C.B.S.E. CLASS–XII–2015
CHEMISTRY (Theory)
SET–I (DELHI BOARD)

Time allowed: 3 hours

Maximum Marks: 70

General Instructions:

(i) All questions are compulsory.

(ii) Q. no. 1 to 5 are very short-answer questions and carry 1 mark each,

(in) Q. no. 6 to 10 are short-answer questions and carry 2 marks each.

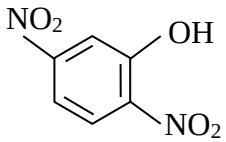
(iv) Q. no. 11 to 22 are also short-answer questions and carry 3 marks each.

(v) Q. no. 23 is a value based question and carry 4 marks.

(vi) Q. no. 24 to 26 are long-answer questions and carry 5 marks each.

1. What is the basicity of H_3PO_4?

2. Write the IUPAC name of the given compound:



3. Which would undergo S_N2 reaction faster in the following pair and why?

$$CH_2-CH_2-Br \text{ and } CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

4. Out of $BaCl_2$ and KCl, which one is more effective in causing coagulation of a negatively charged colloidal Sol ? Give reason.

5. What is the formula of a compound in which the element Y forms ccp lattice and atoms of X occupy 1/3rd of tetrahedral voids?

6. What are the transition elements? Write two characteristics of the transition elements.

7. (i) Write down the IUPAC name of the following complex:

$[Cr(NH_3)_2Cl_2(en)]Cl$

(en = ethylenediamine)

(ii) Write the formula for the following complex:

Pentaamminenitrito-o-Cobalt (III).

8. Name the reagents used in the following reactions:

(i)

$$CH_3-CO-CH_3 \xrightarrow{?} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

(ii)

$$C_6H_5-CH_2-CH_3 \xrightarrow{?} C_6H_5-COO^-K^+$$

(iii) $C_6H_5-CH_2-CH_3 \xrightarrow{?} C_6H_5-COO^-K^+$

9. What is meant by positive deviations from Raoult's law? Give an example. What is the sign of $\Delta_{mix}H$ for positive deviation?

OR

Define azeotropes. What type of azeotrope is formed by positive deviation from Raoult's law? Give an example.

10. (a) Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution:

$$Ag^+(aq)+e^- \longrightarrow Ag(s) \quad E^o=+0.80V$$

$$H^+(aq)+e^- \longrightarrow \frac{1}{2}H_2(g) \quad E^o=0.00V$$

On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why?

(b) Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with the decrease in concentration ?

11. 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K Calculate the van't Hoff factor and predict the nature of solute (associated or dissociated).

(Given : Molar mass of benzoic acid = 122 g mol^{-1}, K_f for benzene = 4.9 K kg mol^{-1})

12. (i) Indicate the principle behind the method used for the refining of zinc.

(ii) What is the role of silica in the extraction of copper?

(iii) Which form of the iron is the purest form of commercial iron?

13. An element with molar mass 27 g mol^{-1} forms a cubic unit cell with edge length 4.05×10^{-8} cm. If its density is 2.7 g cm^{-3}, what is the nature of the cubic unit cell?

14. (a) How would you account for the following:

(i) Actionoid contraction is greater than lanthanoid contraction.

(ii) Transition metals form coloured compounds.

(b) Complete chemical equation is given below :

$$2MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow$$

15. (i) Draw the geometrical isomers of complex $[Pt(NH_3)_2Cl_2]$.

(ii) On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_o < P$.

(iii)Write the hybridization and magnetic behaviour of the complex $[Ni(CO)_4]$.

(At no. of Ni = 28).

16. Calculate emf of the following cell at 25°C:

Fe $|Fe^{2+}(0.001M) \| H^+ (0.01M) | H_2(g)$ (1bar) | Pt(s)

$E° (Fe^{2+} | Fe) = -0.44$ V $E° (H^+ | H_2) = 0.00$ V

17. Give reasons for the following observations:

(i) Leather gets hardened after tanning.

(ii) Lyophilic sol is more stable than lyophobic soil.

(iii) It is necessary to remove CO when ammonia is prepared by Haber's process.

18. Write the names and structures of the monomers of the following polymers :

(i) Nylon–6, 6

(ii) PHBV

(iii) Neoprene

19. Predict the products of the following reactions :

(i) $CH_2-\underset{\underset{CH_3}{|}}{C}=O \xrightarrow[(ii)KOH/Glycol,\Delta]{(i)H_2N-NH_3} ?$

(ii) $C_6H_5-CO-CH_3 \xrightarrow{NaOH/I_2} ?$

(iii) $CH_3COONa \xrightarrow[\Delta]{NaOH/CaO} ?$

20. How do you convert the following :

(i) Phenol to anisole

(ii) Propan–2–ol to 2–methylpropan–2–ol

(iii) Aniline to phenol

OR

(a) Write the mechanism of the following reaction :

$$2CH_3CH_2OH \xrightarrow{H^+} CH_3CH_2–O–CH_2CH_3$$

(b) Write the equation involved in the acetylation of Salicylic acid

21.

(i) Which one of the following is a disaccharide : Starch, Maltose, Fructose, Glucose ?

(ii) What is the difference between fibrous protein and globular protein ?

(iii) Write the name of vitamin whose deficiency causes bone deformities in children

22. Give reasons:

(a) n–Butyl bromide has higher boiling point than t–butyl bromide.

(b) Racemic mixture is optically inactive.

(c) The presence of nitro group (– NO_2) at o/p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.

23. Mr. Roy, the principal of one reputed school organized a seminar in which he invited parents and principals to discuss the serious issue of diabetes and depression in students. They all resolved this issue by strictly banning the junk food in schools and to introduce healthy snacks and drinks like soup, lassi, milk etc in school canteens. They also decided to make compulsory half an hour physical activities for the students in the morning assembly daily. After six months, Mr. Roy conducted the health survey in most of the schools and discovered a tremendous improvement in the health of students.

After reading the above passage, answer the following:

(i) What are the values (at least two) displayed by Mr. Roy?

(ii) As a student, how can you spread awareness about this issue?

(iii) What are tranquilizers? Give an example.

(iv) Why is use of aspartame limited to cold foods and drinks?

24.

(a) Account for the following:

(i) Acidic character increases from HF to HI.

(ii) There is large difference between the melting and boiling points of oxygen and sulphur.

(iii) Nitrogen does not form pentahalide.

(b) Draw the structures of the following:

(i) ClF_3, (ii) XeF_4

OR

(i) Which allotrope of phosphorus is more reactive and why?

(ii) How the supersonic jet aeroplanes are responsible for the depletion of ozone layers?

(iii) F_2 has lower bond dissociation enthalpy than Cl_2. Why?

(iv) Which noble gas is used in filling balloons for meteorological observations ?

(v) Complete the equation:

$$XeF_2 + PF_5 \longrightarrow$$

25. An aromatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown belowWrite the structures of A, B, C, D and E in the following reactions:

$$(C_7H_7OH)A \xrightarrow{Br_2+KOH} C_6H_5NH_2 \xrightarrow[273K]{NaNO_2+HCl} B \xrightarrow{CH_3CH_2OH} C$$

$$C_6H_5NH_2 \downarrow CHCl_3 + NaOH \quad D$$

$$B \downarrow KI \quad E$$

OR

(a) Write the structures of main products when aniline reacts with the following reagents :

(i) Br_2 water, (ii) HCl,

(iii) $(CH_3CO)_2O$/pyridine.

(b) Arrange the following in the increasing order of their boiling point:

$C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$

(c) Give a simple chemical test to distinguish between the following pair of compounds: $(CH_3)_2NH$ and $(CH_3)_3N$

26. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained:

t/s	0	30	60
$[CH_3COOCH_3]$ /mol L^{-1}	0.60	0.30	0.15

(i) Show that it follows pseudo first order reaction, as the concentration of water remains constant.

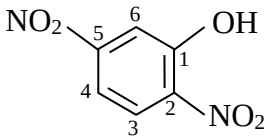
(ii) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

(Given log 2 = 0.3010, log 4 = 0.6021)

SOLUTION

1. H_3PO_4 has three ionisable hydrogen atoms Hence, its basicity is 3.

2.



2, 5-Dinitrophenol

3. Primary alkyl halides prefer to undergo S_N2 reactions than tertiary alkyl halides because of less steric hindrance experienced by the approaching nucleophile.

Hence, out of the given pair ($CH_3–CH_2–Br$) would undergo S_N2 reaction faster.

4. According to the Hardy-Schulze rule, the greater the valency of a flocculating ion, the greater is its power to cause precipitation Between Ba^{2+} (from $BaCl_2$) and IO (from KCI), Ba^{2+} has greater valency Therefore, $BaCl_2$ will be more effective in causing the coagulation of a negatively charged colloidal sol.

5. Number of tetrahedral voids formed = 2 Number of atoms of element Y

Number of atoms of element Y in the ccp unit cell = 4

Number of tetrahedral voids formed = 2= 4 = 8

Number of tetrahedral voids occupied by atoms of X = Ratio of the number of atoms of X and Y

$= \frac{8}{3} : 4 = 2 : 3$

Hence, the formula of the compound is X_2Y_3.

6. Elements that possess incompletely filled d-orbitals either in their ground state orin any of their oxidation states are known as transition elements. The name 'transition'given to the elements of d–block is only because of their position between s–block and p-block elements.

Characteristics of transition elements are as follows :

1. They show paramagnetic behaviour.
2. They show variable oxidation states.
3. They exhibit catalytic properties.
4. They generally form complex compounds.
5. They generally form coloured compounds.

7.

(i) $[Cr(NH_3)_2Cl_2(en)]Cl$

IUPAC Name : Diamminedichloridobis (ethane-l,2-diamine) chromium (III) chloride

(ii) Pentaamminenitrito–O–Cobalt (III)

Formula: $[Co(NH_3)_5(ONO)]^{2+}$

8. (i)

$$CH_3-CH-CH_3 \xrightarrow{NaBH_4} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

(i)

$$C_6H_5-CH_2-CH_3 \xrightarrow[\text{Heat}]{KMnO_4-KOH} C_6H_5-COO^-K^+$$

Name of the reagent: Alkaline potassium permanganate ($KMnO_4$ – KOH)

9. The solutions that do not obey Raoult's law over the entire range of concentration are known as non–ideal solutions. They have vapour pressures either higher or lower than those predicted by Raoult's law. If the vapour pressure is higher, then the solution is said to exhibit a positive deviation from Raoult's law.

OR

Azeotropes are the binary mixtures of solutions that have the same composition in liquid and vapour phases and that have constant boiling points.

A minimum-boiling azeotrope is formed by solutions showing a large positive deviation from Raoult's law at a specific composition.

Example : An ethanol–water mixture containing approximately 95% ethanol by Volume.

10. (a) Given:

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \quad E^o = +0.80V$$

$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g) \quad E^o = 0.00V$$

The relationship between the standard tree energy change and *emf* of a cell reaction is given by $\Delta G° = – nFE°$

Thus, the more positive the standard reduction potential of a reaction the more negative is the standard free energy change associated with the process and, consequently, the higher is the feasibility of the reaction.

Since $E^\circ_{Ag^+/Ag}$ has a greater positive value than $E^\circ_{H^+/H}$ the reaction which is feasible at the cathode is given by

$Ag^+(aq) + e^- \rightarrow Ag(s)$

(b) The limiting molar conductivity of an electrolyte is defined as its molar conductivity when the concentration of the electrolyte in the solution approaches zero.

The conductivity of an electrolyte solution is the conductance of ions present in a unit volume of the solution. The number of ions (responsible for carrying current) decreases when the solution is diluted of the concentration is decreased. As a result, the conductivity of an electrolyte solution decreases with the decrease in the concentration.

11. We know that the depression in freezing point is given by

$$\Delta T_f = iK_f \frac{w_s \times 100}{M_S \times W}$$

Here,

van't Hoff factor = *i*

Depression in freezing point, $\Delta T_f = 1.62$ K

K_f for benzene = 4.9 K kg mol^{-1}

Mass of benzoic acid, w_s = 3.9 g

Mass of benzene, W = 49 g

Molar mass of benzoic acid, M_s = 122g mol^{-1}

Substituting the values, we get

$$1.62 = i \times 4.9 \times \frac{3.9 \times 1000}{122 \times 49}$$

$$\Rightarrow i = \frac{1.62 \times 122 \times 49}{4.9 \times 3.9 \times 1000} = 0.51$$

As the value of i < 1, benzoic acid is an associated solute. 12. (i) Zinc is refined using electrolytic refining process. In this process, pure zinc is transported to cathode from the impure sample at anode. The more basic metal remains in the electrolytic solution and the less basic metals, present as impurities, precipitate as anode mud.

Electrode	Chemical Reaction
Anode	$Zn \rightarrow {}^{+} + 2e^-$ (From Zn^2anode)
Cathode	$Zn^{2+} + 2e^- \rightarrow Zn$ (From electrolyte)

(ii) Ores of copper contain iron oxide as impurity. Silica reacts with iron oxide and forms iron silicate, which is removed as slag.

FeO	+	SiO_2	$\rightarrow$	$FeSiO_3$
Iron oxide		Silica (slag)		Iron silicate

(iii) Wrought iron is the purest form of commercial iron. 13. Molar mass of the given element,

M = 27 g mol^{-1} = 0.027 kg mol^{-1}

Edge length,

a = 4.05 x 10^{-8} cm

= 4.05 × 10^{-10}m

Density, d = 2.7g cm^{-3}

= 2.7 × 10^3 kg m^{-3}

Applying the relation,

$$d = \frac{Z \times M}{a^3 \times N_A}$$

Where, Z is the number of atoms in the unit cell and N_A is the Avogadro number.

Thus,

$$Z = \frac{d \times a^3 \times N_A}{M}$$

$$= \frac{2.7 \times 10^3 \times (4.05 \times 10^{-10})^3 \times 6.022 \times 10^{23}}{0.027}$$

= 4

Since the number of atoms in the unit cell is four, the given cubic unit cell has a face-centered cubic (fcc) or cubic-closed packed (ccp) structure.

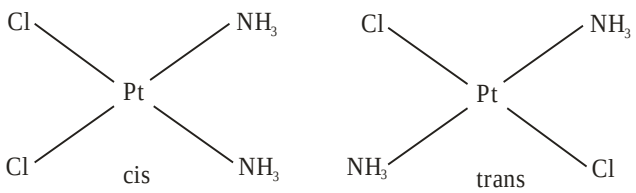
14. (a) (i) In actinides, 5 f-orbitals are filled. These 5 f-orbitals have a poorer shielding effect than 4 f-orbitals (in lanthanoids). Thus, the effective nuclear charge experienced by electrons in valence shells in case of actinoids is much more than that experienced by electrons in valence shells in case of case of actinoids is much more than that experienced by electrons in valence shells in case of lanthanoids. Hence, the size contraction in actinoids is greater than that in lanthanoids.

(ii) In the presence of ligands, the d-orbitals of transition metal ions split up into two sets of orbitals having different energies. Thus, the transition of electrons takes place from one set to another. The energy required for these transitions is quite less and falls in the visible region of radiation. The ions of transition metals absorb the radiation of a particular wavelength and the rest is reflected, imparting colour to the solution.

(b) The complete chemical equation is given below :

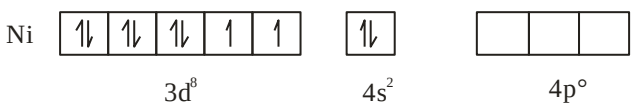
$$2MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

15. (i) Geometrical isomers of complex $[Pt(NH_3)_2Cl_2]$

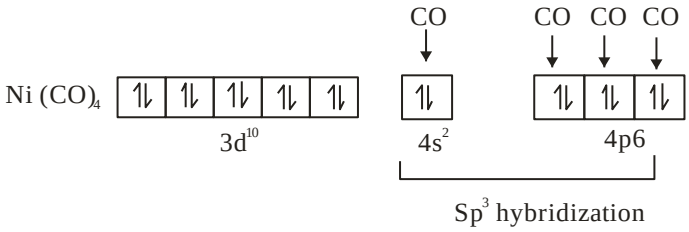


(ii) On the basis of crystal field theory, for a d^4 ion, if Δ_o < P, then the complex is a high spin complex formed by association of weak field ligands with the metal ion. As a result, the fourth election enters one of the e_g orbitals, thereby exhibiting the electronic configuration $t_{2g}3^e{}_{g^1}$.

(iii) Outer electronic configuration of Ni atom in ground state



Outer electronic configuration of Ni atom in Ni $(CO)_4$



Carbonyl, CO being a strong field ligand causes the pairing of up valence electrons in the Ni atom against the Hund's Rule of Maximum Multiplicity. This results in the formation of an inner orbital complex, $[Ni(CO)_4]$ having diamagnetic character $[Ni(CO)_4]$ has sp^3 hybridization.

16. For the given cell representation, the cell reaction will be

$$Fe(s) + 2H^+(aq) \longrightarrow Fe^{2+}(aq) + H_2(g)$$

The standard emf of the cell will be

$$E^\circ_{cell} = E^\circ_{H^+/H_2} - E^\circ_{Fe^{2+}/Fe}$$

$$\Rightarrow E^o_{cell} = 0-(-0.44) = 0.44\ V$$

The Nernst equation for the cell reaction at 25 °C will be

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log\frac{[Fe^2]}{[H^+]^2}$$

$$= 0.44\ \frac{0.0591}{2}\log\frac{0.001}{(0.01)^2}$$

$= 0.44 - 0.02955$ (log 10)

$= 0.44 - 0.02955(1)$

$= 0.41045\ V \approx 0.41V$

17. (i) Animal skin (hide) is colloidal in nature and has positively charged particles, whereas tanning consists of negatively charged colloidal particles. When a hide is soaked in tanning, mutual coagulation takes place and as a result, leather gets hardened.

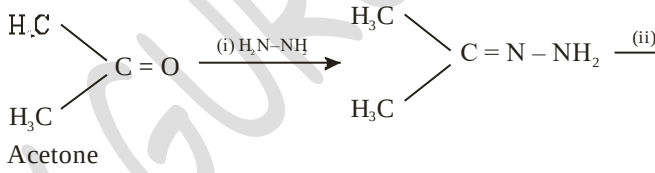
(ii) The stability of lyophilic sols is a result of two factors, the presence of a charge and the solvation of colloidal particles. On the other hand, the stability of lyophobic sols is only because of the presence of a charge. Thus, lyophilic sol is more stable than lyophobic sol due to the extensive solvaltion.

(iii) It is necessary to remove CO when ammonia is prepared by Haber's process because CO acts as a poison and adversely affects the activity of iron catalyst, used in the process.

18.

Polymers	Name of Monomer(s)	Structure
(i) Nylon –6, 6	Hexamethylenediamine and adipic acid	$H_2N-CH_2-CH_2-CH_2-CH_2-NH_2$ Hexamethylenediamine $HOOC–CH_2–CH_2–CH_2–CH_2–COOH$ Adipic acid
(ii) PHBV	3–Hydroxypentanoic acid and 3–Hydroxybutanoic acid	$CH_3-CH_2-CH(OH)-CH_2-COOH$ 3–Hydroxypentanoic acid $CH_3-CH(OH)-CH_2-COOH$ 3–Hydroxybutanoic acid
(iii) Neoprene	Chloroprene	$H_2C=C(Cl)-C(H)=CH_2$ Chloroprene

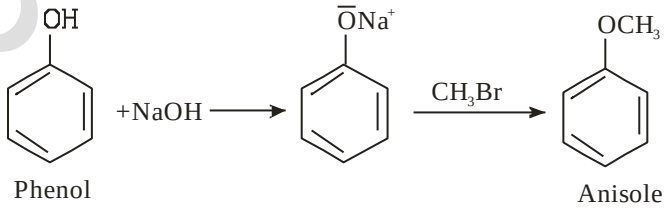
19. (i)

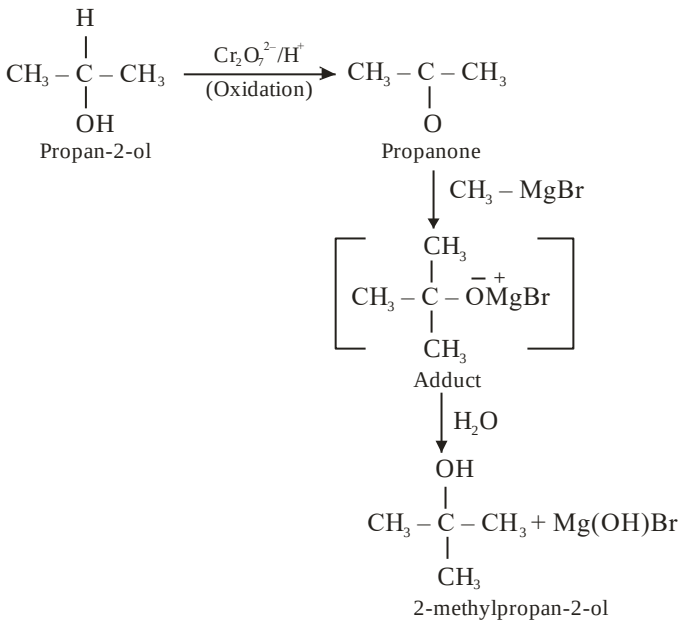


(ii)

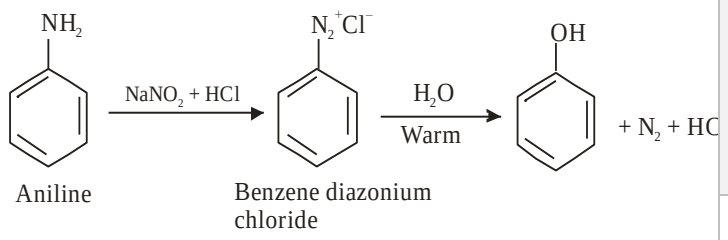
$$\underset{\text{Acetophenone}}{C_6H_5-CO-CH_3} \xrightarrow{NaOH/I_2} \underset{\substack{\text{Iodoform}\\(\text{Yellow})}}{CHI_3\downarrow} + C_6H_5COONa$$

20. (i)





(iii) Aniline to phenol



OR

(a)

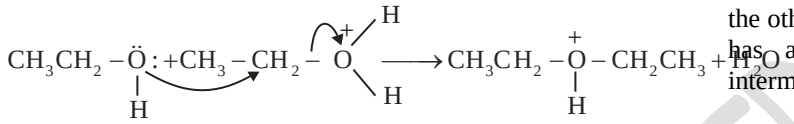
$$2CH_3CH_2OH \xrightarrow{H^+} CH_3CH_2-O-CH_2CH_3$$

The given reaction follows S_N2 mechanism as shown below:

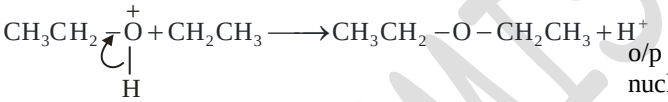
Step 1

$$CH_3-CH_2-\ddot{\underset{..}{O}}-H + H^+ \rightarrow CH_3-CH_2-{}^+\overset{H}{\overset{..}{\underset{..}{H}}}-H$$

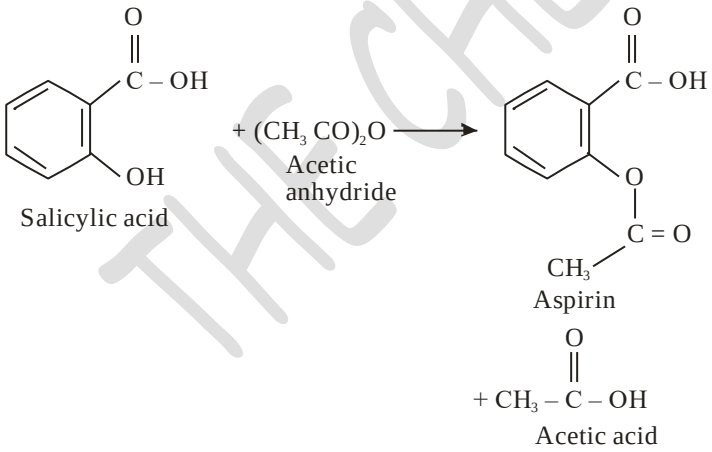
Step 2



Step 3



(b) Acetylation of salicylic acid:



21. (i) Maltose is a disaccharide, as it consists of two α-D-glucose units. Starch is a polysaccharide, while glucose and fructose are monosaccharides.

(ii)

	Fibrous Proteins	Globular Proteins
1.	They are fibre-like structures formed by polypeptide chains. Such proteins are held together by strong hydrogen and disulphide bonds.	The polypeptide chains in these proteins are folded around themselves, giving these proteins a spherical structure.
2.	They are usually insoluble in water.	They are usually soluble in water.
3.	They are structural proteins. For example, keratin is present in nails and hair, collagen is present in tendons and myosin is present in muscles.	They are functional proteins. For example, most enzymes and some hormones like insulin.

(iii) Deficiency of vitamin D causes bone deformities in children

22. (a) The boiling point of n–butyl bromide is higher than that of t–butyl bromide because n-butyl bromide is a straight chain molecule having larger surface area and therefore, has stronger intermolecular forces. On the other hand, t–butyl bromide is branched molecule, so it has a smaller surface area. Hence, it has weaker intermolecular force.

(b) Racemic mixture contains two enantiomers (d and / forms) in equal proportions and thus, the rotation due to one isomer is cancelled by the rotation due to another. Therefore, it has zero optical rotation and hence, it is optically inactive.

(c) The presence of nitro groups (– NO_2) at o/p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions because nitro groups (– NO_2) at o/p positions withdraw the electron density from the benzene ring facilitating the attack of the nucleophile. The negative charge in the carbanion formed, at ortho and para positions with respect to halogen atom, is stabilised through resonance and the presence of nitro groups (– NO_2), respectively.

23.

(i) The values displayed by Mr. Roy are:

Care – He showed concern for the health of the students.

Selfless service – He conducted seminars and health surveys in most of the schools.

(ii) Awareness regarding diabetes and depression among students can be spread by conducting seminars, health camps, debates, distribution of pamphlets, organizing workshops by doctors, etc. to highlight the need to follow healthy eating habits and importance of physical activity in day to day life of students.

(iii) Tranquillisers are those class of organic compounds that are neurologically active drugs. They perform their function by inhibiting the message transfer mechanism from nerve to receptor. They induce a sense of well being and are used in treatment of stress, anxiety, irritability and mental diseases. For example, chlordiazepoxide, iproniazid, phenelzine, meprobamate, equanil, etc.

(iv) Use of aspartame is limited to cold food

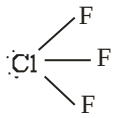
and drinks because it is unstable at temperatures achieved during cooking of food.

24. (a) (i) The acidic strength of the hydrohalic acids increases from HF to HI because the stability of the acids decreases from HF to HI on account of decrease in bond dissociation enthalpy of H–X bond from HF to HI.

(ii) The oxygen exists as a diatomic molecule, O_2, while sulphur exists as a polyatomic molecule, S_8. Hence, there is a large difference between the melting point and the boiling point of oxygen and sulphur.

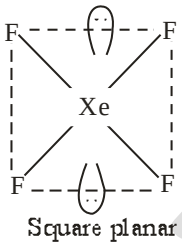
(iii) Group 15 elements form pentahalides when they have empty d–orbitals, which are can be used for forming coordinate bonds. Since nitrogen does not have d–orbitals, it cannot form petahalides.

(b) (i) Structure of $C1F_3$



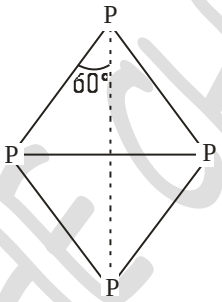
Bent T-shaped

(ii) Structure of $XeFe_4$



OR

(i) White phosphorus is most reactive of all the allotropes of phosphorus because it is unstable due to the angular strain on P_4 molecule with the bond angle of 60°.



(ii) Nitrogen oxide emitted from the exhausts of supersonic jet aeroplanes readily combine with ozone to form nitrogen dioxide and diatomic oxygen.

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

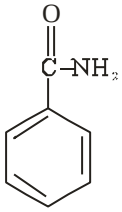
Since supersonic jets fly in the stratosphere near the ozone layer, they are responsible for the depletion of ozone layer.

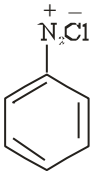
(ii) The size of a fluorine atom is very small as compared to a chlorine atom. Therefore, the repulsion between electrons in the outer most shell of the two atoms in a fluorine molecule is much greater than that in a chlorine molecule. Hence, it requires less energy to break up the fluorine molecule, making its bond dissociation energy lesser than that of chlorine molecule.

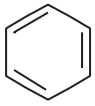
(iv) Helium, being light, non–inflammable and unreactive, is used for filling of balloons for metrological observations.

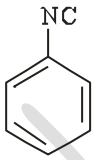
(v) $XeF_2 + PF_5 \rightarrow [XF]+[PF_6]^-$

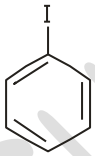
25.

(A) 

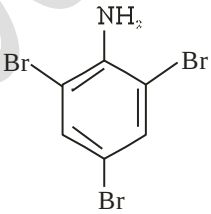
(B) 

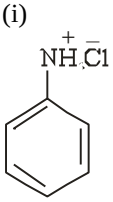
(C) 

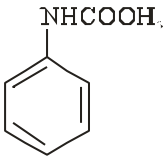
(D) 

(E) 

OR

(a) (i) 

(ii) 

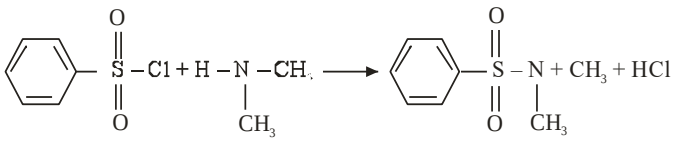
(iii) 

(b) Increasing order of boiling point.

$(CH_3)_3N < C_2H_5NH_2 < C_2H_3OH$

Alcohols have higher boiling point as compared to that of amines because oxygen, being more electronegative, forms strong hydrogen bond as compared to that of nitrogen. In tertiary amine, there is no hydrogen to form hydrogen bond and hence, has the lowest boiling point.

(c) $(CH_3)_2$ NH reacts with benzene sulphonyl chloride as follows:



N, N-Dimethylbenzenesulphonamide

$(CH_3)_3N$ does not react with benzene sulphonyl chloride.

26. (i) For the hydroylsis of methyl acetate to be a pseudo first order reaction, the reaction should be first

order wth respect to ester when $[H_2O]$ is constant. The rate constant K for a first order reaction is given by

$$K = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

Where –

$[R]_0$ = Initial concentration of reactant

[R] = Final concentration of reactant

At t_1 = 30s,

$$K_1 = \frac{2.303}{30}\log\frac{0.60}{0.30} = 2.30\times10^{-2}S^{-1}$$

At t_2 = 60s,

$$\frac{2.303}{60}\log\frac{0.60}{0.15} = 2.31\times10^{-2}S^{-1}$$

It can be seen that the rate constant K for the reaction has a constant value under any given time interval.

Hence, the given reaction follows the pseudo first order Kinetic.

(ii) Average rate of reaction between the time interval 30 – 60. Second is given by–

$$\text{Average rate} = \frac{\Delta[\text{Ester}]}{\Delta t}$$

$$= -\left(\frac{0.15-0.30}{60-30}\right) = \frac{0.15}{30} = 0.005 \text{ mol } L^{-1}S^{-1}$$

OR

(a) For a reaction $A+B \rightarrow P$, the rate is given by $\text{Rate}=k[A][B]^2$

(i) How is the rate of reaction affected if the concentration of B is doubled ?

(ii) What is the overall order of reaction if A is present in large excess ?

(a) $A + B \rightarrow P$, Rate = K [A] [B]

(i) Since the given reaction has order two with respect to reactant B, thus, if the concentration of B is doubted in the given reaction, then the rate of reaction will becomes four times.

(ii) If A is present in large excess then the reaction will be independent of the concentration of A and will be dependent only on the concentration of B. As $[B]^2$ will be the only determining factor in the order of reaction, the over all order of the reaction will be two.

(b) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction, (log 2 = 0.3010)

Ans. (b) For the given first order reaction, the rate constant for 50%. Completion is given by

$$K= \frac{2.303}{t}\log\frac{[R]_0}{[R]} \quad \text{... (1)}$$

Here, t = Time taken for 50% completion = 30 min.

$[R]_0$ = Initial concentration of the reactant

[R] = Final concentration of the reactant.

Let $[R]_0$ be 100 and due to 80% completion of reaction [R] will be 100 – 50,

i.e., 50.

Putting values in (1) we get

$$K = \frac{2.303}{30}\log\frac{100}{50} = \frac{2.303}{30}\log = 0.23 \text{ min}^{-1}$$

For the same reaction, the time required for 90% completion of the reaction can be computed using the expression

$$K = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

Here,

[R] = Final concentration of reactant

= 100 – 90 = 10

$$0.023 = \frac{2.303}{t}\log = \frac{1010}{10}$$

$$\Rightarrow t = \frac{2.303}{0.023}\log 10 = 100.13 \text{ min.}$$

Therefore, the time required for 90% completion of the given first order reaction is 100.13 min.t for order of questions.