Al-Mustaqbal University College
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Chemical Reaction Kinetics
3rd Stage

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Lecture 3

Stoichiometry for a batch system of constant volume

In formulating our stoichiometric table we shall take species A 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 "per mole of A."

Next, we develop the stoichiometric relationships for reacting species that give the change in the number of moles of each species (i.e., A, B, C, and D).

At time t = 0 we will open the reactor and place a number of moles of species A, B, C, D, and I (Inert)$(N_{Ao}, N_{Bo}, N_{Co}, N_{Do}$ and N_I respectively) into the reactor.

Species A is our basis of calculation and N_{Ao} is the number of moles of A initially present in the reactor. Of these, $N_{Ao} X$ moles of A are consumed in the system as a result of the chemical reaction, leaving $(N_{Ao} - N_{Ao} X)$ moles of A in the system. That is, the number of moles of A remaining in *the* reactor after conversion *X* has been achieved is

$N_A = N_{Ao} - N_{Ao} X = N_{Ao} (1-X)$,

$$C_A = \frac{N_{Ao}\ (1-X)}{V_O} = C_{Ao}(1 - X)$$

Let $M_i = C_i / C_{AO}$

$$C_B = \frac{N_{AO}\left[M_B - \left(\frac{b}{a}\right)X\right]}{V_O} = C_{Ao}\left[M_B - \left(\frac{b}{a}\right)X\right]$$

$$C_c = \frac{N_{AO}\left[M_C - \left(\frac{c}{a}\right)X\right]}{V_O} = C_{Ao}\left[M_C + \left(\frac{c}{a}\right)X\right]$$

$$C_D = \frac{N_{AO}\left[M_D - \left(\frac{d}{a}\right)X\right]}{V_O} = C_{Ao}\left[M_D + \left(\frac{d}{a}\right)X\right]$$

The complete stoichiometric table for the reaction shown taking place in a batch reactor is presented in Table ;

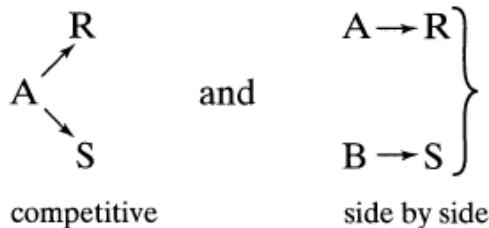| Species	Initial moles	Change(reacted or Produced, mol)	Remaining mol
A	N_{Ao}	$- N_{Ao} X$	$N_A = N_{Ao} - N_{Ao} X$
B	N_{Bo}	$- (b/a) N_{Ao} X$	$N_B = N_{Bo} - (b/a)N_{Ao} X$ $= N_{AO} \left[M_B - \left(\frac{b}{a}\right) X \right]$
C	N_{Co}	$(c/a) N_{Ao} X$	$N_C = N_{Co} + (c/a)N_{Ao} X$ $= N_{AO} \left[M_C + \left(\frac{c}{a}\right) X \right]$
D	N_{Do}	$(d/a) N_{Ao} X$	$N_D = N_{Do} + (d/a)N_{Ao} X$ $= N_{AO} \left[M_D + \left(\frac{d}{a}\right) X \right]$
I (inerts)	N_{Io}	------------------	$N_I = N_{Io}$
Total	N_{To}		$N_T = N_{To} + [(d/a)+(c/a) - (b/a) -1]N_{Ao} X$

Single and Multiple Reactions

First of all, when materials react to form products it is usually easy to decide after examining the stoichiometry, preferably at more than one temperature, whether we should consider a single reaction or a number of reactions to be occurring.

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
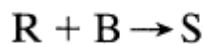
Multiple reactions may be classified as: *series reactions,*

$$A \rightarrow R \rightarrow S$$

parallel reactions, which are of two types

$$A \overset{\nearrow R}{\searrow S} \qquad \text{and} \qquad \left.\begin{array}{l} A \rightarrow R \\ B \rightarrow S \end{array}\right\}$$

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

Consider a single reaction with stoichiometric equation

$$A + B \rightarrow R$$ If we postulate that the rate-controlling mechanism involves the collision or interaction of a single molecule of A with a single molecule of B, then the number of collisions of molecules A with B is proportional to the rate of reaction. But at a given temperature the number of collisions is proportional to the concentration of reactants in the mixture; hence, the rate of disappearance of A is given by

$$-r_A = kC_A C_B$$

Such reactions in which the rate equation corresponds to a stoichiometric equation are called **elementary** reactions. When there is no direct correspondence between stoichiometry and rate,

then we have **nonelementary** reactions. The classical example of a nonelementary reaction is that between hydrogen and bromine,

$$H_2 + Br_2 \rightarrow 2HBr$$
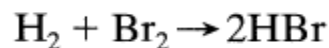
which has a rate expression*

$$r_{HBr} = \frac{k_1[H_2][Br_2]^{1/2}}{k_2 + [HBr]/[Br_2]}$$

- ## Molecularity and order of the 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:

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

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where a, b, . . . , d are not necessarily related to the stoichiometric coefficients. We call the powers to which the concentrations are raised the order of the reaction. Thus, the reaction is**;**

  *a*th order with respect to A

  *b*th order with respect to B

  *n*th order overall

Since the order refers to the empirically found rate expression, it can have a fractional value and need not be an integer. However, the molecularity of a reaction must be an integer because it refers to the mechanism of the reaction, and can only apply to an elementary reaction.

The term *molecularity* refers to number of atoms, ions, or molecules involved in the rate-limiting step of the reaction.

Unimolecular – one reactant involved in reaction
Bimolecular – two reactants must collide to react
Trimolecular – three reactants must interact for reaction to occur

Concentration – Dependent Term of a Reaction Rate Law

Before we can find the form of the concentration term in a rate expression, we must distinguish between different types of reactions. This distinction is based on the form and number of kinetic equations used to describe the progress of reaction. Also, since we are concerned with the concentration-dependent term of the rate equation, we hold the temperature of the system constant.

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

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

-rA=k C_A^n

$$k = \frac{(Concentration)^{1-n}}{Time} \, or$$

For the nth order of reaction mol/vol.s =k. (mol/vol)^n

k=(s^{-1}) (mol/vol)$^{1-n}$

which for a first-order reaction becomes simply

$$(time)^{-1}$$

Representation of an Elementary Reaction

In expressing a rate we may use any measure equivalent to concentration (for example, partial pressure), in which case

$$r_A = kp_A^a p_B^b \ . \ . \ . p_D^d$$

Whatever measure we use leaves the order unchanged; however, it will affect the rate constant k.
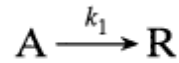
For brevity, elementary reactions are often represented by an equation showing both the molecularity and the rate constant. For example,

$$2A \xrightarrow{k_1} 2R$$
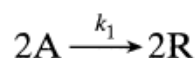
represents a biomolecular irreversible reaction with second-order rate constant k_1, implying that the rate of reaction is

$$-r_A = r_R = k_1 C_A^2$$

It would not be proper to write the equation as

$$A \xrightarrow{k_1} R$$

for this would imply that the rate expression is

$$-r_A = r_R = k_1 C_A$$

Thus, we must be careful to distinguish between the one particular equation that represents the elementary reaction and the many possible representations of the stoichiometry.

For example, consider the reaction,

$$B + 2D \rightarrow 3T$$

If the rate is measured in terms of B, the rate equation is

$$-r_B = k_B C_B C_D^2$$

If it refers to D, the rate equation is

$$-r_D = k_D C_B C_D^2$$

Or if it refers to the product T, then
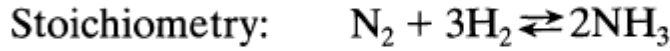
$$r_T = k_T C_B C_D^2$$

But from the stoichiometry

$$-r_B = -\frac{1}{2} r_D = \frac{1}{3} r_T$$

hence,

$$k_B = \frac{1}{2} k_D = \frac{1}{3} k_T$$

Representation of a Nonelementary Reaction

A nonelementary reaction is one whose stoichiometry does not match its kinetics. For example,

$$\text{Stoichiometry:} \quad N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$\text{Rate:} \quad r_{NH_3} = k_1 \frac{[N_2][H_2]^{3/2}}{[NH_3]^2} - k_2 \frac{[NH_3]}{[H_2]^{3/2}}$$

This nonmatch shows that we must try to develop a multistep reaction model to explain the kinetics.

o Do not follow law of mass action(is the proposition that the rate of a chemical reaction is directly proportional to the product of the activities or concentrations of the reactants.
o proceeds in more than one step.
o Involves the appearance of intermediates.

Intermediates cannot be observed as they are highly reactive and present in minute quantities, intermediates could be:
- Free radicals: CH_3^*, $C_2H_5^*$ etc.
- Ions & Polar substances: Na^+, OH^-, NH_4^+
- Highly reactive molecules: $A \rightarrow R \rightarrow S$
- Transition State Complexes

Homogeneous Reactions :
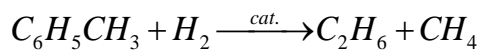
Gas phase synthesis of phosgene

$$CO + Cl_2 \longrightarrow COCl_2$$
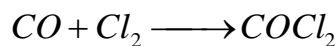
$$-r_{CO} = k_{CO} C_{CO} C_{Cl_2}^{3/2}$$

Heterogeneous Reactions :Gas-solid catalyzed: Hydrodemethylation of toluene (T) , form benzene (B) and methane (M)

$$C_6H_5CH_3 + H_2 \xrightarrow{cat.} C_2H_6 + CH_4$$

$$-r_T' = \frac{k\, P_{H_2} P_T}{1 + K_B P_P + K_T P_T}$$

$$k = \frac{mol\ toluene}{kg_{cat}.s.kPa^2}$$