Sample Paper 19 Solutions

Class XII 2023-24

Chemistry

Time: 3 Hours **Max. Marks: 70**

General Instructions:

1. There are 33 questions in this question paper with internal choice.
2. SECTION A consists of 16 multiple-choice questions carrying 1 mark each.
3. SECTION B consists of 5 very short answer questions carrying 2 marks each.
4. SECTION C consists of 7 short answer questions carrying 3 marks each.
5. SECTION D consists of 2 case-based questions carrying 4 marks each.
6. SECTION E consists of 3 long answer questions carrying 5 marks each.
7. All questions are compulsory.
8. Use of log tables and calculators is not allowed.

SECTION-A

Directions (Q. Nos. 1-16) : The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1. When one Faraday of electric current is passed, the mass deposited, equal to

(a) One gram equivalent

(b) One gram mole

(c) Electrochemical equivalent

(d) Half gram equivalent

Ans : (a) One gram equivalent

The mass deposited is equal to one gram equivalent. Because "Faraday" is not a measure of current. The ampere is the measure of current. The mass of metal transferred in plating depends on the metal and the process.

2. The most convenient method to protect the bottom of ship made of iron is

(a) Coating it with red lead oxide

(b) White tin plating

(c) Connecting it with Mg Block

(d) Connecting it with Pb block

Ans : (c) Connecting it with Mg Block

For bottom of ship to be protected it is connected with more reactive metal than iron like magnesium. This technique is called cathodic protection.

3. Aldehydes and ketones will not form crystalline derivatives with

(a) Sodium bisulphite

(b) Phenylhydrazine

(c) Semicarbazide hydrochloride

(d) Dihydrogen sodium phosphate

Ans : (d) Dihydrogen sodium phosphate

Dihydrogen sodium phosphate (NaH_2PO_4) does not have a lone pair of electrons on the P atom. As such it can not act as a nucleophile and hence not react with aldehydes and ketones.

4. Actinides;

(a) Are all synthetic elements

(b) Include element 104

(c) Have any short lived isotopes

(d) Have variable valency

Ans : (d) Have variable valency

Actinides have variable valence due to very small difference in energies of $5f$, $6d$ and $7s$ orbitals. Actinides are the elements from atomic number 89 to 103.

5. $AgNO_3$ does not give precipitate with $CHCl_3$ because

(a) $CHCl_3$ does not ionise in water

(b) $CHCl_3$ does not react with $AgNO_3$

(c) $CHCl_3$ is chemically inert

(d) None of these

Ans : (a) $CHCl_3$ does not ionise in water

Chloroform is an organic compound which does not ionise in water. Since it can not provide Cl^-, therefore, it is not precipitated with $AgNO_3$.

6. At 25°C, the highest osmotic pressure is exhibited by 0.1 M solution of :

(a) $CaCl_2$ (b) KCl

(c) Glucose (d) Urea

Ans : (a) $CaCl_2$

Conc. of particles in $CaCl_2$ sol. will be max. as

$$i = 3 \text{ is max.}$$

Glucose and Urea do not dissociate into ions, as they are non-electrolytes.

7. The bad smelling substance formed by the action of alcoholic caustic potash on chloroform and aniline is:

(a) Acetic acid (b) Acetone

(c) Methanol (d) Methylamine

Ans : (a) Acetic acid

Primary amides react with nitrous acid to form carboxylic acids with the evolution of nitrogen gas.

$$\underset{\text{Ethanamide}}{CH_3CONH_2} + HONO \longrightarrow \underset{\text{Ethanoic acid}}{CH_3COOH} + N_2 + H_2O$$

In this reaction, nitrogen is eliminated quantitatively and its volume can be easily measured. Therefore, this reaction is used for the quantitative estimation of primary amides.

8. RNA is different from DNA because RNA contains

(a) ribose sugar and thymine

(b) ribose sugar and uracil

(c) deoxyribose sugar and thymine

(d) deoxyribose sugar and uracil.

Ans : (b) ribose sugar and uracil

In RNA, the sugar is D-ribose and base is uracil where as in DNA, the sugar is D-2 de oxyribose and the nitrogenous base is thymine.

9. For a first order reaction $A \longrightarrow B$ the reaction rate at reactant concentration of 0.01 M is found to be 2.0×10^{-5} mol $L^{-1}s^{-1}$. The half life period of the reaction is

(a) 30 s (b) 220 s

(c) 300 s (d) 347 s

Ans : (d) 347 s

Given, $[A] = 0.01$ M

$$\text{Rate} = 2.0 \times 10^{-5} \text{ mol } L^{-1}s^{-1}$$

For a first order reaction

$$\text{Rate} = k[A]$$

$$k = \frac{2.0 \times 10^{-5}}{[0.01]} = 2 \times 10^{-3}$$

$$t_{1/2} = \frac{0.693}{2 \times 10^{-3}} = 347 \text{ s}$$

10. Correct name of $K_4[Fe(CN)_6]$ is

(a) Potassium ferricyanide

(b) Potassium ferrocyanide

(c) Potassium hexacyanoferrate (II)

(d) Potassium hexacyanoferrate (III)

Ans : (c) Potassium hexacyanoferrate (II)

Oxidation state of iron is +2 in $K_4[Fe(CN)_6]$

So, its correct name is potassium hexacyanoferrate (II).

11. Which of the following compounds is oxidised to prepare methyl ethyl ketone ?

(a) 2-Propanol (b) l-Butanol

(c) 2-Butanol (d) t-Butyl alcohol

Ans : (c) 2-Butanol

Secondary alcohols oxidise to produce kenone.

$$\underset{2-\text{Butanol}}{CH_3CHOHCH_2CH_3} \xrightarrow{(O)} \underset{\text{Ethyl methyl ketone}}{CH_3COCH_2CH_3}$$

12. For the reaction $A \longrightarrow B$, the rate law expression is : rate $= k[A]$. Which of the following statements is incorrect?

(a) The reaction follows first order kinetics

(b) The $t_{1/2}$ of reaction depends on initial concentration of reactants.

(c) k is constant for the reaction at a constant temperature.

(d) The rate law provides a simple way of predicting the concentration of reactants and products at any time after the start of the products at any time after the start of the reaction.

Ans : (b) The $t_{1/2}$ of reaction depends on initial concentration of reactants

For 1st order reaction $t_{1/2}$ independent of initial concentration.

$$t_{1/2} = \frac{0.693}{K}$$

Directions (Q. No. 13-16) : Each of the following questions consists of two statements, one is Assertion and the other is Reason. Give answer :

13. **Assertion :** Isobutanal does not give iodoform test.
Reason : It does not have α-hydrogen

(a) Both Assertion and Reason are correct and Reason is a correct explanation of the Assertion.

(b) Both Assertion and Reason are correct but Reason is not the a correct explanation of the Assertion.

(c) Assertion is correct but Reason is incorrect.

(d) Both the Assertion and Reason are incorrect.

Ans : (c) Assertion is correct but Reason is incorrect.

Isobutanal does not give iodoform test because it does not have $-COCH_3$ group.

14. **Assertion :** The rate of a reaction sometimes does not depend on concentrations.
Reason : Lower the activation energy faster is the reaction.

(a) Both Assertion and Reason are correct and Reason is a correct explanation of the Assertion.

(b) Both Assertion and Reason are correct but Reason is not the a correct explanation of the Assertion.

(c) Assertion is correct but Reason is incorrect.

(d) Both the Assertion and Reason are incorrect.

Ans : (b) Both Assertion and Reason are correct but Reason is not the a correct explanation of the Assertion.

The rate of reaction sometimes does not depend upon concentration pseudo-first order reaction. Activation energy is an energy barrier for reaction to occur. So, lower the activation energy, faster is the reaction.

15. **Assertion :** $[Co(NH_3)_5Br]SO_4$ gives white precipitate with barium chloride.
Reason : The complex dissociates in the solution to give Br^- and SO_4^{2-}.

(a) Both Assertion and Reason are correct and Reason is a correct explanation of the Assertion.

(b) Both Assertion and Reason are correct but Reason is not the a correct explanation of the Assertion.

(c) Assertion is correct but Reason is incorrect.

(d) Both the Assertion and Reason are incorrect.

Ans : (c) Assertion is correct but Reason is incorrect.

The complex dissociates to give $[Co(NH_3)_5Br]^{2-}$ and SO_4^{2-} ions. SO_4^{2-} ion reacts with barium chloride to give white ppt. of $BaSO_4$.

$$SO_4^{2-} + BaCl_2 \longrightarrow BaSO_4 + 2Cl^-$$

16. **Assertion :** Nitration of benzoic acid gives *m*-intro-benzoic acid.
Reason : Carboxyl group increases the electron density at meta-position.

(a) Both Assertion and Reason are correct and Reason is a correct explanation of the Assertion.

(b) Both Assertion and Reason are correct but Reason is not the a correct explanation of the Assertion.

(c) Assertion is correct but Reason is incorrect.

(d) Both the Assertion and Reason are incorrect.

Ans : (c) Assertion is correct but Reason is incorrect.

Carboxyl group only marginally decreases the electron density at *m*-position relative to *o*-and *p*-positions.

SECTION-B

Directions (Q. Nos. 17-21) : This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

17. Define ideal solution.

Ans :

The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions. For ideal solutions, $\Delta H(\text{mixing}) = 0$n and $\Delta V(\text{mixing}) = 0$, e.g. solution of *n*-hexane and *n*-hepane, bromoethane and chloroethane, etc.
In these solution (binary solutions), $A - B$ type (i.e. solute-solvet) interactions.

18. What are symmetrical and unsymmetrical ether ?

Ans :

Ether are classified as simple or symmetrical if the alkyl or aryl groups attached to the oxygen atom are the same and mixed or unsymmetrical, if the two groups are different. Diethyl ether $CH_3CH_2OCH_2CH_3$ is a symmetrical. Ether whereas $CH_3CH_2OCH_3$ is an unsymmetrical ether.

19. Name the two half-cell reactions that are taking place in the Daniel cell.

Ans :

The two half cell reactions that are takes place in the Daniel cell are oxidation and reduction.

$$Zn \longrightarrow Zn^{+2} + 2e^- \qquad \text{(Oxdiation)}$$

$$Cu^{+2} \longrightarrow Cu \qquad \text{(Reduction)}$$

20. Name the following compounds according to IUPAC system of nomenclature :

1. $CH_3CH(CH_3)CH_2CH_2CHO$
2. $CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl$
3. $CH_3CH = CHCHO$
4. $CH_3COCH_2COCH_3$

Ans :

1. 4-Mthylpentanal.
2. 6-Chloro-4-ethylhexan-3-one.
3. But-2-enal.
4. Pentane-2, 4-dione.

or

Write natural sources of formic acid, acetic acid and butyric acid.

Ans :

Formic acid (HCOOH) was first obtained from red ants (Latin formica means ant), acetic acid (CH_3COOH) from Vinegar (Latin; acetum), butyric acid ($CH_3CH_2CH_2COOH$) from rancid butter (Latin : butyrum, means butter).

21. Predict the geometrical shapes of all following :
(a) sp^3
(b) d^2sp^3

Ans :

(a) sp^3 → As 4-orbitals undergo for hybridisation, the geometry is tetrahedral.
(b) d^2sp^3 → As 6-orbitals undergo for hybridisation and the geometry is octahedral.

SECTION-C

Directions (Q. Nos. 22-28) : This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each.

22. Identify the compounds A, B, C and D in the following sequence of reactions :

$$C_2H_5OH \xrightarrow[443\,K]{\text{conc. } H_2SO_4} A \xrightarrow{HBr} B \xrightarrow[443\,K]{KOH\,(aq)} C \xrightarrow{I_2,NaOH} D$$

Ans :

$$C_2H_5OH \xrightarrow[443\,K]{\text{conc. } H_2SO_4} \underset{(A)}{CH_2=CH_2} \xrightarrow{HBr} \underset{(B)}{CH_3CH_2Br}$$

$$\underset{(B)}{CH_3CH_2Br} \xrightarrow{KOH(aq.)} \underset{(C)}{CH_3CH_2OH} \xrightarrow{I_2/NaOH} \underset{\text{yellow ppt.}}{\underset{(D)}{CHI_3}}$$

23. How is a galvanic cell represented on paper as per IUPAC convention? Give one example.

Ans :

Representation of a Galvanic cell :
As per IUPAC convention
→ Oxidation half cell represented on the left side.
→ Reduction half cell represented on the right side.
→ Oxidation half cell and reduction half cell are connected by a salt bridge indicated by two vertical parallel lines.
Eg. : $Cu_{(s)} \mid Cu^{+2}_{(aq)} \parallel Ag^{+}_{(aq)} \mid Ag_{(s)}$

24. Derive equilibrium constant from Nernst equation

Ans :

Consider the following cell reaction :

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

Nernst equation for this cell reaction at 298 K is

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$= E^{\circ}_{cell} - \frac{0.0591}{n}\log Q_C$$

Where Q_C is concentration quotient.

At equilibrium, $E_{cell} = 0$ and $Q_C = K_C$

or $E^{\circ}_{cell} = \frac{0.0591}{n}\log K_C (\text{at } 298\,K)$

25. (a) Give the IUPAC name of the complex salt $K_3[Fe(CN)_6]$.
(b) Calculate EAN (Effective Atomic Number) of Fe in this complex salt.

Ans :

(a) $K_3[Fe(CN)_6]$ = Potassium hexacynoferate(III).
(b) **The effective atomic number (EAN) of Fe is calculated as follows :** The oxidation state of Fe in the complex $= +3$.
Number of electrons in Fe^{3+}ion $= 23$.
Number of electrons gained by coordination with $6(CN^-)$ ligands $= 2 \times 6 = 12$ (Since one CN ion gives 2 electrons).
Total number of electrons in Fe^{+3} ion after coordination $= 23 + 12 = 35$.
Therefore, EAN of Fe in complex is (35).

26. Point out the difference between :
(i) Chirality and chiral centre.
(ii) Diastereoisomers and Enantiomers.

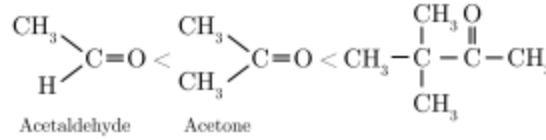
Ans :

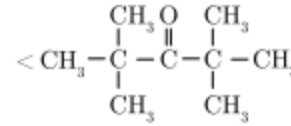
(i) **Chirality :** The phenomena of a molecule containing a carbon atom attached to four different atoms or groups of atom and thus making the mirror image of the molecule non-superimposable on the molecule is called chirality.
Chiral Centre : The carbon atom which is attached to four different atoms or groups of atoms is called the chiral centre.
(ii) **Diastereoisomers :** Those pairs of stereoisomers which are not mirror images of each other and differ in optical rotation.
Enantiomers : They are non-superimposable mirror images of molecules with each other. They have optical rotation equal in magnitude but opposite in sign.

27. Arrange the following compounds in increasing order of their reactivity toward HCN.
Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone.

Ans :

The order of +I effect and steric hindrance is-





Reactivity towards HCN addition decreases with increases in +I effect and steric hindrance. Thus the increasing order of reactivity is

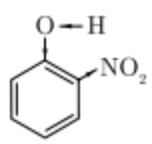
Di-tert-cutyl ketone<Methyl-tert-butyl ketone>Acetone <Acetaldehyde.

or

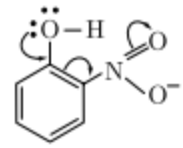
Explain why is ortho-nitrophenol more acidic than ortho-methoxy phenol ?

Ans :

Due to strong $-R$ and $-I$ effect of the $-NO_2$ group, electron density in the O–H bond decreases and hence the loss of proton becomes easy.

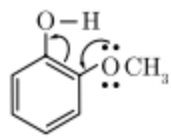


–I Effect



–R Effect

In ortho-methoxyphenol due to + R effect of the OCH_3 group, the electron density in the O–H bond increases which makes the loss of a proton difficult.



Thus, o-nitrophenol is more acidic than o-methoxyphenol.

28. In a reaction, the rates of disappearance of different reactants or rates of formation of different products may not be equal but rate of reaction at any instant of time has the same value expressed in terms of any reactant or product. Further, the rate of reaction may not depend upon the stoichiometric coefficients of the balanced chemical equation. The exact powers of molar concentrations of reactants on which rate depends are found experimentally and expressed in terms of 'order of reaction: Each reaction has a characteristic rate constant depends upon temperature. The units of the rate constant depend upon the order of reaction.

Answer the following questions :

(a) The rate constant of a reaction is found to be $3 \times 10^{-3} \text{mol}^{-2}\text{L}^2\,\text{sec}^{-1}$. What is the order of the reaction?

(b) Rate of a reaction can be expressed by following rate expression, Rate $= k[A]^2[B]$, if concentration of A is increased by 3 times and concentration of B is increased by 2 times, how many times rate of reaction increases?

(c) The rate of a certain reaction is given by, rate $= k[\text{H}^+]^n$. The rate increases 100 times when the pH changes from 3 to 1. What is the order (n) of the reaction ?

or

(d) In a chemical reaction $A + 2B \rightarrow$ products, when concentration of A is doubled, rate of the reaction increases 4 times and when concentration of B alone is doubled rate continues to be the same. What is the order of the reaction ?

Ans :

(a) Unit of k for n^{th} order

$$= (\text{mol L}^{-1})^{1-n}\text{sec}^{-1} \quad \ldots(1)$$

Here, $k = 3 \times 10^{-3}\,\text{mol}^{-2}\,\text{L}^2\,\text{sec}^{-1}$

Unit of $k = \text{mol}^{-2}\,\text{L}^2\,\text{sec}^{-1}$

$$= (\text{mol L}^{-1})^{-2}\,\text{sec}^{-1} \quad \ldots(2)$$

Comparing (i) and (ii) we get,

$$1 - n = -2$$

$$n = 3$$

(b) Given,

$$R_1 = k[A]^2[B]$$

According to question,

$$R_2 = k[3A]^2[2B]$$

$$= k \times 9[A]^2 \times 2[B]$$

$$= 18 \times k[A]^2[B] = 18R_1$$

(c) Rate, $r = k[\text{H}^+]^n$

When, $\text{pH} = 3;\ [\text{H}^+] = 10^{-3}$

and when, $\text{pH} = 1;\ [\text{H}^+] = 10^{-1}$

$$\frac{r_1}{r_2} = \frac{k(10^{-3})^n}{k(10^{-1})^n}$$

$$\frac{1}{100} = \left(\frac{10^{-3}}{10^{-1}}\right)^n \qquad (r_2 = 100r_1)$$

$$(10^{-2})^1 = (10^{-2})^n$$

$$n = 1$$

or

(d) Let the order of reaction w.r.t. A is x and w.r.t. B is y

$$r_1 = k[A]^x[B]^y \quad \ldots(1)$$

$$r_2 = k[2A]^x[B]^y \quad \ldots(2)$$

$$r_3 = k[A]^x[2B]^y \quad \ldots(3)$$

$$\frac{r_1}{r_2} = \frac{k[A]^x[B]^y}{k[2A]^x[B]^y}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^x$$

$$\left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^x$$

$$x = 2$$

Similarly, $\frac{r_1}{r_3} = \frac{k[A]^x[B]^y}{= k[A]^x[2B]^y}$

$$1 = \left(\frac{1}{2}\right)^y$$

$$\left(\frac{1}{2}\right)^0 = \left(\frac{1}{2}\right)^y$$

$$y = 0$$

SECTION-D

Directions (Q. Nos. 29-30) : The following questions are case-based questions. Each question has an internal choice and carries 4 marks each. Read the passage carefully and answer the questions that follow.

29. The solubility of gases increases with increase of pressure. William Henry made a systematic investigation of the solubility of a gas in a liquid. According to Henry's law "the mass of a gas dissolved per unit volume of the solvent at constant temperature is directly proportional to the pressure of the gas in equilibrium with the solution".
Dalton during the same period also concluded independently that the solubility of a gas in a liquid solution depends upon the partial pressure of the gas. If we use the mole fraction of gas in the solution as a measure of its solubility, then Henry's law can be modified as "the partial pressure of the gas in the vapour phase is directly proportional to the mole fraction of the gas in the solution."
Read the above passage and answer the following questions:
(a) What is the relation of K_H with temperature ?
(b) Write expression for Henry's law.
(c) Calculate solubility of methane in benzene at 298 K under 760 mm Hg. (Given Henry's constant = 4.27×10^5 mm Hg) ?

or

(d) The partial pressure of ethane over a saturated solution containing 6.56×10^{-2} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane then what will be the partial pressure (in bar) of the gas ?

Ans :

(a) K_H, increases with temperature.

(b) $p = K_H \times x$

(c) $K_H = 4.27 \times 10^5$ mm Hg

$p = 760$ mm Hg

According to Henry's law,

$$p = K_H \times x_{CH_4}$$

$$x_{CH_4} = \frac{p}{K_H} = \frac{760}{4.27 \times 10^5}$$

$$= 1.78 \times 10^{-3}$$

or

(d) According to Henry's law,

$$m = K_H \times p$$

$$6.56 \times 10^{-2} = K_H \times 1$$

$$K_H = 6.56 \times 10^{-2}$$

For another case,

$$5 \times 10^{-2} = 6.56 \times 10^{-2} \times p$$

$$p = \frac{5 \times 10^{-2}}{6.56 \times 10^{-2}} = 0.762 \text{ bar}$$

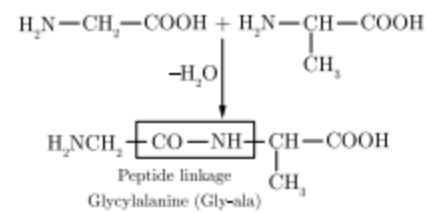
30. Proteins are high molecular mass complex biomolecules of amino acids. The important proteins required for our body are enzymes, hormones, antibodies, transport proteins, structural proteins, contractile proteins etc. Except for glycine, all α −amino acids have chiral carbon atom and most of them have L-configuration. The amino acids exists as dipolar ion called zwitter ion, in which a proton goes from the carboxyl group to the amino group. A large number of α-amino acids are joined by peptide bonds forming polypeptides. The peptides having very large molecular mass (more than 10,000) are called proteins. The structure of proteins is described as primary structure giving sequence of linking of amino acids; secondary structure giving manner in which polypeptide chains are arranged and folded; tertiary structure giving folding, coiling or bonding polypeptide chains producing three dimensional structures and quaternary structure giving arrangement of sub-units in an aggregate protein molecule.
Answer the following questions :
(a) What do you mean by proteins ?
(b) What is Zwitter ion ?
(c) Which type of bond is present in polypeptide? Give example ?

or

(d) Which type of bonding is present in α-helix and (β -pleated structure of proteins.

Ans :

(a) Proteins are high molecular mass complex biomolecules of amino acids these are the polymer of amino acid joined together through amide linkages.
(b) In aqueous solution, carboryl ion loses a proton and amino group can accept a proton, dipolar ion is formed called zwitter ion.
(c) Peptide linkage is present in polypeptides.



or

(d) Intramolecular H-bonding is present in helix and intermolecular H-bonding is present in β −pleated structure of proteins.

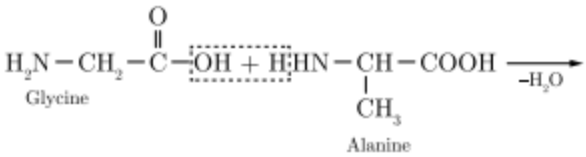
SECTION-E

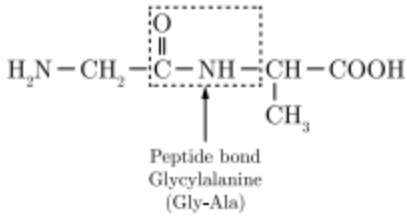
Directions (Q. Nos. 31-33) : The following questions are long answer type and carry 5 marks each. Two questions have an internal choice.

31. Define the following as related to proteins.
(i) Peptide linkage.
(ii) Primary structure.
(iii) Denaturation.

Ans :

(i) **Peptide Linkage :** Proteins are condensation polymers of α-amion acids, these amino acids are connected by peptide bond or peptide linkage.
Chemically peptide linkage is an amide formed between $-COOH$ group of one amino acids and $-NH_2$ group of the other amino acid by loss of a molecule of water.





(ii) **Primary Structure (1°) :** Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other. The specific sequence in which the various α-amino acids forming a protein are linked to one another is called its primary structure.

(iii) **Denaturation :** When a protein is subjected to physical changes such as change in temperature, pH etc. hydrogen bonds are broken. Due to cleavage of hydrogen bonds, unfolding of protein molecule occurs and the protein loses in biological activity. This loss of biological activity is called denaturation. The coagulation of egg white on boiling is common example of denaturation.

32. Define order of reaction and molecularity of reaction. Derive a general expression for specific rate constant of first order reaction.

Ans :

Order of reaction : Order of reaction is the sum of exponents of the molar concentrations of the reactants in the rate equation :
For a general reaction $aX - bY \rightarrow$ Product

$$\text{Rate} = k[X]^m.[Y]^n$$

$$\text{Order of reaction} = m + n$$

Molecularity of reaction : It is the number of atoms, ions or molecules that collides with one another simultaneously so as to result into a chemical reaction.
General Expression

$$A \longrightarrow \text{Product}$$

A is $(a - X)\text{mol}\,l^{-1}$
For First order reaction

$$\frac{dX}{dt} = k(a - X) \quad \text{Where k is the rate constant}$$

Hence, $\frac{dX}{a - X} = kdt$ (integrating)

$$\int \frac{dx}{a - X} = k\int dt$$

$$-\ln(a - X) = Kt + C \qquad ...(1)$$

C is the constant of integration
At $t = 0,\ x = 0$ then equation (1) we have

$$C = \ln a$$

Putting the value of C in equation (1),

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

$$K = \frac{1}{t}\ln\frac{a}{a - x}$$

Hence, $$K = \frac{2.303}{t}\log\frac{a}{a - x} \qquad ...(2)$$

Above is the general expression for specific rate constant of first order reaction.

or

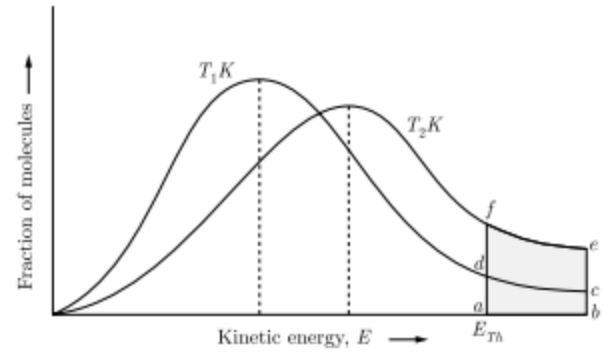
Explain the effect of temperature on rate of a reaction.

Ans :

Temperature coefficient is the ratio of two rates of reactions or rate constants that differ by 10 K.

$$\text{Temperature coefficient} = \frac{\text{Rate of reaction at } 310K}{\text{Rate of reaction at } 300K}$$

For most of the reaction its value is approximately 2. This can be explained as follows :
Explantion : All the reacting molecules do not have the same kinetic energy. However, fractions of molecule having a particular kinetic at a particular temperature remains constant. At a particular temperature, if fractions of molecules are plotted versus corresponding kinetic energies, a graph of the type shown in fig. is obtained (called Maxwell's distribution of energies). The peak of the curve represents the kinetic energy possessed by the maximum fraction of molecules and is called most probable kinetic energy. If the point a represent threshold energy, the shaded area abed represents the fraction of molecules having energy greater than threshold value.



When the temperature is increased to $T + 10°$, the curve shift as shown in Fig. Now the fraction of molecule having

kinetic energy greater than threshold value is represented by the shaded area abef which is almost double than the area abed. Thus the increase in the rate of reaction with increase in temperature is mainly due to increase in the number of effective collisions.

33. Explain giving reasons:

1. Transition metals and many of their compounds show paramagnetic behaviour.
2. The enthalpies of atomisation of the transition metals are high.
3. The transition metals generally form coloured compounds.
4. Transition metals and their many compounds act as good catalysts.

Ans :

1. Transition elements have unpaired electrons. Each unpaired electron has a magnetic moment associated with its spin angular momentum and orbital angular momentum. This is the reason of paramagnetism in transition metals.
2. The reason for the high enthalpy of atomisation is the presence of large number of unpaired electrons in their atoms. These atoms have strong interatomic interaction and hence, stronger bonding between them.
3. Formation of coloured compounds by transition metals is due to partial adsorption of visible light. The electron absorbs the radiation of a particular frequency (of visible region) and jumps into next orbital.
4. Catalysts, at the solid surface, involve the formation of bonds between reactants molecules and atoms of the surface of the catalyst (I row transition metal utilise $3d$and $4s$-electrons for bonding). This has the effect of increasing the concentration of the reactant at the catalyst surface and also lowering of the activation energy.
   Transition metal ions show variable oxidation states, so they are effective catalysts.
   e.g. Reaction,
   $2I^- + S_2O_8^{2-} \xrightarrow{Fe^{3+}} I_2 + 2SO_4^{2-}$
   Mechanism of catalysing action of Fe^{3+} in the above reaction.
   (a) $2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$
   (b) $2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$

or

Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) ion (II) ions (ii) SO_2 and (iii) oxalic acid? Write the ionic equations.

Ans :

Preparation of $KMnO_4$ potassium permanganate is prepared by the fusion of MnO_2 with and alkali metal hydroxide and an oxidising agent like KNO_3. It forms dark green, K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.

1. $2MnO_2 + 4KOH + O_2 \xrightarrow{KNO_3} 2K_2MnO_4 + 2H_2O$

2. $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$
   or $3K_2MnO_4 + 2H_2SO_4 \longrightarrow \underset{\text{Potassium permanganate}}{2KMnO_4} + 2K_2SO_4 + MnO_2 + 2H_2O$

   Reactions of $KMnO_4$ in acidic medium,

   $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ ...(1)

1. Iron (II) ions ferrous is oxidise to ferric.

   $[Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 5$ ...(2)

   From equation (1) and (2),

   $5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

2. SO_2 : It is oxidised to SO_4^{2-} by acidified $KMnO_4$

   $SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$ ...(3)

   From equation (i) and (3)

   $5SO_2 + 2MnO_4^- + 2H_2O \longrightarrow 2Mn^{2+} + 4H^+ + 5SO_4^{2-}$

   Oxalic acid : $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$ ...(4)

   From equation (1) and (4),

   $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

□□□□□□□