

# PHYSICAL CHEMISTRY

CHM 100L/CHEMISTRY DEPARTMENT

DR. MRS BAMGBOSE



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## Chemical Kinetics

How fast does the reaction go?

This is the concern of kinetics. It also examines the detailed pathway that a reaction goes through in going from reactants and products, thus giving us an insight into the reaction mechanism.

The rate of chemical reactions is usually followed by:

- measuring either the decrease in concentration of the reactants
- or an increase in the concentration of the products with time.

A unit of rate is  $\text{Ms}^{-1}$  ( $\text{mol dm}^{-3} \text{s}^{-1}$ ).

### Measurements of reaction rates

It is usual to conduct a preliminary investigation to establish:-

- The nature and extent of possible side reaction
- The position of equilibrium
- That the reaction proceeds at a conveniently measurable rate.

The rate is then measured at constant temperature by one of the following methods which allow the concentration of either reactants or products to be followed with time.

- Volumetric or Gravimetric Analysis
- Measurement of Pressure Change and
- Measurement of Change in some Physical Property etc.

## Analysis of Experimental results

### The Rate Expression

$A + B \rightarrow \text{Product}$

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[P]}{dt} = k[A][B], \quad k = \text{rate constant (M}^{-1}\text{s}^{-1}\text{)}$$

Since  $[A]$  and  $[B]$  decreases with time, rate must also decrease. The rate constant,  $k$ , remains unchanged throughout the reaction and provides a more convenient measure of reaction velocity than does the experimentally measured.

**Rate Law:** - Expression which gives the rate of reaction as a function of the concentrations of some of the reactants e.g.  $\frac{dx}{dt} = k[A][B]$  etc. which is rate law,  $k = \text{rate constant}$   $[A]$  or  $[B] = \text{concentrations of A or B}$ .

**Order of a Reaction:** This is the sum of the power of the concentration terms in the differential rate law or rate determining step. This is experimental quantity which cannot be predicted from the equation of the reaction.

## Differential Rate Equations

$A + B + C \rightarrow \text{Product}$

If experimentally we found that  $\frac{d[P]}{dt} = k[A]$ , the reaction is 1<sup>st</sup> order,  $k$  is first order rate constant.

$\frac{d[P]}{dt} = k[A][B]$ , overall reaction is 2<sup>nd</sup> order;  $k$  is second order rate constant. If  $\frac{d[P]}{dt} = k[A]^2[B]^2$ ,  $k$  is 2<sup>nd</sup> order with respect to A or B but overall order is 4<sup>th</sup> order.  $\frac{d[P]}{dt} = k[A][B][C]$  or  $[A]^3$ , reaction is 3<sup>rd</sup> order,  $k$  is 3<sup>rd</sup> order rate constant.

**Molecularity:** - This is the number of chemical species which are involved in the rate determining step. It is a theoretical quantity 1, 2, 3, unimolecular, bimolecular and termolecular

## Derivation of Rate Equation by Integration Method

First order rate equations,  $A \rightarrow \text{Products}$

$$\begin{array}{ccc} t = 0 & a & 0 \\ t = t & a - x & x \end{array}$$

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{d(a-x)}{dt} = k_1[a-x]$$

$$\text{Rate} = \frac{dx}{dt} = k(a-x)$$

$$\frac{dx}{a-x} = kdt$$

$$\int_0^x \frac{dx}{a-x} = \int_0^t kdt$$

$$-\ln(a-x) = kt + c, \text{ when } x=0, t=0, c = -\ln a$$

$$-\ln(a-x) = kt - \ln a$$

$$\ln a - \ln(a-x) = kt$$

$$\ln \frac{a}{a-x} = k_1 t, \text{ where } k = \text{rate constant or}$$

$$\log(a-x) = \log a - \frac{k_1 t}{2.303}$$

A plot of  $\log(a-x)$  versus  $t$  gives a straight line with slope  $= -\frac{k_1}{2.303}$  and intercept  $= \log a$ .

### Differential Rate Equations

$A + B + C \rightarrow \text{Product}$

If experimentally we found that: (i)  $\text{Rate} = \frac{d[P]}{dt} = k(\text{mol dm}^{-3} \text{s}^{-1})$ . This indicates that the reaction is zero order i.e. it does not depend on the concentration of any of the reactants,  $k = \text{zero order rate constant}$ .

(ii)  $\text{Rate} = \frac{d[P]}{dt} = k[A](\text{mol dm}^{-3} \text{s}^{-1})$ . The reaction is first order,  $k = \text{first order rate constant (s}^{-1}\text{)}$

(iii)  $\text{Rate} = \frac{d[P]}{dt} = k[A][B]$  or  $k[A]^2$  or  $k[B]^2$  ( $\text{mol dm}^{-3} \text{s}^{-1}$ ). The reaction is second order,  $k = (\text{mol}^{-1} \text{dm}^3 \text{s}^{-1})$  or ( $\text{M}^{-1} \text{s}^{-1}$ )

(iv)  $\text{Rate} = \frac{d[P]}{dt} = k[A][B][C]$  or  $k[A]^2[B]$  or  $k[A][B]^2$  ( $\text{mol dm}^{-3} \text{s}^{-1}$ ). The reaction is third order,  $k = (\text{mol}^{-2} \text{dm}^3 \text{s}^{-1})$  or ( $\text{M}^{-2} \text{s}^{-1}$ ).

**Half-life:** The time taken for half of the reactants to go to products designated by  $t_{1/2}$ .

$$t_{1/2} = (a-x) = \left(\frac{a}{2}\right) \quad x = \left(\frac{a}{2}\right)$$

$$kt_{1/2} = 2.303 \log \left( \frac{a}{\frac{a}{2}} \right) = 2.303 \log 2 = 0.69$$

$$t_{1/2} = \frac{0.69}{k_1}$$

Half-life period of any first order reaction is independent of the initial concentration i.e. it takes a

First order reaction just as much time to go halfway to completion when the initial concentration is high as when is low.

**Second order rate equations**

$2A \rightarrow \text{Product}$ , e.g. Dimerization of butadiene  $2C_4H_6 \rightarrow C_8H_{12}$  OR

$A + B \rightarrow \text{Product}$

For Second order reaction, the rate equation is:

$$k_2 t = \frac{1}{a-x} - \frac{1}{a}$$

Plot of  $\frac{1}{(a-x)}$  against  $t$  gives a straight line with a slope  $= k_2$ .

#### Determination of Order of Reaction

1.

**Question 1:-** From the following data obtained at  $20^\circ\text{C}$  shows that the decomposition of hydrogen peroxide in aqueous solution is a first order.

Time (min)	0	5	10	20
KMnO <sub>4</sub>	46.1	37.1	29.8	19.6
<b>Solution</b>				

$$k = \frac{2.303}{t} \log \left( \frac{a}{a-x} \right)$$

$$t = 5$$

$$k = \frac{2.303}{5} \log \left( \frac{46.1}{37.1} \right) = 4.34 \times 10^{-2} \text{ min}^{-1}$$

$$t = 10$$

$$k = \frac{2.303}{10} \log \left( \frac{46.1}{29.8} \right) = 4.36 \times 10^{-2} \text{ min}^{-1}$$

$$t = 20$$

$$t = \frac{2.303}{20} \log \left( \frac{46.1}{19.6} \right) = 4.36 \times 10^{-2} \text{ min}^{-1}$$

This shows that the reaction is conform to equation which is first order.

2.

The following data in the hydrolysis of acetate at  $25^\circ\text{C}$  in the presence of 0.35 N HCl used as catalyst produces the following data,

Time (min)	0	1200	4500	7400	$\infty$
Alkaline (ml)	24.36	25.85	29.32	31.72	47.15

From the above data shows that the hydrolysis of acetate is first order.

Let  $V_\infty$  = titre value at time  $t = 0$  and  $V_\infty$  = titre value at  $t = \infty$ , therefore

$$V_\infty - V_t = a \quad \& \quad V_\infty - V_t = a - x, \quad V_\infty - V_t = x, \quad k = \frac{2.303}{t} \log \left( \frac{V_\infty - V_t}{V_\infty - V_\infty} \right)$$

The rate constant is obtained from the slope of the plot of  $\log \left( \frac{V_\infty - V_t}{V_\infty - V_\infty} \right)$  versus  $t$  which gives a

$$\text{slope} = \frac{2.303}{k}$$

#### Theoretical treatment of Reaction Rates

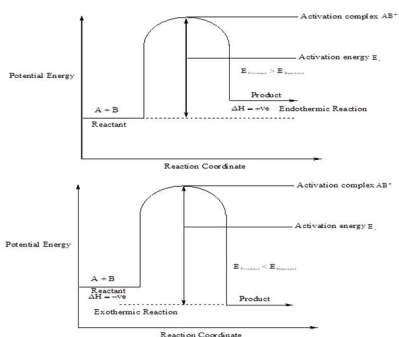
**Collision theory:** - The application of the simple kinetic theory of gases to the rate of the bio molecular process  $A + B \rightarrow \text{Product}$ , is based on the reasonable assumption that for the reaction to take place;

(a) Molecules A & B must collide

(b) The energy of the colliding molecules must be at least equal to the activation energy ( $E_a$ ).

The rate of the reaction is therefore equal to the number of effective collisions per second in unit volume of the reacting gas.

quantity.  $E_a = \Delta H + RT$ . Where  $\Delta H$  is the change in the enthalpy of the reaction, R is the Gas constant and T is Temperature,



#### Factors Determining the Rate of Reaction

**Nature of the reactant:** - surface area of the reactant affects the rate of reaction. Faster in powdered form than in granular form.

**Concentration of the reacting molecules:** - increase in the concentration of the reactant increase the rate of the reaction. Because collision is increased leading to increase in rate. Not all collisions are effective. Only those molecules which have a certain minimum energy (activation energy) to overcome the repulsive forces generated by the electron clouds of the reactants are able to form the product.

**Temperature:** - An increase in temperature result in an increase in rate because at higher temperature, the kinetic energy of the reactant increase making their collision more violent & therefore more probable to cause reaction.

Increase in temperature also alter the distribution of molecular energy to the extent that one molecule acquire higher kinetic energy. At higher temperature the energies of molecules are distributed and more molecules acquire more kinetic energies greater than activation energy leading to increase in the rate of reaction.

Arrhenius equation shows the temperature dependence of rate of reactions as  $k = Ae^{-\frac{E_a}{RT}}$ . Where  $k$  = rate constant,  $A$  = frequency factor concerned with the number of collisions per unit time, and the orientation of the reacting species during collision,  $E_a$  = Activation energy,  $R$  = Universal gas constant and  $T$  = Temperature in kelvin.

Enthalpy of activation complex can be calculated from  $E_a = \Delta H^\ddagger + RT$ .

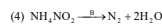
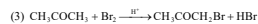
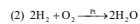
### Catalysis

A catalyst increases the rate of chemical reaction. Since the addition of a catalyst does not change the stoichiometry of the reaction,  $A + B \rightarrow C + D$

Otherwise the reaction would not be the same one, the catalysed reaction may be represented by  $A + B + \text{Catalyst} \rightarrow C + D + \text{Catalyst}$ . From which it follows that

- The catalyst remains chemically unchanged at the end of the reaction
- A catalyst does not alter the position of chemical equilibrium but accelerates the approach to chemical equilibrium by equally affecting the forward and reverse rates
- A small amount of catalyst will promote a large amount of chemical change

Examples:-

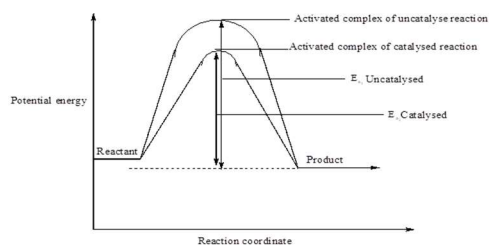


(5) Many reactions in biological systems are catalysed by enzymes.

Two broad types of catalysis are recognized depending on the kinetic classification of reaction types.

**Homogeneous catalysis:** - This is when all the reactants are in the same phase, gases, liquids, solids with catalyst. Examples 3, 4, 5 are representation of this type.

**Heterogeneous catalysis:** - This is when all the reactants including the catalyst are not in the same phase. The catalyst constitutes an additional phase as in example 2.



Since  $E_a < E_{a_u}$ , the reaction in the presence of catalyst proceeds faster than in its absence.

### Equilibrium

A reversible reaction is one which proceeds in both forward and backward direction i.e.

$A + B \rightleftharpoons C + D$ , (where  $k_f$  &  $k_b$  are the equilibrium constant for both forward and backward reaction respectively). Equilibrium is achieved when the forward rate is equal to reverse rate and in such case, the concentration of A, B, C & D are constants. Supply of reactants in both directions is constantly reviewed so that equilibrium is dynamic. The position of equilibrium is measured by equilibrium constant  $K$ .

#### Measurement of Equilibrium constant ( $K$ ) under Standard Condition

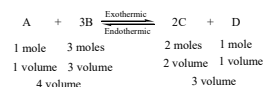
At  $25^\circ\text{C}$  and 1 atm pressure, the equilibrium constant is written as  $K^\circ$  and is related to the standard free energy change as follows,  $\Delta G^\circ = -RT \ln K^\circ = -2.303RT \log K^\circ$ .  $\Delta G^\circ$  also measures the position of equilibrium.  $\Delta G^\circ = -ve$ ,  $K^\circ = 1$ , and equilibrium lies to the right.

#### Unit of $K_{eq}$

- For reactions in solution,  $K_{eq}$  is expressed in terms of concentration
- For gaseous reaction ( $\text{mol dm}^{-3}$ ), partial pressure ( $\text{Nm}^{-2}$ , mmHg)

### Le Chatelier Principle

Effect of a stress on equilibrium such as (a) change in concentration (b) pressure (c) temperature can be predicted by applying Le Chatelier principle. Le Chatelier Principle states that 'A system in equilibrium react to any change in its conditions in a manner that would tend to abolish this change'. Let us apply this principle to hypothetical examples:



**Change of Pressure:** - If in a system in equilibrium, the pressure is raised, then Le Chatelier principle predicts that the system will respond to this external change as to oppose its effect i.e. the position of equilibrium will alter by promoting that reaction which results in lower pressure because it proceeds with a reduction in volume. So in this case a higher pressure will cause a shift in the position of equilibrium from left to right and lead to a higher proportion of C & D in the reaction mixture. Lowering the pressure of the system will have opposite effect.

**Change in Temperature:** - By similar reasoning, if the system is in equilibrium and the temperature is raised, this change will be opposed by promoting the reaction which proceeds with the absorption of heat i.e. Endothermic reaction, causing a shift in the position of the equilibrium to the left thereby increasing the proportion of A & B.

**Change in Concentration:** - Partial or complete removal of D from the equilibrium mixture will upset the system in equilibrium. Le Chatelier principle predicts that the consequence of such a change will be a shift in the position of equilibrium to the right with production of more C & D thereby opposing the reduction in the concentration of D that has been made.

#### Examples:

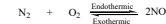
Examples high pressure and low temperature



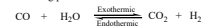
High pressure, low temperature and large excess of oxygen



Alternating pressure has no effect and high temperature leads to the formation of NO



Alternating pressure has no effect and low temperature leads to the formation of  $\text{CO}_2$  &  $\text{H}_2$



### Questions

- The rate of hydrolysis of isobutane in an acidic aqueous solution is given by  $-\frac{d[\text{Isobutane}]}{dt} = k[\text{Isobutane}]$  and the value of rate constant is  $k = 2.2 \times 10^{-4} \text{ s}^{-1}$  at  $25^\circ\text{C}$ 
  - What is the half-life of the reaction
  - How long will it take for the concentration of isobutane to decrease to 0.1% of its initial value at  $25^\circ\text{C}$
  - If the concentration of isobutane in the solution  $1.00 \times 10^{-3} \text{ M}$  after the reaction has proceeded for 3600 seconds at this temperature. What was its concentration when the reaction began?
- A substance decomposes according to first order rate law with half-life of 40min. What fraction of the sample remains after 100mins of the reaction

### Answer 1

$$t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{2.2 \times 10^{-4}} = 3150 \text{ s}$$

$$kt = 2.303 \log \left( \frac{a}{a-x} \right)$$

$$2.2 \times 10^{-4} t = 2.303 \log \left( \frac{100}{0.1} \right)$$

$$t = \frac{2.303 \times 3}{2.2 \times 10^{-4}} = 31404.5 \text{ s}$$

$$kt = 2.303 \log \left( \frac{a}{a-x} \right)$$

$$2.2 \times 10^{-4} \times 3600 = 2.303 \log \left( \frac{a}{1.00 \times 10^{-3}} \right)$$

$$a = 2.207 \times 1.0 \times 10^{-3} = 2.207 \times 10^{-3} \text{ M}$$

### Answer 2

$$t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{40} = 1.73 \times 10^{-2} \text{ s}^{-1}$$

$$kt = 2.303 \log \left( \frac{a}{a-x} \right)$$

$$1.73 \times 10^{-2} \times 00 = 2.303 \log \left( \frac{a}{a-x} \right)$$

$$\log \left( \frac{a}{a-x} \right) = 0.752$$

$$\frac{a}{a-x} = \frac{56}{10}$$

$$\frac{a-x}{a} = \frac{5}{28} = 0.178 = \frac{1}{5.6}$$