LIBERTY PAPER SET

STD. 12 : Chemistry

Full Solution

Time : 3 Hours **ASSIGNMENT PAPER 14**

Part A

1. (D) **2.** (C) **3.** (A) **4.** (C) **5.** (D) **6.** (B) **7.** (B) **8.** (A) **9.** (D) **10.** (A) **11.** (B) **12.** (D) **13.** (B) **14.** (A)
15. (D) **16.** (D) **17.** (C) **18.** (C) **19.** (D) **20.** (C) **21.** (B) **22.** (A) **23.** (B) **24.** (B) **25.** (C) **26.** (C)
27. (C) **28.** (A) **29.** (B) **30.** (D) **31.** (C) **32.** (D) **33.** (A) **34.** (C) **35.** (D) **36.** (C) **37.** (D) **38.** (B)
39. (A) **40.** (B) **41.** (A) **42.** (B) **43.** (A) **44.** (D) **45.** (D) **46.** (B) **47.** (A) **48.** (B) **49.** (C) **50.** (A)

Part B

Section A

➢ **Write the answer of the following questions : (Each carries 2 Mark)**

1.

➥ n = 2

$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[Ni^{2+}]}{[Ag^+]^2}$$

$$= 1.05 - \frac{0.059}{2} \log \frac{0.160}{(0.002)^2}$$

$$E_{cell} = 1.05 - \frac{0.059}{2} \log (40000)$$

$$= 1.05 - \frac{0.059}{2} \times 4.6021$$

$$= 1.05 - 0.1358$$

$$= 0.91\ V$$

2.

➥ $$\text{Average rate} = \frac{\text{Decrease in concentration of R}}{\text{time taken}}$$

$$= -\frac{\Delta[R]}{\Delta t}$$

$$= -\frac{0.02 - 0.03}{25}$$

$$= \frac{0.01}{25}$$

$$= 4 \times 10^{-4}\ M\ min^{-1}$$

$$\text{Rate of reaction in terms of second} = \frac{4 \times 10^{-4}\ M}{60\ sec} = 6.67 \times 10{-6}\ M\ s{-1}$$

3.

➥ Manganese ($_{25}Mn$) shows largest number of oxidation states because it has maximum number of unpaired electrons.

4.

➥ Potassium permanganate is used as a favourite oxidant in preparative organic chemistry.

➥ Its uses are for the bleaching of wool, cotton, silk and other textile fibres and for the decolourisation of oils are also dependent on its strong oxidising power.

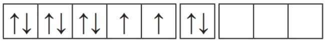
➥ An aqueous solution of potassium permanganate is used for gargling to keep mouth germfree as it is antiseptic.

➥ It is useful as titrant in redox titrations to know the proportion of metal ions like iron (II) and organic compounds like oxalic acid.

5.

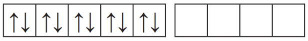
➥ In $[Ni(CO)_4]$ Ni is in the zero oxidation state. It's Electronic configuration is

$_{28}Ni$: [Ar] $3d^8$ $4s^2$ 4p



➥ But CO is a strong field ligand. Therefore, it causes the pairing of unpaired 3d electrons. Also, it causes the 4s electrons to shift to the 3d orbital, thereby giving rise to sp^3 hybridization.

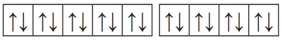
$_{28}Ni$: [Ar] $3d^{10}$



4 Sp^3 hybrid orbitals

- Each CO donate electron pair to Sp^3 hybrid orbital.

$[Ni(CO)_4]$: $[Ar]\ 3d^{10}$



4 pairs of electrons form 4 CO

- Since no unpaired electrons are present in this case, $[Ni(CO)_4]$ is diamagnetic.

6.

- Solution :
  - (i) $[Co(NH_3)_4(H_2O)_2]Cl_3$
  - (ii) $K_2[Ni(CN)_4]$
  - (iii) $[Cr(en)_3]Cl_3$

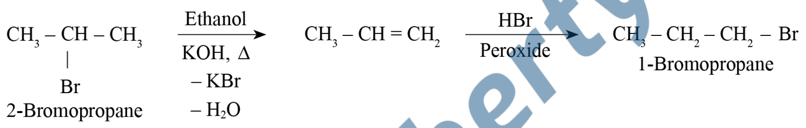
7.

- Propene to propan-l-ol

$$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[\text{Peroxide}]{\text{HBr}} \underset{\text{1-Bromopropane}}{CH_3-CH_2-CH_2-Br} \xrightarrow[\text{KOH} \atop -\text{KBr}]{\text{Aquous}} \underset{\text{Propan-1-Ol}}{CH_3-CH_2-CH_2-OH}$$

8.

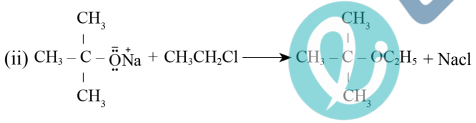
- 2-Bromopropane to 1-bromopropane



$$\underset{\text{2-Bromopropane}}{CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3} \xrightarrow[\text{KOH, }\Delta \atop {-\text{KBr} \atop -H_2O}]{\text{Ethanol}} CH_3-CH=CH_2 \xrightarrow[\text{Peroxide}]{\text{HBr}} \underset{\text{1-Bromopropane}}{CH_3-CH_2-CH_2-Br}$$

9.

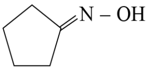
- (i) The major product of the given reaction is 2-methylprop-1-ene. It is because sodium ethoxide is a strong nucleophile as well as a strong base. Thus, elimination reaction predominates over substitution.



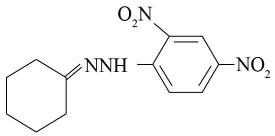
$$\text{(ii) } CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-\ddot{\overset{..}{O}}\overset{+}{N}a + CH_3CH_2Cl \longrightarrow CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OC_2H_5 + Nacl$$

10.

- (i)



- (ii)



11.

- Vitamins are classified into two groups depending upon their solubility in water or fat.
- (i) Fat soluble vitamins :
  - Vitamins which are soluble in fat and oils but insoluble in water are kept in this group. These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues.
- (ii) Water soluble vitamins :
  - B group vitamins and vitamin C are soluble in water so they are grouped together. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot be stored (except vitamin B_{12}) in our body.
  - Vitamin K increases blood clotting time.

12.

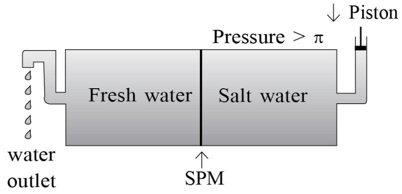
- A polymer made up of pentose sugar, Heterocyclic bases and phosphate ion containing nucleotide is known as nucleic acids.
- Nucleic acids are responsible for protein synthesis in a cell. It is responsible for the transmission of inherent characters from one generation to the next. This process of transmission is called heredity.

Section B

- **Write the answer of the following questions : (Each carries 3 Mark)**

13.

- *The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. That is, now the pure solvent flows out of the solution through the semi permeable membrane. This phenomenon is called reverse osmosis.*



- Reverse osmosis is used in desalination of sea water.
- When pressure is more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane. A variety of polymer membranes are available for this purpose.
- The pressure required for the reverse osmosis is quite high. A workable porous membrane is a film of cellulose acetate placed over a suitable support. Cellulose acetate is permeable to water but impermeable to impurities and ions present in sea water.
- These days many countries use desalination plants to meet their potable water requirements.

14.

- $A = \pi r^2 = 3.14 \times 0.5^2 cm^2$

$= 0.785\ cm^2 = 0.785 \times 10^{-4}\ m^2$

$l = 50\ cm = 0.5\ m$

$R = \frac{\rho l}{A}$ or

$\rho = \frac{RA}{l} = \frac{5.55 \times 10^3\ \Omega \times 0.785\ cm^2}{50\ cm}$

$= 87.135\ \Omega\ cm$

Conductivity $= \kappa = \frac{l}{\rho} = \left(\frac{1}{87.135}\right) S\ cm_{-1}$

$= 0.01148\ S\ cm^{-1}$

Molar conductivity,

$\Lambda m = \frac{\kappa \times 1000}{c}\ cm^3\ L^{-1}$

$= \frac{0.01148\ S\ cm^{-1} \times 1000\ cm^3\ L^{-1}}{0.05\ mol\ L^{-1}}$

$= 229.6\ S\ cm^2\ mol^{-1}$

If we want to calculate the values of different in terms of ‘m’ instead of ‘cm’.

$\rho = \frac{RA}{l}$

$$= \frac{5.55 \times 10^3 \Omega \times 0.785 \times 10^{-4} \text{ m}^2}{0.5 \text{ m}}$$

$$= 87.135 \times 10^{-2} \, \Omega \text{ m}$$

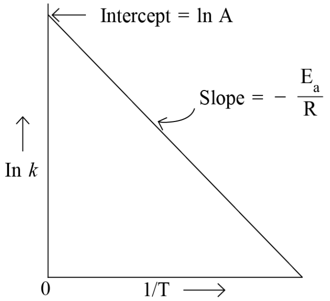
$$\kappa = \frac{l}{\rho} = \frac{100}{87.135} \, \Omega \text{ m} = 1.148 \text{ S m}^{-1}$$

$$\text{and } \Lambda_m = \frac{\kappa}{c} = \frac{1.148 \text{ S m}^{-1}}{50 \text{ mol m}^{-3}}$$

$$= 229.6 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

15.

- Activation energy using graph :
- Taking natural logarithm on both the side of Arrhenius equation $k = A e^{-\frac{E_a}{RT}}$
- $\ln k = -\frac{E_a}{RT} + \ln A$ ... ... Eq. (1)
- The plot of ln k vs 1/T gives a straight line as shown in figure.



- In figure, slope = $-\frac{E_a}{R}$ and intercept = ln A. So, we can calculate activation energy (E_a) and Arrhenius constant A using these values.
- Formula of activation energy :
- It has been found from Arrhenius equation that increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in rate constant.
- Thus, at temperature T_1, equation (1) is

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \text{ ... ... Eq. (2)}$$

- at temperature T_2, equation (1) is

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \text{ ... ... Eq. (3)}$$

(since A is constant for given reaction)

k_1 and k_2 are rate constant at temperatures T_1 and T_2 respectively.

- Subtracting equation (2) from (3), we obtain

$$\ln k_2 - \ln k_1 = \frac{-E_a}{RT_2} + \frac{E_a}{RT_1}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

- From above formula activation energy can be calculate using measured values of rate constants at different temperatures.

16.

- The transition metals and their compounds are known for their catalytic activity.
- This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes.
- Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in Catalytic Hydrogenation) are some of the examples.
- Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3d and 4s electrons for bonding).
- This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering).
- The Transition metal ions can change their oxidation states, they become more effective as catalysts.
- For example, iron (lll) catalyses the reaction between iodide and persulphate ions.

$$2\,I^- + S_2O_8^{2-} \rightarrow I_2 + 2\,SO_4^{2-}$$

- An explanation of this catalytic action can be given as :

$$2\,Fe^{3+} + 2\,I^- \rightarrow 2\,Fe^{2+} + I_2$$

$$2\,Fe^{2+} + S_2O_8^{2-} \rightarrow 2\,Fe^{3+} + 2SO_4^{2-}$$

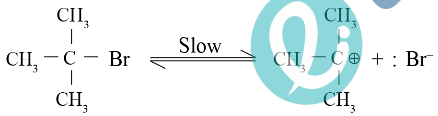
17.

- S_N1 reactions are generally carried out in polar protic solvents (like water, alcohol, acetic acid etc.)
- The reaction between tert- butyl bromide and hydroxide ion yields tert-butyl alcohol and follows the first order kinetics,
- The rate of reaction depends upon the concentration of only one reactant, which is tert- butyl bromide.
- Rate = $K[(CH_3)_3\,C\,Br]$

$$(CH_3)_3CBr + {}^-OH \longrightarrow (CH_3)_3\,COH + Br^-$$

2-Bromo-2-methylpropane 2-methylpropane-2-01

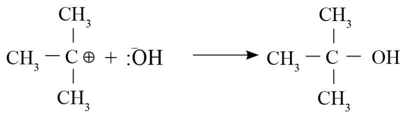
- It occurs in two steps. In step I, the polarised C–Br bond undergoes slow cleavage to produce a carbocation and a bromide ion.
- Step 1 :



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br \xrightleftharpoons{\text{Slow}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\oplus + :Br^-$$

tert-butyl bromide

- The carbocation formed is then attacked by nucleophile in step II to complete the substitution reaction.
- Step 2 :



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\oplus + :\bar{O}H \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$$

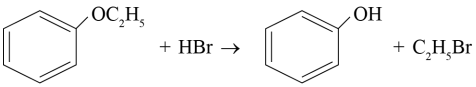
tert-butyl alcohol

- Step I is the slowest and reversible. It involves the C–Br bond breaking for which the energy is obtained through solvation of halide ion with the proton of protic solvent.
- Since the rate of reaction depends upon the slowest step, the rate of reaction depends only on the concentration of alkyl halide and not on the concentration of hydroxide ion.
- Further, greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction. In case of alkyl halides, 3^o alkyl halides undergo SN^1 reaction very fast because of the high stability of 3^o carbocations.
- Reactivity order for S_N1 reaction
- 3^0 – halide > 2^0 – halide > 1^0 – halide > $CH_3 - X$

18.

➥ (i) $CH_3-CH_2-CH_2-O-CH_3 + HBr \rightarrow CH_3CH_2CH_2OH + CH_3Br$

(ii)



(iii) $(CH_3)_3\,C-OC_2H_5 \xrightarrow{HI} (CH_3)_3\,C-I + C_2H_5OH$

19.

➥ (i) Butane-1,3-diol

$$2CH_3CHO \xrightarrow{\text{Dil NaOH}} \underset{\text{3-Hydroxy butanal}}{CH_3CH(OH)CH_2CHO} \xrightarrow{NaBH_4} \underset{\text{Butan-1,3-diol}}{CH_3CH(OH)CH_2CH_2OH}$$

(ii) But-2-enal

$$2CH_3CHO \xrightarrow{\text{Dil NaOH}} CH_3CH(OH)CH_2CHO \xrightarrow[-H_2O]{H_3O^+} \underset{\text{But-2-enal}}{CH_3-CH=CH-CHO}$$

(iii) But-2-enoic acid

$$\underset{\text{Ethanal}}{2CH_3CHO} \xrightarrow[\text{(ii) }H_3O^+]{\text{(i) Dil NaOH}} CH_3CH=CHCHO \xrightarrow[\text{Tollens' reagent}]{[Ag(NH_3)_2]^+OH^-} \underset{\text{But-2-enoic acid}}{CH_3CH=CHCOOH}$$

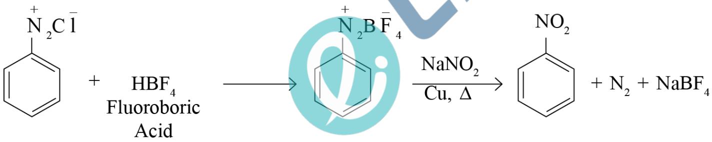
20.

➥ Replacement by hydroxyl group :

➥ If the temperature of the diazonium salt solution is allowed to rise upto 283 K, the salt gets hydrolyzed to phenol.

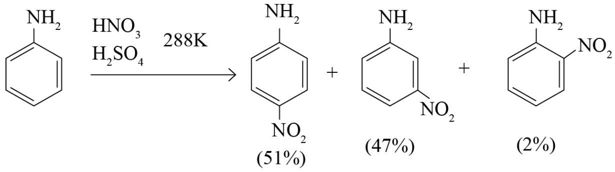
$$Ar\overset{+}{N}_2\overset{-}{Cl} + H_2O \rightarrow ArOH + N_2 + HCl$$

➥ Replacement by nitrogroup : When diazonium fluroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by $-NO_2$ group.

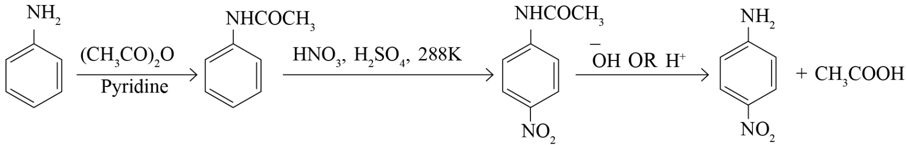


21.

➥ Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives. Moreover in the strongly acidic medium, aniline is protonated to form the anilinium ion which is meta directing. That is why besides the ortho and para derivatives, significant amount of meta derivative is also formed.



➥ However by protecting the $-NH_2$ group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the P-nitro derivative can be obtained as the major product.



Acetanilide P-nitroacetanilide P-nitroaniline

Section C

- **Write the answer of the following questions : (Each carries 4 Mark)**

22.

- Henry give a quantitative relation between pressure and solubility of a gas in a solvent which is known as Henry's law.
- *"At a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution."*
- If we use the mole fraction of a gas in the solution as a measure of its solubility, then it can be said that the mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution.

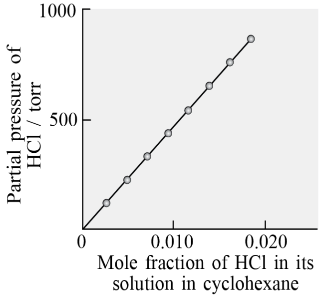
$p = K_H x$

Where, p = Partial pressure of gas.

K_H = Henry's constant

x = Solubility of gas

- If we draw a graph between partial pressure of the gas versus mole fraction of the gas in solution, then we should get a plot of the type as shown in Fig.



- Different gases have different K_H values at the same temperature
- Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.
- If temperature increases the value of K_H increases so solubility decreases.
- Values of Henry's Law Constant for Some Selected Gases in Water (information only)

Gas	Temperature/K	KH / kbar
He	293	144.97
H_2	293	69.16
N_2	293	76.48
N_2	303	88.84
O_2	293	34.86
O_2	303	46.82
Argon	298	40.3
CO_2	298	1.67
Formaldehyde	298	1.83×10^{-5}
Methane Vinyl	298	0.413
Chloride	298	0.611

- Applications :

  (1) To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

  (2) Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood. When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends, which are painful and dangerous to life.

- To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

  (3) At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.

23.

- Cell B : $AgNO_3 \rightarrow Ag^+ + NO_3^-$

  Cathode : $Ag^+ + e^- \rightarrow Ag$

  1F gives → 108 g Ag

  ∴ 108 g Ag obtain by 1F

  ∴ 1.45 g Ag obtain by (?)

  $$F = \frac{1.45 \times 1}{108} = 0.01342\ F$$

  $$F = \frac{I \times t}{96,500}$$

  $$\therefore 0.01342 = \frac{1.5 \times t}{96,500}$$

  $$\therefore t = \frac{0.01342 \times 96500}{1.5} = 863.73\ \text{sec.}$$

- Cell A : $ZnSO_4 \rightarrow Zn^{+2} + SO_4^{-2}$

  Cathode : $Zn^{+2} + 2e^- \rightarrow Zn$

  2F give → 65.3 g Zn

  ∴ 0.01342 F give → (?)

  $$W_{Zn} = \frac{0.01342 \times 65.3}{2} = 0.438\ g\ Zn$$

- Cell C : $CuSO_4 \rightarrow Cu^{+2} + SO_4^{-2}$

  Cathode : $Cu^{+2} + 2e^- \rightarrow Cu$

  2F give → 63.5 g Cu

  ∴ 0.01342 F give → (?)

  $$W_{Cu} = \frac{0.01342 \times 63.5}{2} = 0.426\ g\ Cu$$

24.

- Average Rate

  $$= \frac{1}{2}\left\{-\frac{\Delta[N_2O_5]}{\Delta t}\right\} = \frac{-1}{2}\left[\frac{2.08 - 2.33\ \ \text{mol L}^{-1}}{184\ \text{min}}\right]$$

  $= 6.79 \times 10^{-4}$ mol L^{-1}/min

  $= (6.79 \times 10^{-4}$ mol L^{-1} $\text{min}^{-1}) \times (60$ min/1h)

  $= 4.07 \times 10^{-2}$ mol L^{-1}/h

  $= 6.79 \times 10^{-4}$ mol L^{-1} × 1 min/60s

  $= 1.13 \times 10^{-5}$ mol L^{-1} s^{-1}

It may be remembered that

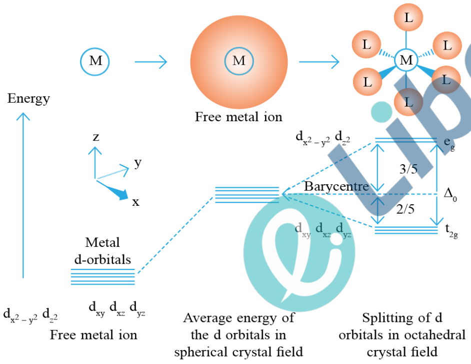
$$\text{Rate} = \frac{1}{4}\left\{\frac{\Delta[NO_2]}{\Delta t}\right\}$$

$$\frac{\Delta[NO_2]}{\Delta t} = 6.79 \times 10^{-4} \times 4 \text{ mol L}^{-1}\text{ min}^{-1}$$

$$= 2.72 \times 10^{-3}\text{ mol L}^{-1}\text{ min}^{-1}$$

25.

- In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal d orbitals and the electrons (or negative charges) of the ligands.
- Such a repulsion is more when the metal d orbital is directed towards the ligand than when it is away from the ligand.
- Thus, the $dx^2\text{–}y^2$ and dz^2 orbitals which point towards the axes along the direction of the ligand will experience more repulsion and will be raised in energy.
- The d_{xy}, d_{yz} and d_{xz} orbitals which are directed between the axes will be lowered in energy relative to the average energy in the spherical crystal field.
- Thus, the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set.
- This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δo.
- Thus, the energy of the two e_g orbitals will increase by (3/5) Δo and that of the three t_{2g} will decrease by (2/5)Δo.



d-orbital splitting in an octahedral crystal field

- The crystal field splitting, Δo, depends upon the field produced by the ligand and charge on the metal ion.
- Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently, result in small splitting of d orbitals.
- In general, ligands can be arranged in a series in the order of increasing field strength as given below

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$$

- Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands.
- Let us assign electrons in the d orbitals of metal ion in the octahedral coordination entities.
- The single d electron occupies one of the lower energy t_{2g} orbitals. In d^2 and d^3 coordination entities, the d electrons occupy the t_{2g} orbitals singly accordance with the Hund's rule.
- For d^4 ions, two possible patterns of electron distribution arise:

(i) The fourth electron could either enter the t_{2g} level and pair with an existing electron,

(ii) It could avoid paying the price of the pairing energy by occupying the e_g level.

- Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting, Δo and the pairing energy, P

  (i) If $\Delta_0 < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_0 < P$ are known as weak field ligands and form high spin complexes.

  (ii) If $\Delta_0 > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as strong field ligands and form low spin complexes.

26.

- (i) Acidic potassium dichromate or neutral/acidic/alkaline $KMnO_4$.

  (ii) Pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl.

  (iii) Bromine water Br_2/H_2O.

  (iv) Acidic or alkaline potassium permanganate.

27.

- (A) forms 2,4-DNP derivative. Therefore, it is an aldehyde or a ketone. Since it does not reduce Tollens' or Fehling reagent, (A) must be a ketone. (A) responds to iodoform test. Therefore, it should be a methyl ketone. The molecular formula of (A) indicates high degree of unsaturation, yet it does not decolourise bromine water or Bayer's reagent. This indicates the presence of unsaturation due to an aromatic ring.

- Compound (B), being an oxidation product of a ketone should be a carboxylic acid. The molecular formula of (B) indicates that it should be benzoic acid and compound (A) should, therefore, be a monosubstituted aromatic methyl ketone. The molecular formula of (A) indicates that it should be phenyl methyl ketone (acetophenone). Reactions are as follows: