It is the branch of chemistry which deals with the rate & mechanism of chemical reactions proceeding under given conditions of temperature, pressure and concentration.

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Chemistry

**Alpha Classes**

**Chemicial Kinetics**

**Chemical Kinetics:** It is the branch of chemistry which deals with the rate & mechanism of chemical reactions proceeding under given conditions of temperature, pressure and concentration. The study of chemical kinetics has been useful in determining the factors which affect rate of reactions as well as in understanding mechanisms of a number of chemical reactions. Chemical kinetic supplement chemical thermodynamics.

Based upon their rates, all chemical reactions have been classified into the following three groups.

**1. Fast Reactions:** These reactions occur almost instantaneously requiring just 10-6 to 10—10 seconds for completion and hence the rate of such reactions cannot be measured. These are mostly ionic reactions and do not involve any cleavage of bonds. This is due to the fact that the ionic reactants are already present in ionic state in aqueous solution and thus such reactions occur instantaneously. Therefore, the rate of such reactions is extremely fast e.g.

(a)  

Besides ionic reactions, nuclear reactions are also fast reactions.

**2. Extremely Slow Reactions:** These reactions take months or years to produce any detectable change. For example, rusting of iron, combination of hydrogen and oxygen at ordinary temperature, conversion of monoclinic sulphur to triclinic sulphur, etc.

**3. Moderate Velocity Reactions:** These reactions occur at conveniently measurable rate i.e. their rates are in between the very slow and fast reactions. For example

(a) C12H22O­11 + H2O H+ C6 H12 O6 + C6 H12O6

glucose fructose

**Rates of Reaction:** The rate of a reaction is defined as the speed with which the reactants are converted into products.

The rate of a reaction may be expressed quantitatively by measuring the decrease in concentration of any one of the reactants or increase in the concentration of any one of the products per unit time.

Let us consider a simple hypothetical chemical reaction,

X Y

The progress of the reaction may be expressed in the following two ways

**(i)** The rate of disappearance of X or decrease in concentration of reactant

Rate of reaction =  =  = 

**(ii)** The rate of appearance of Y or increase in concentration of product

Rate of reaction =  =  = 

Since concentration of reactants decreases with time, its change in concentration per unit time is expressed with negative sign. Like wise, the concentration of product increases with time. So its change in concentration per unit time is expressed with positive sign. Therefore,

Rate of reaction =  =  or

Where Δ[X] represent decrease in concentration of X and Δ[Y] represent increase in concentration of Y. The square bracket signs around the substances are used to express the concentration in mole/litre.

For example, for the reaction

2 NH3 

Rate of reaction = -

However the rate of reaction as stated above, is in fact the average rate of reaction. This is because according to Law of Mass Action the rate of a reaction depends upon the molar concentrations of the reactants. Now as the molar concentrations of reactants decreases with time the rate of reaction also decrease. Thus the rate of reaction as defined above is the average rate of reaction during the time interval chosen.

**Units of Rate of Reaction:** Since concentration of reactants or products are expressed in mol L–1, the rate of reaction has the unit of mol L–1 s–1.

**Instantaneous Rate of a Reaction:** As the rate of a reaction generally keeps on decreasing throughout the reaction, we should talk of the rate of reaction only at a particular instant of time. This is called instantaneous rate of reaction. It can be defined as follows.

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

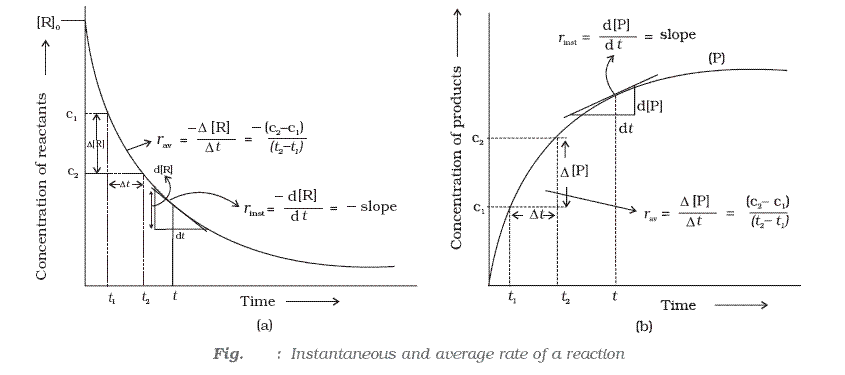
To express the instantaneous rate of reaction, a very small time interval (dt) is chosen at that particular instant of time during which the rate of reaction is supposed to be almost constant. The corresponding small change in concentration is dx. The rate of reaction at that instant is then given by dx/dt.

**Measurement Of Rate Of Reaction:**

We know that the rate of reaction depends upon the molar concentration of the reactants. Since the molar concentration of the reactants keeps on decreasing with the passage of time, therefore, the rate of reaction continuously decreases with time. Thus, the rate of reaction will not be constant throughout the reaction. The rate of a chemical reaction can be determined by two different methods.

**(a)** **Average Rate:** A rate of any reaction can be determined by dividing the total change in concentration of reactant by the total time elapsed during that change.

Average rate = 



**(b)** **Instantaneous Rate:** It is defined as the rate of change of concentration of any one of the reactants or products at a particular moment of time. It is mathematically expressed as  where dx is the change in concentration of any of the species in infinitesimally small interval of time dt

i.e. Instantaneous rate =

Q, From the concentrations of C4H9Cl (butyl chloride) at different times given **(NCERT)**

below, calculate the average rate of the reaction:

C4H9Cl + H2O → C4H9OH + HCl

during different intervals of time.

*t*/s 0 50 100 150 200 300 400 700 800

[C4H9Cl]/mol L–1 0.100 0.0905 0.0820 0.0741 0.0671 0.0549 0.0439 0.0210 0.017

Q. The decomposition of N2O5 in CCl4 at 318K has been studied by monitoring the concentration of N2O5 in the solution. Initially the concentration of N2O5 is 2.33 mol L–1 and after 184 minutes, it is reduced to 2.08 mol L–1. The reaction takes place according to the equation

2 N2O5 (g) → 4 NO2 (g) + O2 (g)

Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of NO2 during this period? **(NCERT)**

Q. For the reaction R → P, the concentration of a reactant changes from 0.03M to 0.02M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds. **(NCERT)**

Q. In a reaction, 2A → Products, the concentration of A decreases from 0.5 mol L–1 to 0.4 mol L–1 in 10 minutes. Calculate the rate during this interval? **(NCERT)**

**Dependence of Rate on Concentration**

The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and products. Therepresentation of rate of reaction in terms of concentration of the reactants is known as **rate law**. It is also called as rate equation or rate expression.

**Rate Expression and Rate Constant**

Consider a general reaction

aA + bB → cC + dD

where a, b, c and d are the stoichiometric coefficients of reactants and products.

The rate expression for this reaction is

Rate ∝ [A]x [B]y

where exponents x and y may or may not be equal to the stoichiometric coefficients (a and b) of the reactants. Above equation can also be written as

Rate = *k* [A]x [B]y

where *k* is a proportionality constant called **rate constant**. The equation like this , which relates the rate of a reaction to concentration of reactants is called rate law or rate expression. Thus, **rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation**.

**Order of a Reaction**

In the rate equation

Rate = *k* [A]x [B]y

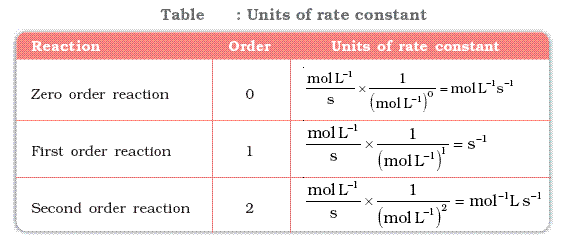
x and y indicate how sensitive the rate is to the change in concentration of A and B. Sum of these exponents, i.e., x + y gives the overall order of a reaction whereas x and y represent the order with respect to the reactants A and B respectively.

Hence, **the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction**.

Q.Calculate the overall order of a reaction which has the rate expression **(NCERT)**

(a) Rate = *k* [A]1/2 [B]3/2

(b) Rate = *k* [A]3/2 [B]–1

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Q. Identify the reaction order from each of the following rate constants. **(NCERT)**

(i) *k* = 2.3 × 10–5 L mol–1 s–1

(ii) *k* = 3 × 10–4 s–1

**Molecularity of a Reaction**

The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

Q. For a reaction, A + B → Product; the rate law is given by, *r* = *k* [ A]1/2 [B]2. What is the order of the reaction? **(NCERT)**

Q.The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y ? **(NCERT)**

**Zero Order Reaction**

**First order Reaction**

**Q.**The initial concentration of N2O5 in the following first order reaction N2O5(g) → 2 NO2(g) + 1/2O2 (g) was 1.24 × 10-2 mol L–1 at 318 K. The concentration of N2O5 after 60 minutes was 0.20 × 10–2 mol L–1. Calculate the rate constant of the reaction at 318 K. **(NCERT)**

Q. The following data were obtained during the first order thermal decomposition of N2O5 (g) at constant volume:

N2O5 g→2N2O4 g+O2 g

S.No. Time/s Total Pressure/(atm)

1. 0 0.5

2. 100 0.512

Calculate the rate constant. **(NCERT)**

## Half Life of a reaction

Q. A first order reaction is found to have a rate constant, *k* = 5.5 × 10-14 s-1.Find the half-life of the reaction. **(NCERT)**

Q. Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life (*t* 1/2) of the reaction. **(NCERT)Q.** A first order reaction has a rate constant 1.15 × 10-3 s-1. How long will 5 g of this reactant take to reduce to 3 g? **(NCERT)**

**Q.** Time required to decompose SO2Cl2 to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction. **(NCERT)**

## Temperature Dependence of Rate of a Reaction

Q. The rate constants of a reaction at 500K and 700K are 0.02s–1 and 0.07s–1 respectively. Calculate the values of *E*a and *A*. **(NCERT)**

Q. The first order rate constant for the decomposition of ethyl iodide by the reaction

C2H5I(g) → C2H4 (g) + HI(g)

at 600K is 1.60 × 10–5 s–1. Its energy of activation is 209 kJ/mol. Calculate the rate constant of the reaction at 700K. **(NCERT)**

**Q.** The rate of the chemical reaction doubles for an increase of 10K in absolute temperature from 298K. Calculate *E*a. **(NCERT)**

**Q.** The activation energy for the reaction

2 HI(g) → H2 + I2 (g)

is 209.5 kJ mol–1 at 581K.Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy? **(NCERT)**

# NCERT Exercises

**P.1** From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.

(i) 3NO(g) → N2O (g) Rate = *k*[NO]2

(ii) H2O2 (aq) + 3I– (aq) + 2H+ → 2H2O (l) + 3 I− Rate = *k*[H2O2][I-]

(iii) CH3CHO (g) → CH4 (g) + CO(g) Rate = *k* [CH3CHO]3/2

(iv) C2H5Cl (g) → C2H4 (g) + HCl (g) Rate = *k* [C2H5Cl]

**P.2** For the reaction:

2A + B → A2B

the rate = *k*[A][B]2 with k = 2.0 × 10–6 mol–2 L2 s–1. Calculate the initial rate of the reaction when [A] = 0.1 mol L–1, [B] = 0.2 mol L–1. Calculate

the rate of reaction after [A] is reduced to 0.06 mol L–1.

**P.3** The decomposition of NH3 on platinum surface is zero order reaction. What are the rates of production of N2 and H2 if *k* = 2.5 × 10–4 mol–1 L s–1?

**P.4** The decomposition of dimethyl ether leads to the formation of CH4, H2 and CO and the reaction rate is given by

Rate = *k* [CH3OCH3]3/2

The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure

of dimethyl ether, i.e.,

Rate = *k( p*CH3OCH3)3/2

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?

**P.5** Mention the factors that affect the rate of a chemical reaction.

**P.6** A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is

(i) doubled

(ii) reduced to half ?

**P.7** What is the effect of temperature on the rate constant of a reaction? How can this temperature effect on rate constant be represented quantitatively?

**P.8** In a pseudo first order hydrolysis of ester in water, the following results were obtained:

t/s 0 30 60 90

[Ester]/mol L–1 0.55 0.31 0.17 0.085

(i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

**P.9** A reaction is first order in A and second order in B.

(i) Write the differential rate equation.

(ii) How is the rate affected on increasing the concentration of B three times?

(iii) How is the rate affected when the concentrations of both A and B are doubled?

**P.10** In a reaction between A and B, the initial rate of reaction (r0) was measured for different initial concentrations of A and B as given below:

A/ mol L–1 0.20 0.20 0.40

B/ mol L–1 0.30 0.10 0.05

r0/mol L–1s–1 5.07 × 10–5 5.07 × 10–5 1.43 × 10–4

What is the order of the reaction with respect to A and B?

**P.11** The following results have been obtained during the kinetic studies of the reaction:

2A + B → C + D

Determine the rate law and the rate constant for the reaction.

**P.12** The reaction between A and B is first order with respect to A and zero order

with respect to B. Fill in the blanks in the following table:



**P.13** Calculate the half-life of a first order reaction from their rate constants given below:

(i) 200 s–1 (ii) 2 min–1 (iii) 4 years–1

**P.14** The half-life for radioactive decay of 14C is 5730 years. An archaeological artifact containing wood had only 80% of the 14C found in a living tree. Estimate the age of the sample.

**P.15** The experimental data for decomposition of N2O5

[2N2O5 → 4NO2 + O2]

in gas phase at 318K are given below:

**

(i) Plot [N2O5] against *t*.

(ii) Find the half-life period for the reaction.

(iii) Draw a graph between log[N2O5] and *t.*

(iv) What is the rate law ?

(v) Calculate the rate constant.

(vi) Calculate the half-life period from *k* and compare it with (ii).

**P.16** The rate constant for a first order reaction is 60 s–1. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?

**P.17** During nuclear explosion, one of the products is 90Sr with half-life of 28.1 years. If 1μg of 90Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

**P.18** For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

**P.19** A first order reaction takes 40 min for 30% decomposition. Calculate t1/2.

**P.20** For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

**

Calculate the rate constant.

**P.21** The following data were obtained during the first order thermal decomposition of SO2Cl2 at a constant volume.

SO2Cl2(g)→SO2(g)+Cl2(g)



Calculate the rate of the reaction when total pressure is 0.65 atm.

**P.22** The rate constant for the decomposition of N2O5 at various temperatures

is given below:

**

Draw a graph between ln *k* and 1/*T* and calculate the values of *A* and *E*a. Predict the rate constant at 30° and 50°C.

**P.23** The rate constant for the decomposition of hydrocarbons is 2.418 × 10–5s–1 at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor.

**P.24** Consider a certain reaction A → Products with *k* = 2.0 × 10–2s–1. Calculate the concentration of *A* remaining after 100 s if the initial concentration of *A* is 1.0 mol L–1.

**P.25** Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with *t*1/2 = 3.00 hours. What fraction of sample of sucrose remains after 8 hours ?

**P.26** The decomposition of hydrocarbon follows the equation

*k* = (4.5 × 1011s–1) e-28000*K*/*T*

Calculate *E*a.

**P.27** The rate constant for the first order decomposition of H2O2 is given by the following equation:

log *k* = 14.34 – 1.25 × 104*K*/*T*

Calculate *E*a for this reaction and at what temperature will its half-period be 256 minutes?

**P.28** The decomposition of A into product has value of *k* as 4.5 × 103 s–1 at 10°C and energy of activation 60 kJ mol–1. At what temperature would *k* be 1.5 × 104s–1?

**P.29** The time required for 10% completion of a first order reaction at 298K is equal to that required for its 25% completion at 308K. If the value of *A* is 4 × 1010s–1. Calculate *k* at 318K and *E*a.

**P.30** The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.