Al-Mustaqbal University College
Chem. Eng. Petr. Ind. Dept.

3rd stage

Lecture 1

Introduction to chemical reaction kinetics

Rates of Reaction and Rate Law

CHEMICAL REACTION KINETICS

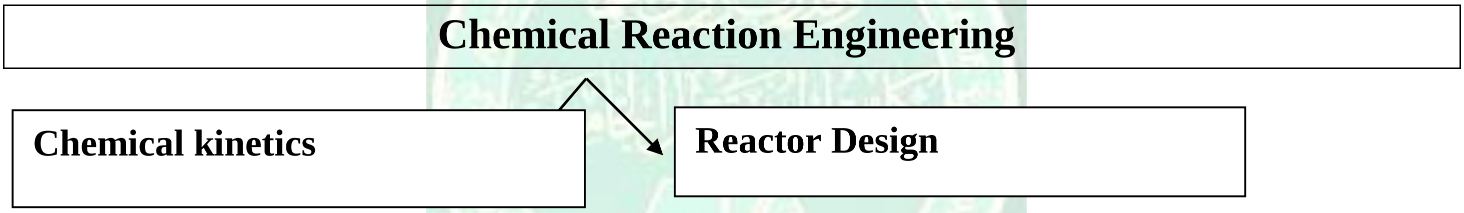
Chapter one: Introduction to chemical reaction kinetics

Chemical kinetics deals with: -

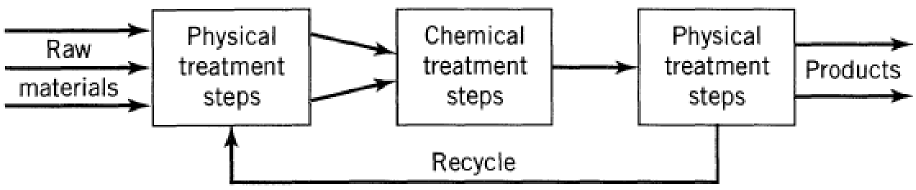
– how fast or slow chemical reactions proceed (occur), i.e. reaction rate,

– what chemical reactions occurs in a chemical process, i.e. reaction mechanisms (reaction mechanisms that cause reactions to occur).

The study of chemical reaction engineering (CRE) combines the study of chemical kinetics with the reactors in which the reactions occur. Chemical kinetics and reactor design are at the heart of producing almost all industrial chemicals.



It is primarily the knowledge of chemical kinetics and reactor design that distinguishes the chemical engineer from other engineers. The selection of a reaction system that operates in the safest and most efficient manner can be the key to the economic success or failure of n chemical plant. Reactor design uses information, knowledge, and experience from a variety of areas-thermodynamics, chemical kinetics, fluid mechanics, heat transfer, mass transfer, and economics. A typical chemical process is shown below:



Chemical reaction engineering is the synthesis of all these factors with the aim of properly designing a chemical reactor.
To find what a reactor is able to do we need to know the kinetics, the contacting pattern and the performance equation.
We show this schematically in Figure (1).

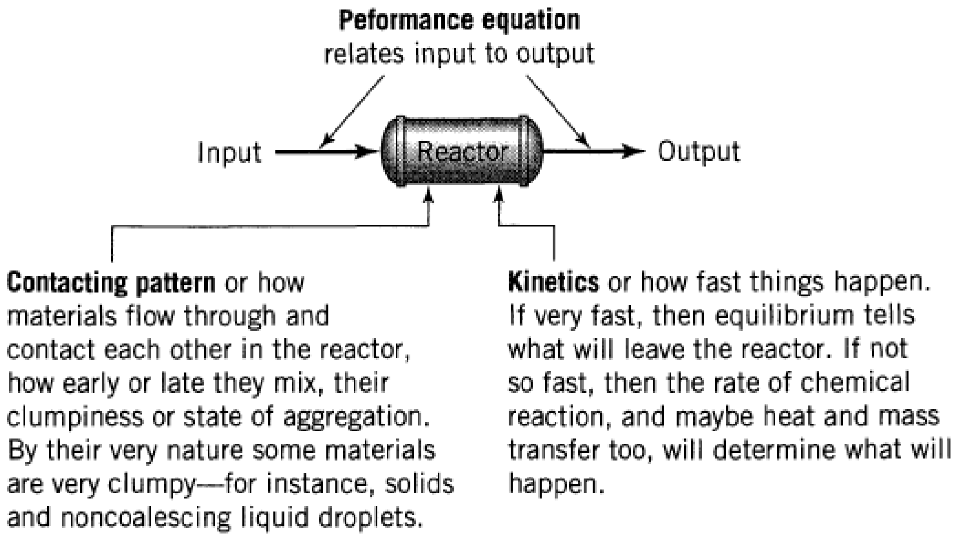


Figure (1). Information needed to predict what a reactor can do.

Much of this lectures deals with finding the expression to relate input to output for various kinetics and various contacting patterns, or

<u>Performance equation</u>

Output = f [input, kinetics, contacting] ……………… (1)

o ***Homogeneous reaction*** **:** it takes place in one phase alone.
o ***Heterogeneous reaction*** : multiple phases, reaction usually occurs at the interface between phases.
Some of the reactions are irreversible as they proceed in only one direction and continue in that direction until the reactants are exhausted, like

Homogeneous reaction

Decomposition N_2O $N_2O\,(g) + 2O_2(g) \rightarrow 2\,N_2(g) + O_2(g)$

Water gas shift reaction $H_2O\,(g) + CO\,(g) \rightarrow H_2(g) + CO_2(g)$

or reversible which can proceed in either direction, depending on the concentrations of reactants and products present relative to the corresponding equilibrium concentration such as ammonia synthesis

Rates of Reaction and Rate Law

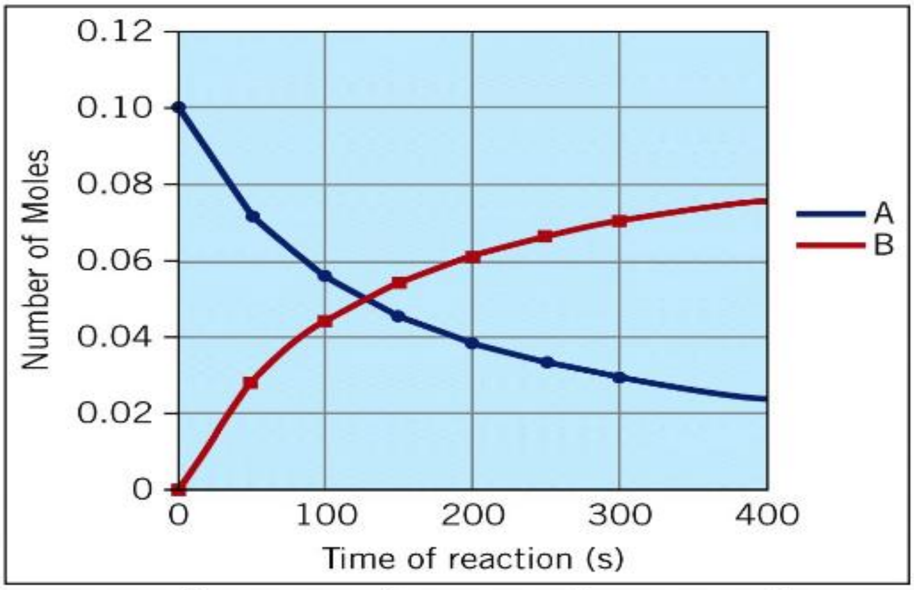
The rate of a chemical reaction is the rate at which reactants are used up, or equivalently the rate at which products are formed. The rate therefore has the units of concentration per unit time, (for gas phase reactions, alternative units of concentration are often used, usually units of pressure – Torr, mbar or Pa).

In homogeneous reactions, the reaction rate **(r_A)** is defined as the change in moles of component A (reactant consumed) or mole of product formed with respect to time per unit volume of the reaction mixture.

In solid-catalyzed reactions (heterogeneous reaction), the reaction rate **(r_A')** is defined as the change in moles of component A with respect to time **per** unit reaction surface area or catalyst weight.

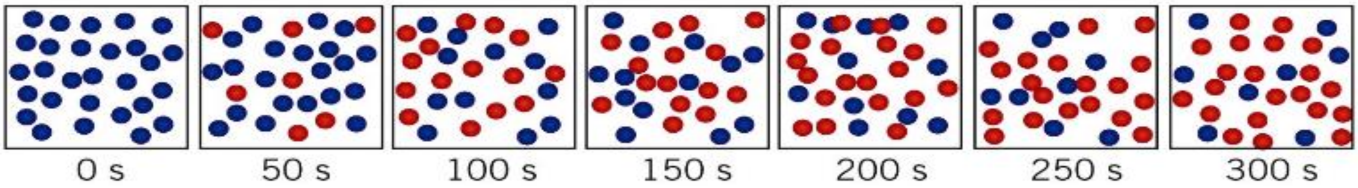
Consider the reaction :

$$A \longrightarrow B$$



Reaction rate is measured by the amount of product produced or reactants consumed per unit time.

- [B] concentration of products will increase over time
- [A] concentration of reactants will decrease over



Factors Affecting Reaction Rates

1- Concentration of the reactants	**When the reactant concentration increases, the reactionrat e increases.**

2- Temperature

- Faster molecules collide more often and collisions have more energy
- Most reactions, even exothermic reactions, require energy to occur

3- Pressure

When the gaseous reactant pressure increases, more reactant is compress ed into a given volume (i.e. the react ant concentration reactant concentration increases), th e reaction rate increases.

4- Presence of Catalysts

- increase rates of chemical reactions without being used up

-Rate-accelerating agents

-Not consumed in the reaction

5. Chemical nature of the reactants

-What are the chemical properti es of the reactants.

-Do the reactants have strong b onds or weak bonds?

-What about the number of bon ds that need to be broken and reformed?

6- Physical State of the Reactants

-Surface area consideration,The greater the surface area, the greater the ability the reactants can meet, and therefore, the greater the reaction rate.

-Phase consideration , Homogeneous or Heterogeneous reaction

$$\text{Rate of Reaction} = \frac{\textit{mole of}\ \text{disappear or formation}}{\textit{volume} \times \textit{time}}$$

$$\text{Rate of Reaction r} = \frac{\Delta\,[\textit{Concentation}]}{\Delta\,\textit{time}}$$

$$\text{Rate of reaction} = \frac{X_{t2} - X_{t1}}{t_2 - t_1}$$

$$= \frac{mol/\text{l}}{s}$$

Definition of Reaction Rate

We next ask how to define the rate of reaction in meaningful and useful ways. To answer this, let us adopt a number of definitions;

Based on unit volume of reacting fluid,

$$r_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of fluid})\,(\text{time})} \tag{2}$$

Based on unit mass of solid in fluid-solid systems,

$$r_i' = \frac{1}{W}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{mass of solid})\,(\text{time})} \tag{3}$$

Based on unit interfacial surface in two-fluid systems or based on unit surface of solid in gas-solid systems,

$$r_i'' = \frac{1}{S}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{surface})\,(\text{time})} \tag{4}$$

Based on unit volume of solid in gas-solid systems

$$r_i''' = \frac{1}{V_s}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of solid})\,(\text{time})} \tag{5}$$

Based on unit volume of reactor, if different from the rate based on unit volume of fluid,

$$r_i'''' = \frac{1}{V_r}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of reactor})\,(\text{time})} \tag{6}$$

In homogeneous systems the **volume of fluid** in the reactor is often identical to the **volume of reactor**. In such a case V and Vr are identical and Eqs. 2 and 6 are used interchangeably. In heterogeneous systems all the above definitions of reaction rate are encountered, the definition used in any particular situation often being a matter of convenience.

$$\begin{pmatrix}\text{volume}\\ \text{of fluid}\end{pmatrix} r_i = \begin{pmatrix}\text{mass of}\\ \text{solid}\end{pmatrix} r_i' = \begin{pmatrix}\text{surface}\\ \text{of solid}\end{pmatrix} r_i'' = \begin{pmatrix}\text{volume}\\ \text{of solid}\end{pmatrix} r_i''' = \begin{pmatrix}\text{volume}\\ \text{of reactor}\end{pmatrix} r_i''''$$

or

$$V r_i = W r_i' = S r_i'' = V_s r_i''' = V_r r_i'''' \tag{7}$$