CHEMISTRY (052) E

Question Paper-III

Total Marks : 100 **Time : 3 Hours**

Instructions :

(1) This question paper contains FIVE questions and all are compulsory.

(2) Figure on the right indicates full marks of the questions.

(3) Answer the questions in short and to the point.

(4) Write equations of the reactions and draw figures wherever necessary.

Q. 1. (A) Answer in brief : **5**

(1) Why does a substance has kinetic energy ?

(2) Write the formula to calculate the change in entropy of system when a liquid evaporates at a constant temperature.

(3) Define : Degree of ionization.

(4) MgO remebles NaCl and TiCl resembles CsCl in their crystal structures. State the coordination number of positive ions in these crystals.

(5) What does $A_{1-x}/\square_A$ indicate ?

(B) Solve [any two] of the following : **6**

(1) Calcualte pOH of 4ml 2×10^{-6} HCl solution diluted to 500 ml.

(2) The concentration of OH^- in a sample of water is 1.75×10^{-8} M. Calculate the minimum quantity of solid $PbCl_2$ that should be added to water to precipitate $Pb(OH)_2$. (Ksp of $Pb(OH)_2 = 2.8 \times 10^{-16}$ molar mass of $PbCl_2$ = 278 g/mole)

(3) Calculate out the K_c of the reaction at 25^0C

$Cu_{(S)} + 2Ag^+_{(aq)} = Cu^{2+}_{(aq)}) + 2Ag_{(S)}$

The standard potential of the cell is 0.54 volt.

(C) Answer any three of the following : **9**

(1) A piece of ice in the atmosphere at 25^0C melts spontaneously; but liquid water does not get converted into ice spontaneously at this temperature. Account for this phenomenon on the basis of the second law of thermodynamics.

(2) What is hydrolysis of salt ? Discuss acidic and basic behaviour of the aqueous salt solution on this basis.

(3) (a) Explain crystalline structure of ZnS. (Figures are not required)

(b) In qualitative analysis to get precipitation of $Al(OH)_3$ NH_4Cl is added before adding NH_4OH solution. Explain.

(4) Explain BCC structure.

Q. 2. (A) Answer in brief :

(1) When two half–cells are connected with each other, electrons flow from anode to cathode. Why ?

(2) What does the following reaction indicate ? Explain on the basis of release of electrons.

$Zn_{(S)} + Cu^{2+}_{(aq)} = Zn^{2+}_{(aq)} + Cu_{(S)}$

(3) Give the usefulness of equation : $t_{1/2} = 0.693/K$.

(4) Give the type of hybrid orbitals and geometrical shape of PCl_5 molecule.

(5) How many orbitals are present if the principal quantum number of an energy level is 3 ?

(B) Solve [any two] examples : **6**

(1) Calculate the potential of the following cell at 25^0C.

Cd / Cd^{2+} (0.26M) // Ag^+ (0.06) / Ag

$E^0_{Cd/Cd^{2+}} = 0.40$ volt, $E^0_{Ag/Ag^+} = -0.80$ volt.

(2) A particle is moving with a kinetic energy of 3.1×10^{-13} erg. Calculate its wavelength. Mass of particle = 8.109×10^{-27} grams.

[Kinetic energy = $\frac{1}{2}mv^2$]

(3) At 300^0C temperature the differential rate of the reaction A + B $\rightarrow$ C, detemined in each of three sets of the experiments, were as under.

(i) Derive the differential rate law. (ii) State the order of the reaction.

(ii) Calculate the specific rate constant of the reaction.

Experiment number	Initial concentration of reactants mole–liter^{-1}		Initial rate of the reaction $-d[B]/dt$ mole. lit^{-1} sec^{-1}
	[A]	[B]	
1	0.02	0.04	7×10^{-5}
2	0.04	0.04	2.8×10^{-4}
3	0.02	0.08	1.4×10^{-4}

(C) Answer the following in detail [any three] **9**

(1) Sketch a cell in which the following reaction occurs.

$Zn_{(S)} + 2Ag^{+}{}_{(aq)} = Zn^{2+}{}_{(aq)} + 2Ag_{(S)}$

Label different parts of the cell, write equations for oxidation and reduction reactions and indicate electrodes on which they occur.

(2) What is meant by order of reaction ? Explain in detail on the basis of the following general equation :

$n_1A + n_2B = n_3C + n_4D$

(3) (a) Explain bonding and anti–bonding molecular orbitals on the basis of molecular orbital theory.

(b) Sketch the shape of 2s orbital. How does 2s orbital differ from 1s orbital ?

(4) (a) Distinguish between covalent bond and coordinate covalent bond.

(b) Write a note on gas electrodes.

Q. 3. (A) Answer in brief : **5**

(1) On exposure to air, yellow phosphorus ignites spontaneously. Why ?

(2) Mention the names of compounds which are not soluble in benzene.

(3) Give the structural formulae of X & Y in following reaction.

$$X \xrightarrow[\text{Conc. } H_2SO_4,\ > 100^0C,\ -H_2O]{\text{Conc. } HNO_3} \text{TNT (Y)}$$

(4) Write the equation and name of product when ethyl cyanide is reduced with Ni or $LiAlH_4$.

(5) Give structural formual of DDT.

(B) Write chemical equation for ANY THREE of the following conversions. Also give the conditions of the reactions, names and structural formula of the main organic compounds. (There should be only two steps of each conversion). **6**

(1) P–methyl acetophenone from benzene.

(2) Isopropyl benzene from phenol

(3) Acetaldehyde from ethyl chloride.

(4) Propene from acetone.

(C) Answer the following [any three] **9**

(1) Compound A on heating with sodalime produced B, which on treatment with a mixture of conc. HNO_3 and conc. H_2SO_4 produced compound C. On reduction with Ni catalyst at 600^0C compound C produced compound D. Give reaction scheme and identify the compound A, B, C & D from the chemical reactions.

(2) Explain in detail about the preparations of the following from toluene.

(a) p–Toluene sulphonic acid (b) p–Dinitro toluene. (c) m–Xylene.

(3) Write a note on polyhalogen compounds.

(4) Give balanced equations of the following chemical reactions :

(a) The equation when potassium carbonate is reacted with nitric acid.

(b) The reaction when potassium hydroxide is reacted with nitric acid.

(c) Give the equation when potassium chlorate is treated with iodine.

Q. 4. (A) Answer in brief : **5**

(1) Which aldehyde is used to prepare various resin type plastics ?

(2) $X \xrightarrow[Br_2/H_2O]{[O]} CH_3COOH$

Give structural formula and IUPAC of X for the above reaction.

(3) Aqueous solutions of amines are basic. Why ?

(4) Which functional groups are present in amino acids ?

(5) Mention the name of inorganic fertilizers and their elements.

(B) Write chemical equations for ANY THREE of the following conversions. Also give the conditions of the reactions, names and structural formula of the main organic compounds. (There should be only two steps of each conversion). **6**

(1) Benzyl chloride from benzoic acid

(2) Ethyl benzoate from toluene

(3) Propane from Iso–propyl alcohol

(4) Ethyl iodide from acetaldehyde.

(C) Answer [any three] of the following : 9

(1) Explain : Confirmative test of primary aromatic amines based on azo coupling.

(2) (a) What are vitamins ? Give sources and uses of vitamin C.

(b) Explain in detail about the role of Chloroform in human life.

(3) Disucuss Grignard reaction of aldehyde and ketones.

$$A \xrightarrow[Br_2/H_2O]{[O]} B \xrightarrow[Conc.[H_2SO_4]]{CH_3-CH_2-OH} C \xrightarrow[\Delta]{NH_3} CH_3-CO-NH_2 + D$$

Give names and structural formulae of A, B, C & D for the above reaction.

Q. 5. (A) Answer in brief : 5

(1) Give the sources of $He_{(g)}$.

(2) The metals absorb hydrogen reversibly during electrolysis. Explain.

(3) Give electronic configuration of Cu_{29} & Cr_{24}

(4) What does secondary valency indicate ?

(5) Which orbitals will be utilized for the hybridization of complex $[Fe(H_2O)_6]^{3+}$? Why ?

(B) Answr the following : 6

(1) Give the IUPAC of the following :

(a) $Na_4[Co(NO_2)_6]$ (b) $[Fe(CO)_6]$

(2) Why is the decrease in the energy of different orbitals irregular ?

(3) Give the names of the following :

(a) As_4O_6 (b) H_3SbO_4 (c) NaH_2AsO_4 (d) P_4O_8

(C) Answer the following : [any three]

(1) Discuss the various oxidation states observed in transition elements with suitable examples.

(2) Explain importance of complexes.

(3) Explain giving reasons :

(1) The formation of coordinate covalent bond is Lewis acid–base reaction.

(2) $K_4[Fe(CN)_6]$ is diamagntic while $[Fe(H_2O)_6]Cl_3$ is paramagnetic.

(4) Write a note on the allotropes of phsphorous and arsenic.

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: ANSWERS :

Q. 1 (A) Answer in brief :

(1) Constituent particles of substance have translation, rotational and vibrational motions. Moreover, electrons and nuclei of these particles have different kind of motions. Therefor substance have kinetic energy.

(2) $\Delta S_{vaporisation} = \dfrac{\Delta H \text{ Vaporisation}}{T}$

(3) The fraction of dissolved compound inonised is known as degree of ionisation.

(4) Co–ordination number of Mg^{+2} and Na^{+} in MgO and NaCl respectively is six.

Co–ordination number of Ti^{+1} and C_s^{+1} in TiCl and C_sCl respcectively is eight.

(5) $A_{1-x/}\square_A$ shows that the atom A occupies $(1 - x)^{th}$ part of its normal site and the remaining part of its site is vacant.

(B) Solve the following :

(1) Given 4.0 ml 2.0×10^{-6}M HCl solution.

Above solution is diluted to 500.0 ml by ading water. Let us calculate concentration of diluted the solution.

$M_1V_1 = M_2V_2$ $\quad$ $M_1 = 2.0 \times 10^{-6}$ mole/lit.

$\therefore \quad M_2 = \dfrac{M_1V_1}{V_2}$ $\quad$ $V_1 = 4.0$ ml.

$= \dfrac{2.0 \times 10^{-6} \times 4.0}{500}$ $\quad$ $V_2 = 500.0$ ml.

$= 16 \times 10^{-9}$ M.

$\therefore$ Concentation of $H^+_{(g)}$ ion after diluting the solution is 16×10^{-9} M.

Since this concentration is less than the ceoncetration of $H^+_{(g)}$ ion produced due to self ionisation of water, the same i. e. 10^{-7} also has to be added.

$\therefore$ Concentration of $H^+_{(g)} = 16 \times 10^{-9} + 10^{-7}$

$= 1.16 \times 10^{-7}$ M

Now, pH $= -\log_{10} [H^+_{(g)}]$

$= -\log_{10} 1.16 \times 10^{-7}$

$= 6.9355$

Now pOH $= 14.0 - pH$

$= 14.0 - 6.9355$

$= 7.0645$

(2) Suppose x mole of $PbCl_2$ should be added to 1.0 lit. of water. Therefor the concentration of Ca^{+2} in water would be x M.

Let us now calcualte the value of x to get IP equal to Ksp.

$Pb(OH)_2 \rightleftharpoons Pb^{+2}_{(aq)} + 2OH^-_{(g)}$

$\therefore$ $Ksp = [Pb^{+2}] [OH^-]^2$

$\therefore$ $2.8 \times 10^{-16} = [x] [1.75 \times 10^{-8}]^2$

$$\therefore \quad x = \frac{2.8 \times 10^{-16}}{1.75 \times 1.75 \times 10^{-16}}$$

$= 0.9145$ M.

If littel more than 0.9145 mole of $PbCl_2$ i.e. 1.0 mole is added to 1.0 lit. of solution, $Pb(OH)_2$ will be precipitated.

$\therefore$ 1.0 mole i.e. 278.0 gm $PbCl_2$ must be added.

(3) As ΔG^0 in terms of electrical work done,

$\Delta G^0 = -nF\Delta E^0$.

Δ in terms of equilibrium constant $\Delta G^0 = -RTlnK$.

$\therefore nF\Delta E^0 = RTlnK$.

$$\therefore \quad \log K = \frac{nF\Delta E^0}{2.303 \times R \times T}$$

$$= \frac{2 \times 96500 \times 0.54}{2.303 \times 8.314 \times 298}$$

$= 18.27$

$\therefore$ $K_c = 1.862 \times 10^{18}$

$Cu_{(s)} + 2Ag^+_{(g)} \rightarrow 2Ag + Cu^{+2}_{(aq)}$

$\Delta E^0 = 0.54V$

$n = 2$

$F = 96,500$

$R = 8.314$

$T = 298\ K^0$

Q. 1. (C)

(1) According to the second law of thermo dynamics in order to know whether a particular reaction will occure sportaneously or not the total entropy change is calcualted as under.

$\Delta S_{total} = \Delta S_{system} + \Delta_{\ srrounding}$.

(i) If $\Delta S_{total} > 0$ i.e. (+) reaction is spontaneous.

(ii) If $\Delta S_{total} < 0$ i.e. (–) reaction is non spontaneous

Now, molar heat of fusion of ice is 1440 cal. $mole^{-1}$.

$\therefore$ $\Delta H = 1440$ cal.$mole^{-1}$

$$\Delta_{system} = \frac{+\Delta H}{T}$$

$$= \frac{1440}{273} = 5.27 \text{ cal.}K^{-1}mole^{-1}$$

As heat is lost by atmosphere,

$$\Delta S_{surrounding} = \frac{-\Delta H}{T} = \frac{-1440}{298} = 4.83 \text{ cal.}k^{-1}.mole^{-1}$$

$\therefore$ $\Delta S_{total} = 5.27 - 4.83 = +0.44$ cal.k^{-1}.$mole^{-1}$

Thus ice melts spontaneously producing water at 0^0C.

For the conversion of water at 25^0C to ice at 0^0C, the system should release energy to atmosphere.

$$\Delta S_{system} = \frac{-1440}{273} = -5.27 \text{ cal}^0K^{-1}.mole^{-1}$$

$$\Delta S_{surronding} = \frac{+1440}{298} = +4.83 \text{ cal } ^0K^{-1}.mole^{-1}$$

$\therefore$ For reversible process,

$\Delta S_{total} = \Delta S_{system} + \Delta_{\ surrounding} = -5.27 + 4.83 = -0.44$ cal.K^{0-1}.$mole^{-1}$

Thus, as ΔS_{total} is negative, liquid water does not get converted into ice spontaneously at 25^0C C temperature.

Q. 2. (2)

The aqueous solutions of salts are either acidic or basic because the ions formed from salts react with ions produced from water. This reaction is known as hydrolysis.

(i) Suppose a salt MA produced by a reaction between a strong base (MOH) and a weak acid (HA) is dissolved in water. The following equilibrium exists in water.

Further, all salts of above type ionize completely in aqueous solution as under :

$MA_{(aq)} \rightarrow M^{+}_{(aq)} + A^{-}_{(aq)}$

As HA is a weak acid, it ionizes only slightly. Therefore, the concentration of A^- present alongwith H^+ would be very low. When a salt dissolves in water, A^- ions are formed in large concentration. As a result, they combin with H^+ ions produced by the self–ionization of water and form undissociated HA. This disturbs the equilibrium in water. As a result, according to the Le Chatelier's principle the equilibrium of water shifts in the forward direction and produces more H^+ and OH^- ions. However as H^+ are removed by A^- the concentratin of OH^- ions exceeds the concentration of H^+ ions in the new state of equilibrium and, therefore the solution becomes basic. The overall reaction in solution may be represented as :

$A^{-}_{(aq)} + H_2O_{(l)} \rightleftharpoons HA_{(aq)} + OH^{-}_{(aq)}$

(ii) When a salt formed by a reaction between a weak base and a strong acid dissolves in waer, M^+ present in solution reacts with OH^- ions formed by the self– ionization of water. This reaction distrubs the equilibrium established between water and its ions. When the following net reaction reaches the state of equilibrium the concentration of H^+ ions exceeds the concentration of OH^- and the solution becomes acidic.

$M^{+}_{(aq)} + H_2O_{(l)} \rightleftharpoons MOH_{(aq)} + H^{+}_{(aq)}$

Q. 3. (A) Crystal Structure of Zinc Sulphide :

There are two crystal forms of zinc sulphide (ZnS) :

Zinc blend and Wurtzite

Just as the carbon atoms are joined tetrahedrally in diamond similarly in both the crystal forms of zinc sulphide Zn^{2+} and S^{2-} ions are arranged in a tetrahedral structure with four other ions surrounding are arranged in a tetrahedral structure with four other ions surrounding them. In Zinc blend, S^{2-} ions have, FCC structue while in Wurtzitee Zn^{2+} ions have hexagonal structure. ions around each S^{2-} ion and they are joined by covalent bonds. However the eight electrons of the covalent bonds are not contributed equally by the zinc and sulphur atoms. The two valence electrons of zinc and the six valence electrons of sulphur together make up the eight electrons which form four covalent bonds. Each ion has a coordination number 4 in these crystal structures.

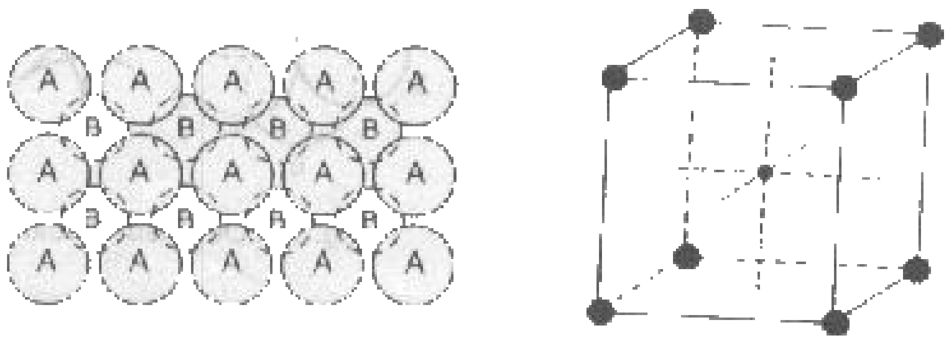
(b) $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$NH_4Cl \longrightarrow NH_4+ + Cl^-$ ...(1/2)

Thus, concentration of common ion NH_4^+ increases. So equilibrium of NH_4OH shifts in reverse direction. As a result, ionization ofr NH_4OH decreases. So the concentration of OH^- ion remains very low. The solubility of $AlCONL_3$ is very low compared to hydroxides of later groups III–B, IV and Mg^{2+}. So only $Al(OH)_3$ precipitate. ...(1)

Q. 1. (C) (4) Body–centered cubic close–packed structure :

In square structure, the spheres in the first layer A remain slightly away from one another. Each sphere is separated by some distance rather than being in mutual contact. Now when the second layer B is placed on the first layer A, then each sphere of the second layer comes in contact with four spheres of the first sphere. The third layer C is arrayed on the second layer B exactly the same way as is the first layehr A. The crystal structure generated by repetition of this ABABAB... kind of arrangement is called the body–centered cubic close– packed (BCC) structure.



Body–centered cubic close–packed structure (BCC)

In this structure, a sphere in any layer is in contact with a total of eight spheres, four of the layer above it and four of the layer beneath it. If we imagine a simple cube and place a Sphere at each of its eight corners and at the center inside the cube, then the structure that results is called the body–centered cubic close–packed (BCC) structure e. g. CsCl crystal in which coordination no. is 8.

Q. 2. (A) Answer in short : **(5)**

(1) Electrons flow from anode to cathode due to electrical pressure produced by a chemical reaction.

(2) Here Zn releases electrons. The tendency of Zn to release electons is greater than the tendency of Cu to release electrons.

(3) It is useful to recognise the first order of reactions.

(4) PCl_5 : Hybridization → sp^3d^2

Shape → Trigonal bipyramidal

(5) Number of orbitals = $n^2 = (3)^2 = 9$

(B)

(1) Cd/Cd^2 (0.26M) || Ag^+ (0.06) / Ag

E^0 Cd/Cd^2 = 0.40V $E^0 Ag/Ag^+$ = –0.80V

C_1 = 0.26M Co_2 = 0.06M

n = 2

ΔE^0 (ed) = E^0 – E^0

Oxi Anode Oxi Cathode

= 0.40 – (–0.8)

= 1.2 volt

$$\therefore \quad \Delta E = \Delta E^0_{cell} - \frac{0.0592}{n} \log \frac{c_1}{c_2}$$

$$= 1.2 - \frac{0.0592}{2} \log \frac{0.26}{0.06}$$

$$= 1.2 - 0.0296 \log \frac{13}{3}$$

$= 1.2 - 0.0296\ (1.1139 - 0.4771)$

$= 1.2 - 0296\ (0.6368)$

$= 1.2 - \text{A.log.}\ (0.4713 + 0.8040) \times 10^{-3}$

$= 1.2 - \text{A.log.}\ (1.2753) \times 10^{-3}$

$= 1.2 - 0.0188$

$= 2.1812$ volt.

$2\ ne = \frac{1}{2}\ mv^2 = 3.1 \times 10^{-13}$ erg. $M = 9.109 \times 10^{-27}$ gm.

$$v^2 = \frac{6.2 \times 10^{-13}}{8.109 \times 10^{-27}}$$

$$\therefore \quad v = \sqrt{\frac{6.2 \times 10^{-13}}{8.109 \times 10^{-27}}}\ \text{cm/s}$$

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.626 \times 10^{-27}}{8.109 \times 10^{-27} \times \sqrt{\frac{6.626 \times 10^{-13}}{8.109 \times 10^{-27}}}}$$

$$= \frac{6.626 \times 10^{-27}}{\sqrt{8.109 \times 6.2} \times 10^{-20}}$$

$$= \text{A.log}\ (0.8213 - \frac{1}{2}\ (0.9090 + 0.7924)) \times 10^{-7}$$

$$= \text{A.log}\ (0.8213 - \frac{1}{2}\ (1.7014)) \times 10^{-7}$$

$= \text{A.log}\ (1.82113 - 0.8507) \times 10^{-8}$

$= \text{A.log}\ (0.9706) \times 10^{-8}$

$= 9.345 \times 10^{-8}$ cm

$= 9.345 \times 10^{-10}$ M

$= 9.345\ A^0$

(3) (i) differential rate law is Rate = $\frac{-d[A]}{dt} = \frac{-d[B]}{dt} = K[A]^x\,[B]^y$

(ii) From given table using different values in above eqn we get.

(1) $7 \times 10^{-5} = K[0.02]^x\,[0.04]^y$

(2) $2.8 \times 10^{-4} = K[0.04]^x\,[0.04]^y$

(3) $1.4 \times 10^{-4} = K[0.02]^x\,[0.08]^y$

$\therefore$ eqn $\frac{1}{2} \Rightarrow \frac{7\times10^{-5}}{2.8\times10^{-4}} = \left(\frac{0.02}{0.04}\right)^x$

$\therefore$ $\frac{.70}{2.8} = \left(\frac{1}{2}\right)^x$

$\therefore$ $2^2 = 2^x$

$\therefore$ $x = 2$

eqn. $\frac{1}{3} \Rightarrow \frac{7 \times 10^{-5}}{1.4 \times 10^{-4}} = \left(\frac{1}{2}\right)^y$

$\therefore$ $.50 = (0.5)^y$

$\therefore$ $y = 1$

$\therefore$ Net order of reaction = x + y = 2 + 1 = 3

putting value of x & g is eqn (1)

$\therefore$ $7 \times 10^{-5} = k[0.02]^2\,[0.04]$

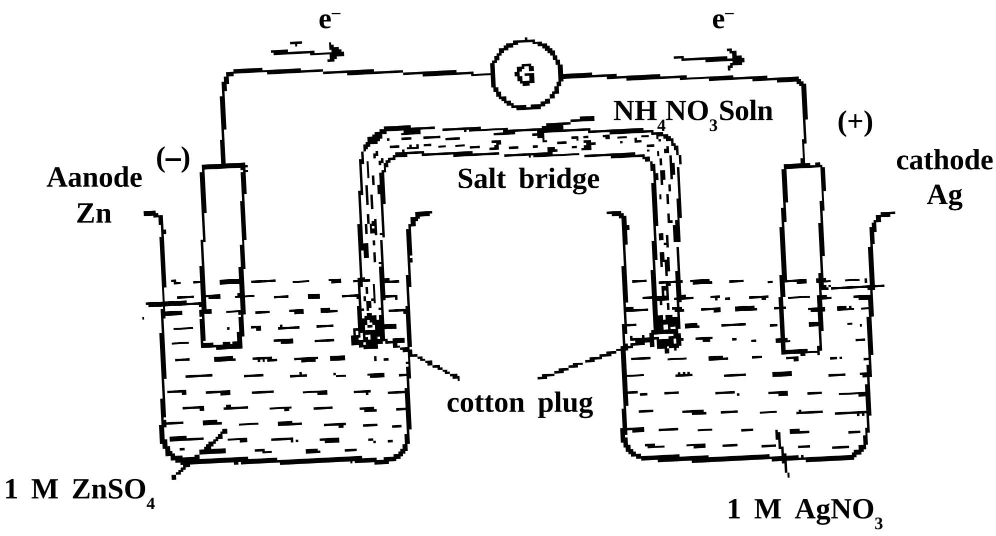
$\therefore$ $7 \times 10^{-5} = k \times [2 \times 10^{-2}]^2\,[4 \times 10^{-2}]$

$\therefore$ $7 \times 10^{-5} = k \times 8 \times 10^{-6}$

$\therefore$ $\frac{70}{8} = k$

$\therefore$ $k = 8.75\ \text{lit}^2\ \text{mole}^{-2}\ \text{sec}^{-1}$

Q. 3. (C) 1



Anode : $Zn_{(s)} \rightarrow Zn^{2+}_{(1M)} + 2e^-$ ... (2)

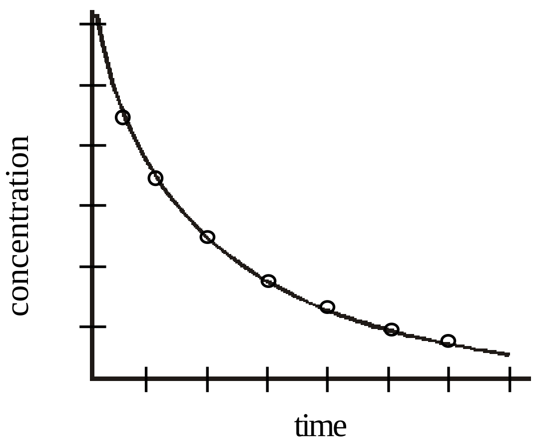
Cathode : $2Ag^{+}_{(1m)} + 2e^- \rightarrow 2Ag_{(s)}$ ... (1)

(2) The value of exponents of concentration term of reactants in differential rate law equation is known as order of reaction. ... (1)

Suppose a general reaction, $n_1A + n_2B = n_3C + n_4D$ occurs at a constant temperature. With the start of the reaction, concentrations of A and B begin to decrease as A and B are consumed in the reaction. The concentrations of C and D go on increasing as C andd D are formed in the reaction. If the decrease in concentrations of A and B are Δ[A] and Δ[B] respectively after time t, then the average rate of reaction of A in time interval $\Delta t = -\frac{\Delta A}{\Delta t}$ and, the average rate of reaction of B in time interval $\Delta t = -\frac{\Delta B}{\Delta t}$. Here negative (–), indicates the decreases in concentration of reactants.

Similarly, the rates of formation of C and D in time Δt can be represented by $+\frac{\Delta[C]}{\Delta t}$ and $+\frac{\Delta[D]}{\Delta t}$ respectively.

The rate of a chemical reaction at a particular moment is proportional to the concentrations of reactants, at the moment. As the concentrations of reactant, go on decreasing continuously the rate of a reaction decreases continuously as time passes; fig. indicates curved graph.



Above tems which indicate the rate of the reaction are related with each other as under :

$$-\frac{1}{n_1}\frac{\Delta[A]}{\Delta t} = -\frac{1}{n_2}\frac{\Delta[B]}{\Delta t} = +\frac{1}{n_3}\frac{\Delta[C]}{\Delta t} = +\frac{1}{n_4}\frac{\Delta[D]}{\Delta t}$$

Differential Rate Law :

The relation between the rate of a reaction and concentrations of reactant at any particular moment is known as the differential rate law of teh reaction. For example, the mathematical form of differential rate law of the general reaction mentioned above can be us under :

$$\frac{1}{n_1}\frac{d[A]}{dt} = -\frac{1}{n_2}\frac{d[B]}{dt} = K[A]^x\ [B]^y$$

Here $\frac{d[A]}{dt}$ is the rate of reaction of A at a moment at which the concentrations of A and B are [A] and [B] respectively. The exponents x and y are known as order of reaction with respect to A and B respectivley. x and y are not related with stoichiometric co–efficients n_1 and n_2 appearing in the balanced equation.

Q. 2. (C)

(3) (a) According to the principles of wave mechanics, a molecular orbital is constructed by the linear combinatin of atomic orbitals of two atoms between which a bond is formed. For example. When H_2 molecule is formed by bonding two H atoms, the acceptable wave function $\Psi_{1s(1)}$ and $\Psi_{1S(2)}$ combine linearly molecular wave functions, Ψ_{m0} and Ψ^0_{m0} are formed.

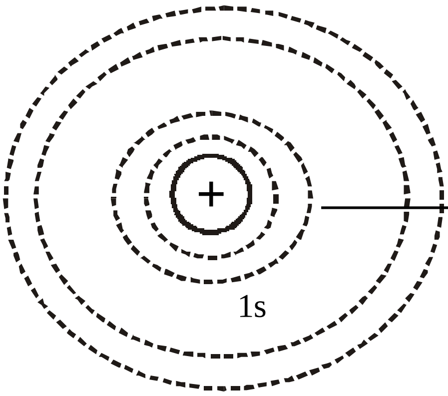
$$\Psi_{m0} = \Psi_{1S(1)} + \Psi_{1S(2)}$$

$$\Psi^*_{m0} = \Psi_{1S(1)} - \Psi_{1S(2)}$$

Here (1) and (2) are serial numbers used to distinguish between two hydrogen atoms. The energy of molecular orbital indicated by Ψ_{m0} is less than the energy of 1s atomic orbital. The energy of molecular orbital indicated by Ψ^*_{m0} has higher energy than the energy of 1s atomic orbital. Here Ψ_{m0} is bonding and Ψ^*_{m0} is antibonding molecular orbitals.

Symbols $\sigma$and π are used to indicate bonding molecular orbitals and σ^* and π^* symbols are used to indicate antibonding molecular orbitals.

(b)



... (1/2)

→ 2S orbital has one node while 1s orbital zero node. ... (1/2)

→ For ds, n = 2, while for 1s, n = 1. Thus, 2s orbital has higher energy than 1s.

(4) (a) The bond formed by overlaping of half–filled valence orbitals of combining atoms is called a covalent bond.

While if one of the two combining atoms has a fully filled valence orbital and another has vacant valence orbital, then the overlapping of these two orbitals forms the special bond is known as coordinate covalent bond.

→ In covalent bond, each atom shares its one electron with only one electron of another atom. While in coordinate bond one atom shares its pair of electron with another atom.

(b) (iii) Gas Electrode : These electrodes resemble inesrt electrodes to a large extent. In these electrodes, a gas is bubbled over the surface of a platinum plate dipped in a solution. For example, hydrogen gas is passed over a platinum plate dipped in a solution containing $H^+_{(aq)}$. In this case eigher $2H^+$ ions are reduced to H_2 by gaining electrons, on the surface of platinum of H_2 is oxidized to $2H_+$, by giving up electrons on the surface of the platinum plate. The platinum plate provides a contact surface for the exchagne of electrons. The reaction occuring on the surface can be represented as under :

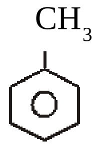
$$H_{2(g)} \rightleftharpoons 2H^+_{(a)} + 2e^- \quad ...(3.4)$$

Q. 3. (A) Answer in brief : (5)

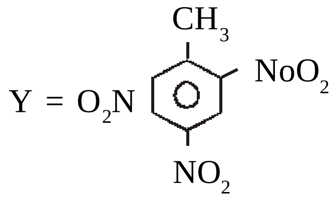
(1) The p–p bonds in P_4 are weak and p–p–p bond angle is very small. So there is strain in P_4 molecule. So it ignites.

(2) Glucose, sugar and inorganic salts.

(3) X =



Toluene

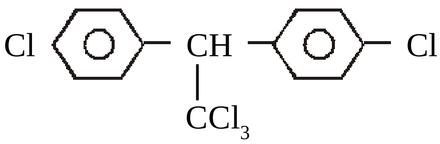


2,4,6–Triniitro toluene

(4) $CH_3–CH_2–CN \xrightarrow[Ni/LiAlH_4]{2H_2} CH_3–CH_2–CH_2–NH_2$

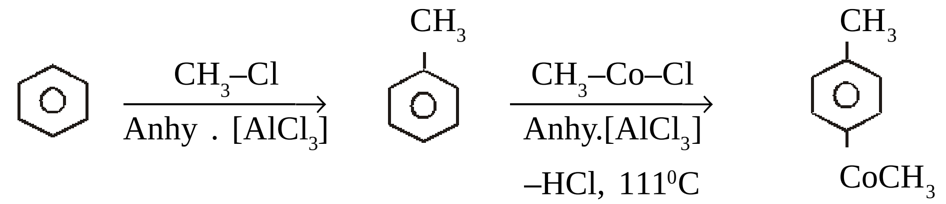
Ethyl cyanide → 1–amino propane

(5)



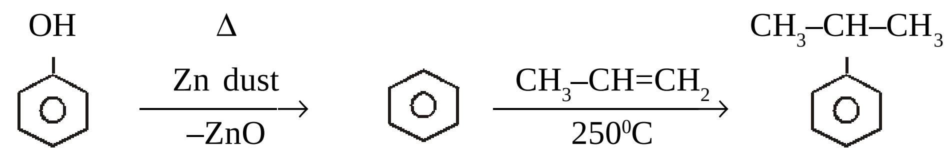
(B) Give conversions (three) (6)

(1)



Benzene –HCl 80^0C Toluene P–methyl acetophenone

(2)



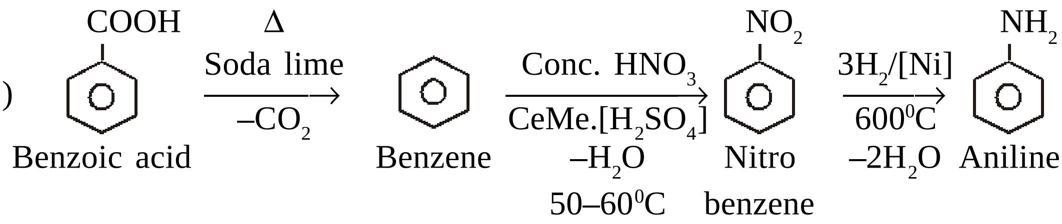
Phenol Benzene $[H_3PO_4]$ Iso–propyl benzene

(3) $$\underset{\text{Ethyl Chloride}}{CH_3–CH_2–Cl} \xrightarrow[\Delta,\ –NaCl]{Aq.NaOH} \underset{\text{Ethanol}}{CH_3–CH_2–OH} \xrightarrow[Na_2Cr_2O_7\ +\ H_2SO_4]{[O]} \underset{\text{Acetaldeayde}}{CH_3–CHO} + H_2O$$

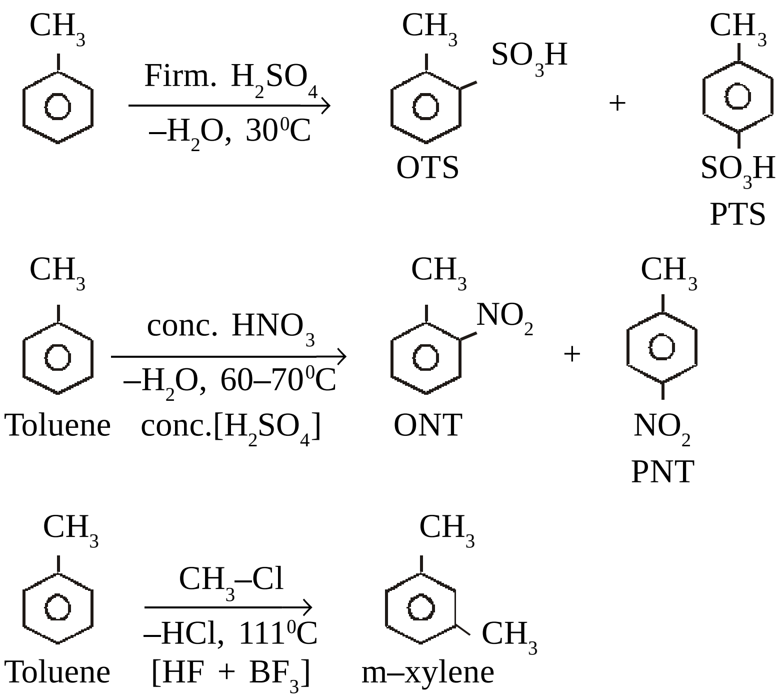
(4) $$\underset{\text{Acetone}}{CH_3–CO–CH_3} \xrightarrow[[Ni]]{H_2} \underset{\text{2–propanol}}{\underset{OH}{CH_3–CH–CH_3}} \xrightarrow[350\ –\ 400^0C\ \ –H_2O]{[Al_2O_3]} \underset{\text{propene}}{CH_3–CH\ =CH_2}$$

(C)

(1)



(2)



(3) Two or more halogen atoms of the same or different kind combine with a metal forming plyhalogen compounds, e.g. $CsBr_3$, CsI_3, $CsICl_2$, $CsIBr_2$. These polyhalogen compounds contain uninegative polyhalide ions like Br_3^-, I_3^-, ICl_3^-, ICl_3^-, IBr_2^- etc.

(4) $K_2CO_3 + HNO_3 \rightarrow KNO_3 + H_2O + CO_2$

$KOH + HNO_3 \rightarrow KNO_3 + H_2O$

$2KClO_3 + I_2 \rightarrow 2KIO_3 + Cl_2$

Q. 4. (A) Answer in brief : **(5)**

(1) Formaldehyde

(2) CH_3CHO – Ethanal

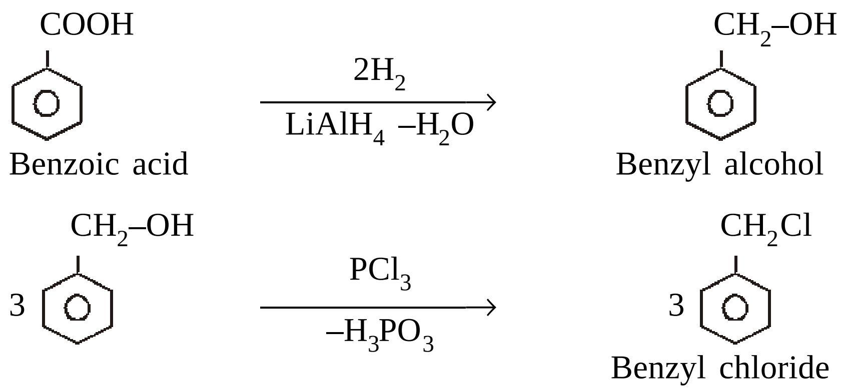
(3) Because, N–atom of amine has non–bonding electron pair and they produce OH^- ions in aqueous solutions.

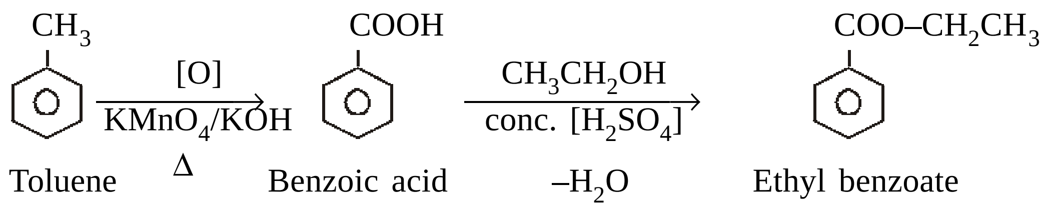
(4) $-NH_2$ and –COOH

(5) Super phosphate of lime → Ca, P, S, O, H atoms

Nitrolime → Ca, C, N atoms.

(B)

(1) 

(2) 

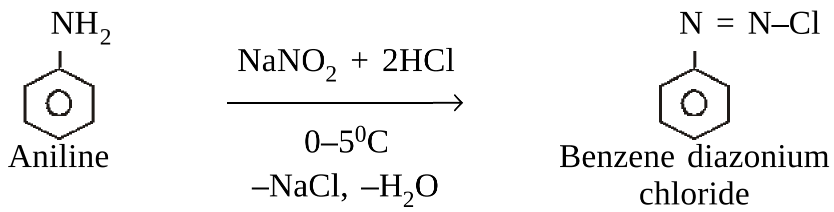
(3) $$\underset{\text{2–propanol}}{CH_3\text{–}\underset{\underset{CH}{|}}{CH}\text{–}CH_3} \xrightarrow[KMnO_4\ |\ KOH]{[O]} \underset{\text{Acetone}}{CH_3\text{–}\underset{\underset{O}{||}}{C}\text{–}CH_3} \xrightarrow[-N_2,\ -H_2O]{N_2H_4/KOH} \underset{\text{Propane}}{CH_3\text{–}CH_2\text{–}CH_3}$$

(4) $$\underset{\text{Acetaldehyde}}{CH_3\text{–}CHO} \xrightarrow[[Ni]]{H_2} \underset{\text{Ethanol}}{CH_3\text{–}CH_2\text{–}OH}$$

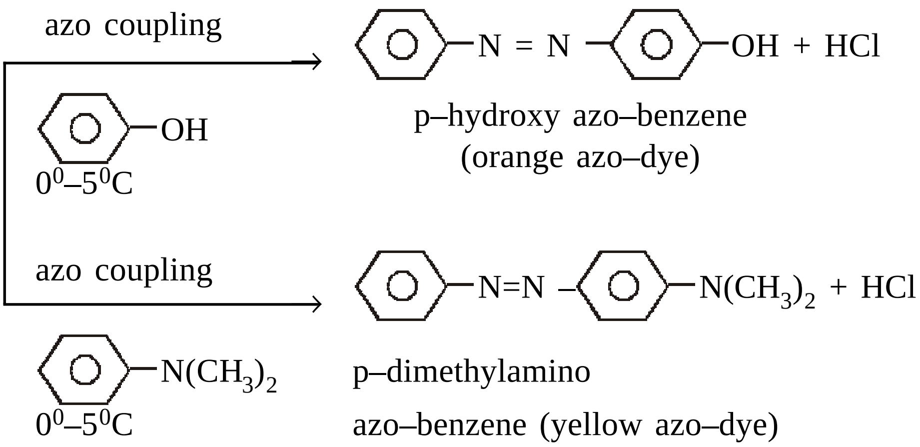
$$3CH_3\text{–}CH_2\text{–}OH \xrightarrow[-H_3PO_3]{PI_3} \underset{\text{Ethyl iodide}}{3CH_3\text{–}CH_2\text{–}I}$$

(C) Answer any three **(6)**

(1) Solution of ailine in dilute hydrochloric acid is prepared and cooled to 0^0–5^0C. Maintaining this low temperature, cold solution of sodium nitrite is added to this very slowly. Benzene diazonium chloride salt is thus formed. Durign this reaction, nitrous acid produced by reaction of hydrochloric acid on sodium nitrite, reacts with amino group of aniline giving benzene diazonium chloride.



phenyl hydrazine



when benzene diazonium chloride is treated with phenol in NaOH at 0–5^0C it gives p–hydroxy azobene and with dimethyl aniline in HCl at 0–5^0C, it gives p–dimethyl amino azo benzene.

(2) For biochemical processes in body, for its normal growth and for the activity of its tissue cells, vitamins are necessary. Lack of vitamins produces defects in body, leading to deficiency dieseases.

Vitamin C is called ascorbic acid. Citrus fruits, lemons, tomatoes and green vegetables contain this vitamin. Its deficiency produces a diseases called scury in which gums get swollen and start bleeding and ulcer occurs with teeth loosening. Vitamin C also gives resistance against common cold.

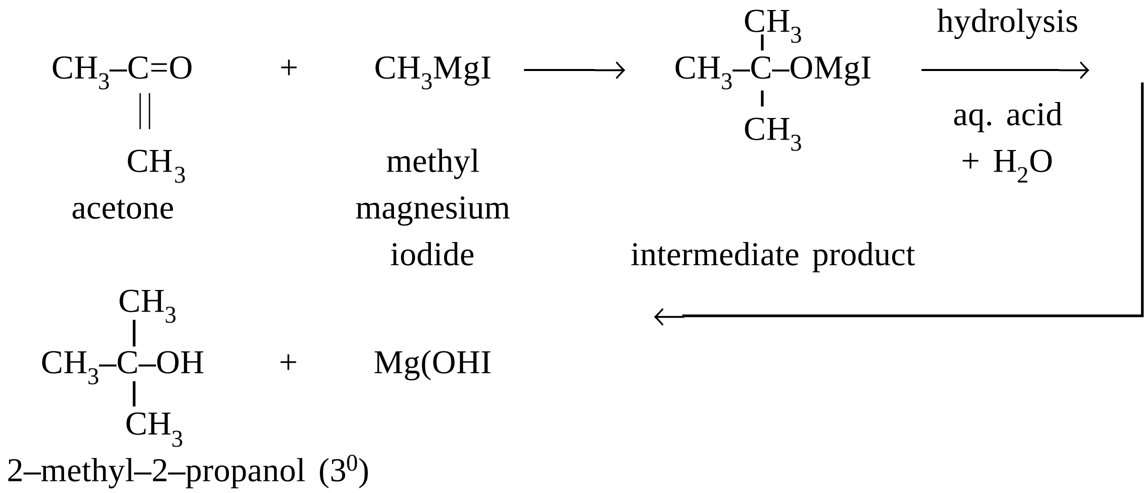
Chlorform :

Drugs like opium, morphine etc. which lower the activity of central nervous system are called central nervous depressants (CND). Drugs like hashish, marijuana, ethanol etc. are called central newrvous stimulants (CNS). Chloroform is central nervous depressant. Its effect blocks the relay in central nervous system and therefore when body parts are operated, no pain is felt. In order to avoid pain during surgery, patient is given chloroform as an anaesthetic. Structure of chloroform is $CHCl_3$ and it is prepared from acetaldehyde or acetone.

Chloroform is a colourless, sweet smelling liquid, heavier than water and sparingly soluble in water. In presence of sunlight it combines with atmospheric oxygen giving cabonyl chloride or phosgene. Hence chloroform used as an anaesthetic containig impurity of phosgene will be fatal. In order to avoid this difficulty, chloroform used in hospitals is mixed with 1% ethanol, which converts phosgene into harmless diethyl carbonate.

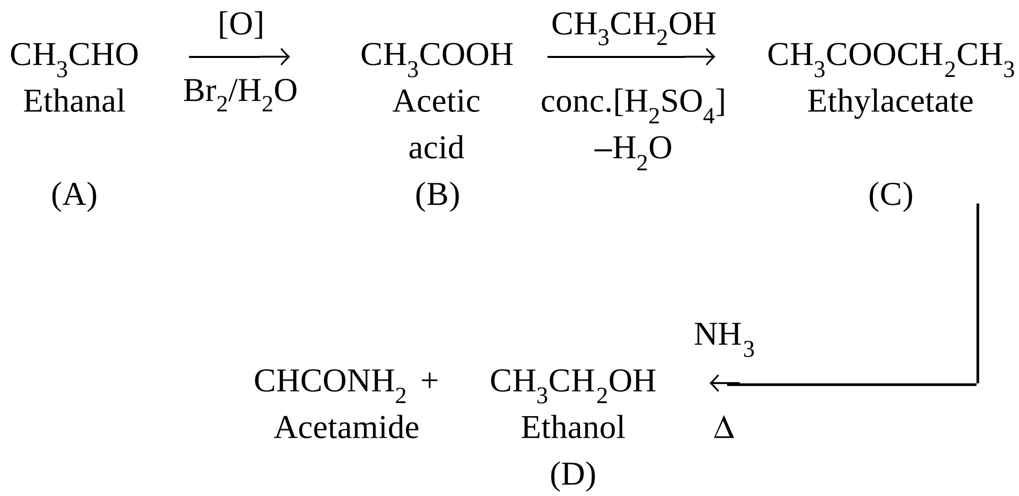
$$\underset{\text{acetaldehyde}}{CH_3\text{–}\underset{|}{\overset{}{C}}(H)\text{=O}} + \underset{\text{methyl magnesium iodide}}{CH_3MgI} \rightarrow \underset{\text{intermediate product}}{CH_3\text{–}C(CH_3)(H)\text{–OMgI}} \xrightarrow[\text{aq. acid} \; +H_2O]{\text{hydrolysis}}$$

$$\underset{\text{2–propanol } (2^0)}{CH_3.CHOH.CH_3} + Mg(OH)I$$



When acetaldehyde and Ketones are reacted with CH_3MgI, they give intermediate products. They an hydrolysis by aqueous acid gives alcohol. By these reactions acetaldehyde gives 2–propanol and acetone give 2–methyl 2–propanol.

(4)



Q. 5. (A) Answer in brief : **(5)**

(1) He is preseent about 7% in volcanic gases.

(2) Ni metal absorbs H atoms in interstitial voids and reversibly releases hydrogen. So Ni metal is used as catalyst.

(3) Cu[29] : [Ar] $3d^{10}\ 4s^1$

Cr[24] : [Ar] $3d^5\ 4s^1$

(4) It indicates co–ordination number of metal ion.

(5) one 4s, three 4p and two 4d orbitals giving sp^3d^2 hybridized orbitals.

(B) Answer the following : **(6)**

(1) (a) Sodium hexanitrito cobaltate (II)

(b) Hexa carbonyl iron (O)

(2) Because the screening effect of the electrous in the inner filled shells is different on different orbitals of the same shell.

(3) (a) $AS_4O_6 \rightarrow$ Arsenic trioxide

(b) $H_3SbO_4 \rightarrow$ Orthoantimonic acid

(c) $P_4O_8 \rightarrow$ Phosphorous tetraoxide

Q. 5. (d)

(1)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3*	(+2)	(+2)	+2	+2*	(+1)	(+1)	+1	+2*	
	+3	+3	+3*	+3	+2	+2	+2*	+2*	
	+4*	+4*	(+4)	+4	+3*	+3*	(+3)		
		+5	(+5)	(+5)	+4	(+4)	(+4)		
			(+6)	(+6)	+6				
				+7					

In the table, the most stable oxidation states are shown by asterisk, while the unstable or rare states are placed in brackets. The oxidation states shown in brackets are the ones found in unstable compound.s These oxidation states are found in common compounds but there are cases known +1, 0 and even negative oxidation states.

The oxidation state of the transition metal atom can be easily calculated in the compounds where the electronegativity difference between the transition element atom and the other atoms combined with it is appreciably large. Generally the ligands possessing N, O, or a halogen form compounds by forming σ–bonds with the metal atom. In the compounds of this type, the oxidation state of the metal atom is positive. But in the compounds of the transition metals with ligands which can accept π–electrons of the metal, the oxidation state of the metal atom is negative but stable. Such liigands are fluoride, cyanide, phosphate, etc.

(2) Complex compounds are of great importance. They are resent in plants, animals and minerals and play a very important role in them. For example, chlorophyll, a magnesium complex present in green plants is important for photosynthesis. Hemoglobin, an iron complex present in animal blood, serves to carry oxygen to the muscles and to remove CO_2 from the blood. The complexes present in minerals are useful as catalysts in the metallurgical industries and as analytical reagents in the laboratory.

The first systematic study of complex compounds was done by Werner in 1892. He prepared several complex compounds by the reaction between cobalt chloride and ammonia and from their exhaustive studies proposed his theory of complex compounds.

(3) (a) The neutral atoms or the cation of the transition elements occupying the centers of the molecules of the complex compounds aer linked with the surrounding anions or neutral molecules by co–ordinate bonds, and these anions or neutral molecules co–ordinated to the central metal ion are called ligands. Ligands function as Lewis bases, sincce they donate electron pairs and the central metal ion of the complex being the acceptor of electron–pairs acts as a Lewis acid.

$CO^{3+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{3+}$

(b)

$[Fe(CN)_6]^{4-}$	⇅ ⇅ ⇅ xx xx	xx	xx xx xx	☐ ☐ ☐ ☐ ☐
$[Fe[H_2O]_6]^{1+}$	↿ ↿ ↿ ↿ ↿	xx	xx xx xx	xx xx ☐ ☐ ☐

→ As Cn^- is strong ligand. So pairing of electorns in 3d–orbitals gives all electrons paird. So it is diamagnetic.

While H_2O is weak ligand. So pairing of electrons does not take place. It gives five unpaired electrons. So it is paramagnetic.

(4) **Phosphorus :** There are three different forms (allotropes) of phosphorus : (1) Yellow phosphorus (2) Red phosphorus and (3) Black phsphorus.

All the three allotropes are solid at ordinary temperature. The yellow phosphorus is wax–like soft and reactive. In air it spontaneously ignites at 35^0C and, therefore has to be kept under water. It causes burns. The tetrahedral P_4 molecules of the solid, liquid nad vapour states decompose into P_2 molecules. When yellow phosphorus is heated to a temperature of 250^0C or lower in presence of sunlight with I_2 as a catalyst and under an inert atmosphere of CO or N_2 red phosphorus is obtained.

Red phosphorus is a plymolecular solid. It does not ignite on exposure to air or on being heated to 400^0C.

Black phosphorus is obtained on heting yellow phosphorus under high pressure. It is a polymolecular solid. It is the most stable form of phosphorus.

Arsenic : There are three allotropic forms of arsenic : (1) grey (2) yellow and (3) black. All three forms are solids at ordinary temperatures. The grey arsenic is crystalline and is a good conductor of electricity showing that this form has a metallic character. Yellow arsenic is a good thermal and electrical conductor but it is unstable. Black arsenic possesses mixed properties of a metal and a non–metal. It is a non–conductor of heat and electricity.

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