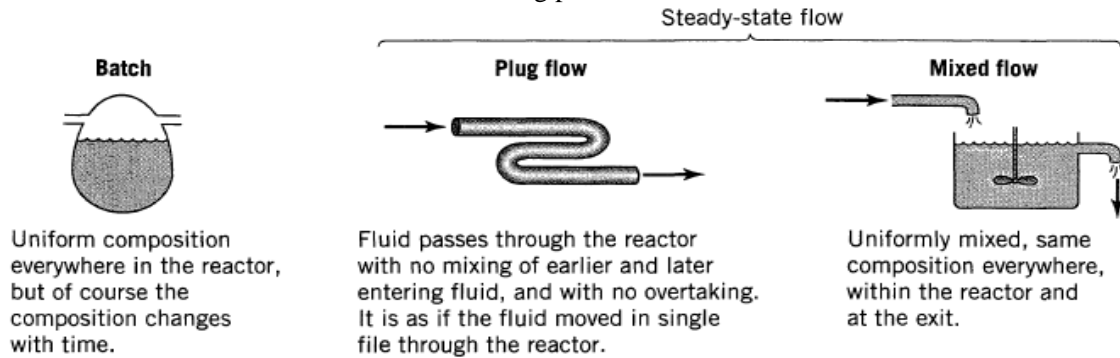# Lecture No. 2:

Kinetics of Homogeneous Reactions:

Simple Reactor Types:

Ideal reactors have three ideal flow or contacting patterns

Steady-state flow

Batch

Plug flow

Mixed flow

Uniform composition everywhere in the reactor, but of course the composition changes with time.

Fluid passes through the reactor with no mixing of earlier and later entering fluid, and with no overtaking. It is as if the fluid moved in single file through the reactor.

Uniformly mixed, same composition everywhere, within the reactor and at the exit.

Figure 2.1 Ideal reactor types.

The Rate Equation:

Suppose a single-phase reaction $aA + bB \rightarrow rR + sS$. The most useful measure of reaction rate for reactant A is then

rate of disappearance of A

$$-r_A = \frac{1}{V}\frac{dN_A}{dt} = \frac{(\text{amount of A disappearing})}{(\text{volume})\,(\text{time})}, \quad \left[\frac{\text{mol}}{\text{m}^3 \cdot \text{s}}\right] \quad (1)$$

note that this is an intensive measure

the minus sign means disappearance

In addition, the rates of reaction of all materials are related by

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_R}{r} = \frac{r_S}{s}$$

Experience shows that the rate of reaction is influenced by the composition and the energy of the material. By energy we mean the temperature (random kinetic energy of the molecules), the light intensity within the system (this may affect

the bond energy between atoms), the magnetic field intensity, etc. Ordinarily we only need to consider the temperature, so let us focus on this factor. Thus, we can write

$$
\left(\frac{mol}{m^3 \cdot s}\right) \quad -r_A = f \begin{bmatrix} \text{temperature} & \text{concentration} \\ \text{dependent} & , & \text{dependent} \\ \text{terms} & \text{terms} \end{bmatrix} \xrightarrow[\text{example}]{\text{as an}} kC_A^a = k_0 e^{-E/RT} C_A^a \tag{2}
$$

$\left(\frac{mol}{m^3}\right)^{1-a} s^{-1}$

activation energy

reaction order

temperature dependent term
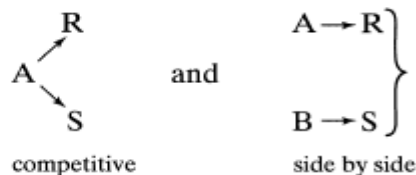
Single and Multiple Reactions:

When a single stoichiometric equation and single rate equation are chosen to represent the progress of the reaction, we have a *single reaction*. When more than one stoichiometric equation is chosen to represent the observed changes, then more than one kinetic expression is needed to follow the changing composition of all the reaction components, and we have *multiple reactions*.
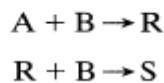**Multiple reactions may be classified as:**

series reactions,

$$A \rightarrow R \rightarrow S$$

parallel reactions, which are of two types

$$
\begin{array}{cc}
A \begin{array}{c} \nearrow R \\ \searrow S \end{array} & \text{and} \quad \left.\begin{array}{c} A \rightarrow R \\ B \rightarrow S \end{array}\right\}
\end{array}
$$

competitive   side by side

and more complicated schemes, an example of which is

$$A + B \rightarrow R$$
$$R + B \rightarrow S$$

Here, reaction proceeds in parallel with respect to B, but in series with respect to A, *R,* and **S.**

Elementary and Nonelementary Reactions:
Such reactions in which the rate equation corresponds to a stoichiometric equation are called *elementary reactions.*

$$A + B \rightarrow R \quad \Longrightarrow \quad -r_A = kC_A C_B$$

When there is no direct correspondence between stoichiometry and rate, then we have *nonelementary reactions.*

$$H_2 + Br_2 \rightarrow 2HBr$$

$$r_{HBr} = \frac{k_1[H_2][Br_2]^{1/2}}{k_2 + [HBr]/[Br_2]} \qquad (3)$$
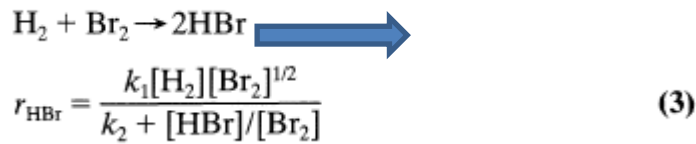
Molecularity and Order of Reaction:

The molecularity of an elementary reaction is the number of molecules involved in the reaction, and this has been found to have the values of one, two, or occasionally three. Note that the molecularity refers only to an elementary reaction.

Often we find that the rate of progress of a reaction, involving, say, materials A, B, . . . , D, can be approximated by an expression of the following type:

$$-r_A = kC_A^a C_B^b \ldots C_D^d, \qquad a + b + \cdots + d = n \qquad (4)$$

We call the powers to which the concentrations are raised the order of the reaction. Thus, the reaction is

ath order with respect to A
bth order with respect to B
nth order overall

$$A \rightarrow \text{products}$$

Order	Rate Equation	Units
Zero	$-r_A = k$	$mol.V^{-1}.s^{-1}$
First	$-r_A = kC_A$	s^{-1}
Second	$-r_A = kC_A^2$	$V.mol^{-1}.s^{-1}$
Third	$-r_A = kC_A^3$	$(V.mol^{-1})2.s^{-1}$
nth order	$-r_A = kC_A^n$	$(concentration)^{1-n}.s^{-1}$

Rate Constant k:

When the rate expression for a homogeneous chemical reaction is written in the form of Eq. 4, the dimensions of the rate constant k for the nth-order reaction are

$$(\text{time})^{-1}(\text{concentration})^{1-n} \qquad (5)$$

which for a first-order reaction becomes simply

$$(\text{time})^{-1} \qquad (6)$$