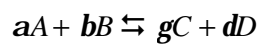


Lecture No: 4

CHEMICAL KINETICS

Chemical Kinetics deals with the stage of the reaction, in which its properties change with time. The time dependence of a chemical reaction is described in terms of the rate of reaction.

1. Rate of Reaction



The rate of reaction is defined as the rate of change of its degree of extent per unit volume with respect to time. The general equation for the rate of reaction is;

$$r = \frac{1}{V} \frac{dx}{dt}$$

The rate of reaction may be written in a more convenient form for calculation. At any time t , the number of moles of each of the substances involving in the reaction may be written as;

$$\begin{aligned} n_A &= n_{oA} - ax & n_C &= n_{oC} + gx \\ n_B &= n_{oB} - bx & n_D &= n_{oD} + dx \end{aligned}$$

Taking the derivative with respect to time, we obtain;

$$\begin{aligned} \frac{dn_A}{dt} &= -a \frac{dx}{dt} & \frac{dn_C}{dt} &= g \frac{dx}{dt} \\ \frac{dn_B}{dt} &= -b \frac{dx}{dt} & \frac{dn_D}{dt} &= d \frac{dx}{dt} \end{aligned}$$

Solving the above equations for dx/dt and substituting the resulting expressions in the general rate equation, we obtain;

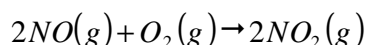
$$r = -\frac{1}{a} \frac{1}{V} \frac{dn_A}{dt} = -\frac{1}{b} \frac{1}{V} \frac{dn_B}{dt} = \frac{1}{g} \frac{1}{V} \frac{dn_C}{dt} = \frac{1}{d} \frac{1}{V} \frac{dn_D}{dt}$$

dn/V is the change in the concentration. In chemical kinetics all the concentration terms are written as $[A]$, $[B]$,....., the symbol of the substance in square brackets.

$$r = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{g} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

The rate of reaction may be expressed in terms of the change of concentration of any of the substances involved in the reaction. In order to write the rate expression, we need a balanced equation for the reaction. The rate is equal to the product of the concentration change of the substance with time and the reciprocal of its stoichiometric coefficient. We use a minus sign for the reactants, while for the products we use a plus sign. So, all the quantities in the above expression are positive.

For example; the rate of reaction for;



may be written as;

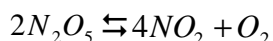
$$r = -\frac{1}{2} \frac{d[NO]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2} \frac{d[NO_2]}{dt}$$

The rate of reaction depends upon the temperature, pressure, the concentrations of the substances and the catalyst.

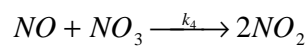
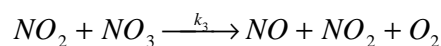
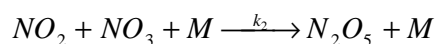
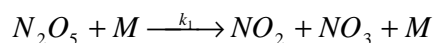
2. Special Terms

- **Homogeneous Kinetics** : Deals with the reactions which occur entirely in one phase.
- **Heterogeneous Kinetics** : Deals with the reactions which occur in more than one phase.
- **Elementary Reactions** : Reactions which take place in a single step as shown by the balanced chemical equation.

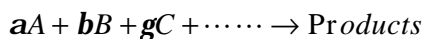
- **Complex Reactions** : Reactions which take place in more than one step. In this case, the balanced chemical equation shows the overall change.
- **Mechanism** : is the sequence of elementary steps that add up to give the overall reaction. For example; the decomposition of N_2O_5 is a complex reaction.



The mechanism for this reaction consists of four elementary reactions;



- **Rate Determining Step**: is the slowest step of the mechanism.
- **Molecularity** : is the number of reactant molecules in an elementary step or in the rate determining step of the mechanism for a complex reaction. Thus, elementary reactions are referred to as unimolecular, bimolecular, trimolecular depending upon whether one, two or three molecules are involved as reactants.
- **Rate Laws** : The concentration dependence of the rate of reaction is expressed with relationships called rate laws. The rate law of a chemical reaction



is of the form ;

$$r = k[A]^a[B]^b[C]^c$$

where;

- $[A]$, $[B]$ and $[C]$ are the concentrations of the various reactants
- a , b and c are the exponents, the powers of the concentrations
- The exponents are called "orders". a is the order of the reaction with respect to A , b is the order with respect to B etc.
- The overall order of the reaction is " $a+b+c$ ".
- " k " in the above expression is the rate constant or specific rate of the reaction. k is the rate if all the concentrations were unity.
- a , b and c are not the stoichiometric coefficients. They are determined experimentally. Only for elementary reactions, the orders are equal to the stoichiometric coefficients.
- The order is not necessarily an integer. It may be a fraction.

3. First-Order Reactions

If the rate of a chemical reaction depends on the concentration of only one reactant, the reaction is a first-order reaction. Consider a reaction of the type;



Suppose that the reaction is first-order with respect to A . Then, the rate law or the differential rate equation may be written as;

$$r = -\frac{d[A]}{dt} = k[A]$$

Rearranging and integrating, we obtain;

$$\ln[A] = -kt + \text{Constant}$$

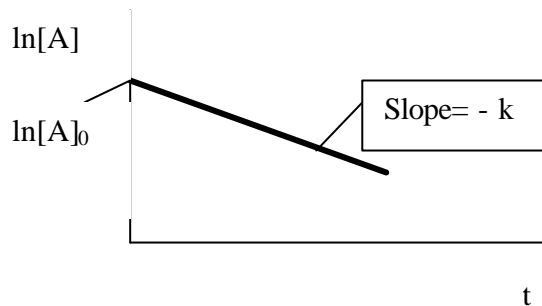
If the concentration of A is $[A]_0$ at time $t=0$, and $[A]$ at time t , the integral constant is;

$$\text{Constant} = \ln[A]_0$$

Then the integral rate equation may be written as;

$$\ln[A] = -kt + \ln[A]_0$$

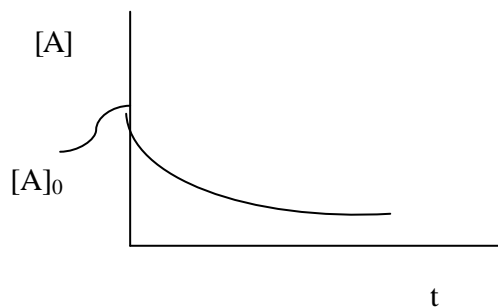
This equation shows that a plot of $\ln[A]$ versus t will yield a straight line with a slope $-k$ and an intercept $\ln[A]_0$



We may express the rate equation in a different way;

$$[A] = [A]_0 e^{-kt}$$

This equation shows that A decays exponentially with time from its initial value $[A]_0$



The **half-life** $t_{1/2}$ of a reaction is the time required for the concentration of the reactant to reach one half of its initial value, for half of the reactant to disappear. When $t = t_{1/2}$ $[A] = [A]_0 / 2$, then for a first-order reaction;

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

For a first-order reaction, the half-life is independent of the initial concentration. 50% of the compound remains after one half-life, 25% after two half-lives and so on.

4. ~~Second-Order~~ Reactions

A reaction is second order, if the rate is proportional to the square of the concentration of one reactant or is proportional to the product of the concentrations of two reactants.

- If the rate is proportional to the square of the concentration of A in the reaction;



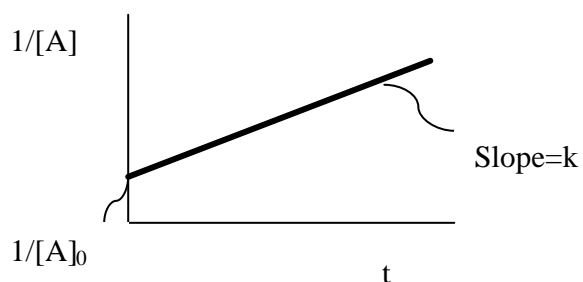
the rate law is;

$$-\frac{d[A]}{dt} = k[A]^2$$

Rearranging, integrating and using the initial conditions, we obtain;

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

Thus, a plot of $1/[A]$ versus time is linear and the slope is equal to the rate constant.

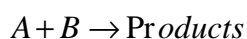


The half-life for a second-order reaction may be calculated to be ;

$$t_{1/2} = \frac{1}{k[A]_0}$$

This equation shows that the half-life of a second-order reaction is dependent upon the initial concentration of the reactant. $t_{1/2}$ is inversely proportional to the initial concentration. Thus, when $[A]_0$ is reduced by a factor of 2, the half-life doubles.

- If the rate is proportional to the product of the concentrations of two reactants. For the reaction;



the rate law is;

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]$$

The rate law is first-order in each reactant and second-order overall. The resulting integral rate equation is;

$$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[A][B]_0}{[B][A]_0}$$

This equation shows that a plot of $\ln [A]/[B]$ versus time gives a straight line.

Reactions of higher order are occasionally important. The differential rate equations for such reactions may be integrated directly or integrated after expressing all the concentrations in terms of a single variable.

Example #1

The reaction



is first order and has a rate constant of $2.24 \times 10^{-5} \text{ s}^{-1}$ at 320°C .

- Calculate the half-life of the reaction.
- What fraction of a sample of $SO_2Cl_2(g)$ remains after being heated for 5.00 hours?
- How long will a sample of $SO_2Cl_2(g)$ need to be maintained at 320°C to decompose 92.0 % of the initial amount present?

Solution:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.24 \times 10^{-5}} = 3.09 \times 10^4 \text{ s}$$

$$\ln[SO_2Cl_2] = -kt + \ln[SO_2Cl_2]_0$$

$$\ln \frac{[SO_2Cl_2]}{[SO_2Cl_2]_0} = -kt = -(2.24 \times 10^{-5})(5hr)(3600 \text{ s.hr}^{-1})$$

$$\frac{[SO_2Cl_2]}{[SO_2Cl_2]_0} = 0.668 \longrightarrow 66.8\%$$

$$\ln(1 - 0.92) = -(2.24 \times 10^{-5})(t)$$

$$t = 1.13 \times 10^5 \text{ s} = 31.3 \text{ hours}$$

Example #2

You order a sample of Na_3PO_4 containing the radioisotope phosphorous -32 ($t_{1/2} = 14.3$ days).

If the shipment is delayed in transit for two weeks, how much of the original activity will remain when you receive the sample?

Solution:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.3 \text{ days}} = 4.85 \times 10^{-2} \text{ days}^{-1}$$

$$[A] = [A]_0 e^{-kt}$$

$$\frac{[A]}{[A]_0} = e^{-(4.85 \times 10^{-2} \times 14)} = 0.507$$

50.6% of the original activity will remain.