CHEMICAL KINETICS

Key Terms the students are expected to know in this chapter:

Activated complex	Activation energy	Average rate
Catalyst	Collision frequency	Complex reactions
Energy barrier	Ester	First order
Frequency factor	Half life period	Hydrolysis
Initial rate method	Instantaneous rate	Inversion of cane sugar
Irreversible reaction	Kinetic stability of fuels	Law of mass action
Molecularity	Order of a reaction	Orientation
Photochemical reaction	Pseudounimolecular	Rate constant
Rate law	Rate of reaction	Reversible reaction
Second order	Simple reactions	Specific rate constant
Temperature coefficient	Thermodynamic stability	Third order
Threshold energy	Units of order	Units of rate
Zero order	Collision theory	

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<u>Rate</u>

The rate of a reaction may be defined as the change in the concentration of any one of the reactants or products per unit time.

<u>Unit of rate</u> Mol/L/Time

<u>Average rate</u>

Total change in concentration by total time taken is known as average rate.

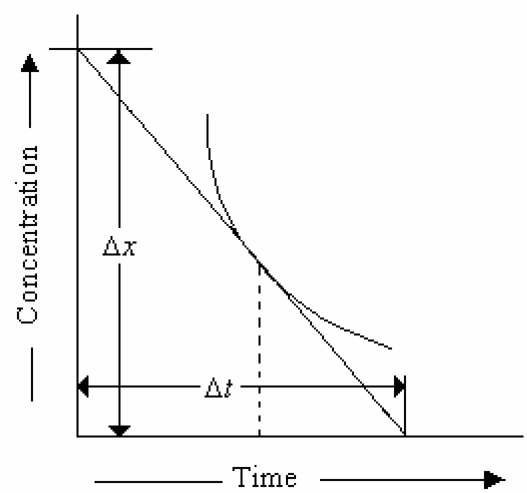
<u>Instantaneous rate</u>

The rate of change of concentration of any one of the reactants or products at that particular instant of time.

$$Rate = \frac{dx}{dt}$$

<u>Graphical method for determination of rate.</u>

The rate can be determined by finding the slope of the tangent to the curve at the point corresponding to that instant of time.



Examples of differential rates:

Write differential rates for the reaction:

$$A + B \rightleftharpoons C + D$$

$$\text{Differential rate for A} = -\frac{d[A]}{dt}$$

$$\text{Differential rate for B} = -\frac{d[B]}{dt}$$

$$\text{Differential rate for C} = +\frac{d[C]}{dt}$$

$$\text{Differential rate for D} = +\frac{d[D]}{dt}$$

Dependence of rate of reaction on the concentration of the reactants:

Rate Law and Order of reaction

The dependence of the rate of a reaction on concentration is seen form the law of mass action. It gives a theoretical dependence of the rate of the reaction on concentration of reactants.

[refer Chemical equilibrium for Law of mass action

Law of mass action

$$aA + bB \rightleftharpoons cC + dD$$

$$Rate_f = k' [A]^a [B]^b$$

$$Rate_b = k'' [C]^c [D]^d$$

$$\text{At equilibrium } Rate_f = Rate_b$$

$$Rate = k \frac{[A]^a [B]^b}{[C]^c [D]^d}$$

The above is the sum of law of mass action]

The rate law is determined experimentally:

In a multi step reaction the rate depends on the slowest step that is the rate-determining step.

Rate α [A] [B]

Rate = k [A] [B]

Where **k** is the rate constant or the specific reaction rate or the velocity constant.

K can be defined as the rate of the reaction when the concentration is unity.

<u>Order</u>

It can be defined as the sum of the exponents of the concentration terms of the rate law

Or

It may be defined as the sum of the powers to which the concentration terms are raised in a rate law expression. This is an experimentally determined factor.

For the reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$Rate = k [A]^x [B]^y$$

$$\textit{order 'n' of the reaction} = x + y$$

Rate = k $[A]^x$ $[B]^y$

The order ‘n’ of the reaction = ‘x’ + ‘y’ where ‘a’ and ‘b’ may or may not be equal to ‘x’ and ‘y’

What are the different orders of reaction?

Zero, First, Second, third etc.

A zero order reaction is independent of the concentration of reactants. The rate of the reaction does not depend on the concentration terms or in other words an increase in the quantity of the reactants does not increase the rate of the reaction.

Photochemical formation of HCl from hydrogen and chlorine is a zero order reaction.

$$H_2 + Cl_2 \xrightarrow{hv} 2HCl$$

$$Rate = k[H_2]^0[Cl_2]^0$$

$$Order\ 'n' = 0 + 0 = 0$$

Units of Zero order reaction:

$$Rate = k[H_2]^0[Cl_2]^0$$

$$Order\ 'n' = 0 + 0 = 0$$

$$k = \frac{Rate}{[H_2]^0[Cl_2]^0}$$

$$k = \frac{molL^{-1}T^{-1}}{[H_2]^0[Cl_2]^0}$$

$$k = molL^{-1}T^{-1}$$

First order reaction the rate of a first order reaction depends on one concentration term only. It is possible that there could be more than one reactants involved in the reaction.

All nuclear fission reactions are first order decay or disintegration.

Hydrolysis of esters: are first order reactions

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

$$Rate = k[CH_3COOC_2H_5]^1$$

$$Order = 1$$

Unit of first order reaction

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

$$Rate = k[CH_3COOC_2H_5]^1$$

$$Order = 1$$

$$k = \frac{Rate}{[CH_3COOC_2H_5]^1}$$

$$k = \frac{molL^{-1}T^{-1}}{[molL^{-1}]}$$

$$k = Time^{-1}$$

Second order reaction:

The rate of a second order reaction is dependent on two concentration terms. This depends on the mechanism of the reaction. Example of a second order reaction is given below

$$2NO_{2(gas)} + F_{2(gas)} \rightarrow 2NO_2F_{(gas)}$$

$$Experimentally\ it\ has\ been\ found$$

$$Rate\ of\ reaction\ \alpha [NO_2]^1[F_2]^1$$

$$Order\ 'n' = 1 + 1 = 2$$

Unit of 'k' for second order reaction:

$$2NO_{2(gas)} + F_{2(gas)} \rightarrow 2NO_2F_{(gas)}$$

$$Experimentally\ it\ has\ been\ found$$

$$Rate\ of\ reaction\ \alpha [NO_2]^1 [F_2]^1$$

$$Order\ 'n' = 1 + 1 = 2$$

$$k = \frac{Rate}{[NO_2]^1 [F_2]^1}$$

$$k = \frac{mol L^{-1} T^{-1}}{[mol L^{-1}][mol L^{-1}]}$$

$$k = L mol^{-1} T^{-1}$$

Molecularity
The number of reacting species (atoms, ions or molecules) that must collide with each other simultaneously so as to result in a chemical reaction is called molecularity.
Pseudo Uimolecular reactions
Reactions in which the ORDER is one but molecularity is two is called pseudounimolecular reactions. E.g. Hydrolysis of Esters.
Equation to be written:

Mechanism of a reaction
A sequence of elementary reactions or steps written to account for the overall reaction is called the mechanism of the reaction.
Example:

The rate-determining step is the slowest step. The rate law is written using this step.

Distinction between rate of reaction rate constant

Rate of reaction	Rate Constant
1. Rate if reaction is the change in concentration of a reactant or product per unit time.	2. It is a constant of proportionality in the rate law equation and is equal to the rate of reaction when the molar concentration of each reactant is unity
3. The rate of reaction at any instant of time depends upon the molar concentration of the reactants at that time.	4. The rate constant is constant for a particular reaction at a particular temperature and does not depend upon the concentrations of the reactants.
5. Its unit is always Mol/L/Time	6. Its units depends upon the order of the reaction.= mol^{1-n} $litre^{n-1}$ $time^{-1}$ n is the order of the reaction.

Life Time
The time taken for the reaction to complete is know as life time (usually 98%)
Half Life '$t^{1/2}$'
The time taken for half of the reaction to complete is called half life period of the reaction.
or
The time taken for the concentration of the reactants to reach 50% of its initial value.

Factors affecting the rates of reactions;

7. Nature of reactants
8. Concentrations of reactants
9. Temperature
10. Catalyst
11. Radiation

Nature of reactants

1. *Physical state of reactants*
   a) Gaseous reactions are faster than liquid reactions which is greater than solid reactions. This is because the chances of interaction of the gaseous molecules is greater than in liquids which is greater than in solids.
2. *Particle size of reactants*
   a) Greater the surface area greater is the chance of interaction of the reactant species. This can be seen from the following reactions.
      i) Powdered coal burns faster than apiece of coal
      ii) powdered sugar dissolves faster than a lump of sugar
      iii) pulverised wood and wood shavings burn faster than wood of the same mass
3. *Chemical nature of reactants*
   a) The rate of a reaction depends on the chemical nature of the reactants.
      i) $MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ (fast)
      ii) $MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow Mn^{2+} + 10CO_2 + 8H_2O$ (slow)

The two reactions occur at different rates due to the difference in the nature of the reducing agents ie Fe^{2+} and $C_2O_4^{2-}$

Concentrations of reactants

The rate of the reaction decreases with decrease in concentration. This is obvious from the law of mass action. When the concentration is large the chance of reactants coming in contact with each other is greater. Hence the rate of the reaction will increase.

Effect of Temperature

As a rule generally speaking a rise in temperature increases the rate of the reaction (whether endothermic or exothermic) this is because all reactions occur only if the reactants molecules possess *Threshold Energ*y.

Threshold Energy

It may be defined as the minimum amount of energy which the colliding molecules must posses in order that the collisions may become effective.

Activation Energy

The extra amount of energy which the molecules of the reactants have to absorb so that their energy becomes equal to the threshold energy is called ***Activation Energy***. (Graph)

Activation Energy = Threshold Energy - Energy possessed by the reactant molecules.

Fast reactions have low activation energy

Slow reactions have high activation energy

Orientation Of Molecules

All collisions does not lead to the formation of the products. Only those molecules which possess *threshold energy* and have a *proper orientation* form the *Transition state* or Activated Complex which can further change into products.

Thermodynamic and Kinetic Stability

Every reaction which is spontaneous on the basis of free energy change (i.e. having ΔG negative) may not take place under ordinary conditions due to high energy of activation such reactions may be thermodynamically unstable but kinetically stable. This is why fuels do not undergo combustion spontaneously.

Presence of Catalyst

A catalyst is a substance that increases the speed of a reaction without itself undergoing any chemical change.

A catalyst provides an alternate path with lower energy barrier. It decreases the *energy of activation* of the reaction.

Effect of radiation

Those reactions which take place only in the presence of electromagnetic radiation's are known as Photochemical reaction's (*In the absence of light the reactions do not occur)*

E.g.

Photography

Photosynthesis

Blue Printing

Reaction between H_2 and Cl_2 in the formation of HCl

There are three steps involved in the reaction

Chain initiation step:

$$Cl_2 + h\nu \rightarrow Cl_2^*$$

$$Cl_2^* \rightarrow Cl^{\cdot} + Cl^{\cdot}$$

Chain Propagation step:

$$Cl^{\cdot} + H_2 \rightarrow HCl + H^{\cdot}$$

$$H^{\cdot} + Cl_2 \rightarrow HCl + Cl^{\cdot}$$

Chain Termination step:

$$H^{\cdot} + Cl^{\cdot} \rightarrow HCl$$

$$H^{\cdot} + H^{\cdot} \rightarrow H_2$$

$$Cl^{\cdot} + Cl^{\cdot} \rightarrow Cl_2$$

Difference between order and molecularity of a reaction

Order of a reaction	Molecularity of a reaction
1. Sum of the exponents of the concentrations in the rate law equation.	1. It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction.
2. It can be a whole number, zero or a fractional value	2. It always has to be a whole number
3. Has to be determined experimentally	3. It can be calculated by adding the molecules present in the slowest step of a reaction
4. Is for the overall reaction	4. The overall molecularity of a complex reaction has no significance, the slowest step is the rate determining step
5. Order of the reaction may or may not be equal to the number of the reactants as represented in the balanced equation	5. The molecularity for simple reactions is obtained from the coefficients of a balanced equation.

Mechanism of Reactions:

A sequence of elementary reactions or steps written to account for the overall reaction is called the mechanism of the reaction.

Example:

$$NO_2 + F_2 \rightarrow NO_2F + \cancel{F} \quad \text{Slow reaction step I}$$

$$NO_2 + \cancel{F} \rightarrow NO_2F \quad \text{Fast reaction step II}$$

$$2NO_2 + F_2 \rightarrow 2NO_2F$$

In the above example the slowest step is the rate determining step. The rate determining step involves only 2 reactants therefore it is a second order reaction.

Rate = k $[NO_2][F_2]$ order n = 2

(The rate-determining step is the slowest step. The rate law is written using this step.)

- **When will you suggest a mechanism for a reaction?**
  When the rate law is not equal to the law of mass action it implies that the reaction does not take place in a single step hence a mechanism should be suggested to satisfy the rate law if known.

- **What are elementary steps in a mechanism?**
  In a multi step reaction the single steps involved are called the elementary steps.
  The different elementary steps should add up to represent the actual reaction.

- **What are reactive intermediates?**
  Reactive intermediates are molecules, atoms or ions formed as a result of molecular interaction of the reactants or the cleavage of the covalent bonds in them. (the F atom in the above reaction is a reactive intermediate with high energy and looking for ways to stabilize ASAP)

- **What happens to the reactive intermediates in a reaction involving a multi step reaction?**
  The reactive intermediates in the elementary steps have very short existence and high energy and usually they change rapidly into other products and will not be present in the final equation as they will cancel out in the subsequent elementary steps.

- **Why is the slowest step an important step in determining the rate of the reaction?**
  The elementary steps that involve cleavage of covalent bonds in aqueous solutions require large amount of energy and hence are slow reactions Energy of activation is high. The quantity of products formed depends on the rate of the slowest step or RDS. The reactive intermediates are formed in the slow steps and hence the rate of reaction of the intermediate does does not alter the rate of the reaction.
  Elementary steps which are slow are the rate determining steps- hence rate law is written using this step.
  (The reactive intermediates are high energy species and hence will change quickly into other products rather fast and such elementary steps will usually be faster than the rate determining steps.)