# Sample Paper 18 Solutions

### Class XII 2023-24

# Chemistry

Time: 3 Hours General Instructions: Max. Marks: 70

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

# SECTION-A

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

- The most durable metal plating on iron to protect against corrosion is
  - (a) nickel plating
- (b) copper plating
- (c) tin plating
- (d) zinc plating

Ans: (d) zinc plating

This is because zinc has higher oxidation potential than Ni, Cu and Sn. The process of coating of iron surface with zinc is known as galvanization. Galvanized iron sheets maintain their lustre due to the formation of protective layer of basic zinc carbonate.

- The rate of reaction between A and B increases by a factor of 100, when the concentration of A is increased 10 folds, the order of reaction with respect to A is
  - (a) 10

(b) 1

(c) 4

(d) 2

Ans: (d) 2

$$(Rate_1) = K[A]^l[B]^m;$$
 $(Rate)_2 = K(10[A])^l[B]^m$ 
Hence,
$$\frac{(Rate)_2}{(Rate)_1} = 100 = 10^l$$
or
$$10^2 = 10^l$$
 $l = 2$ 

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- 3. The rate of a first order reaction is 1.5 × 10<sup>-2</sup> mol L<sup>-1</sup>min<sup>-1</sup> at 0.5 M concentration of the reactant. The half life of the reaction is
  - (a) 0.383 min
- (b) 23.1 min
- (c) 8.73 min
- (d) 7.53 min

Ans: (b) 23.1 min

For a first order reaction,

$$A \longrightarrow \text{products}$$

$$r = k[A]$$

$$k = \frac{r}{[A]}$$

$$k = \frac{1.5 \times 10^{-2}}{0.5} = 3 \times 10^{-2}$$

Further

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3 \times 10^{-2}} = 23.1 \text{ min}$$

- 4. Which one of the following ionic species will impart colour to an aqueous solution?
  - (a) Ti<sup>4+</sup>

(b) Cu<sup>+</sup>

(c) Zn<sup>2+</sup>

(d) Cr3+

Ans: (d) Cr<sup>3+</sup>

We know that chromium (III) salts dissolve in water to give violet solution. The violet colour is due to the hydrated chromium (III) in [Cr(H<sub>2</sub>O<sub>6</sub>]<sup>3+</sup>.

- 5. If 96500 coulomb of electricity is passed through CuSO<sub>4</sub> solution, it will liberate:
  - (a) 63.5 g Cu
- (b) 31.76 g Cu
- (c) 96500 g Cu
- (d) 100 g Cu

Ans: (b) 31.76 g Cu

Molar mass of copper = 63.5

As Copper (Cu) contain (+)2 charge in CuSO<sub>4</sub>, it requires  $2F (= 2 \times 96500 \, C)$  charge to give one mole i.e. 63.5 g of copper. Thus on giving 96500 C of electricity, we get  $63.5/2 = 31.76 \, g$  of copper.

Hence, (b) is the correct option.

- 6. In which of the following conversions, phosphorous 10. pentachloride is used as the reagent?
  - (a)  $H_2C = CH_2 \longrightarrow CH_3CH_2Cl$
  - (b) CH<sub>3</sub>CH<sub>2</sub>OH → CH<sub>3</sub>CH<sub>2</sub>Cl
  - (c)  $H_3C O CH_3 \longrightarrow CH_3Cl$
  - (d) CH ≡ CH − → CH<sub>2</sub> = CHCl

Ans: (b) CH<sub>3</sub>CH<sub>2</sub>OH ---- CH<sub>3</sub>CH<sub>2</sub>Cl

When entryl alcohol is treated with PCl<sub>5</sub>, then ethyl chloride is formed.

$$CH_3CH_2 - OH + PCl_5 \xrightarrow{\Lambda}$$
  
 $CH_3CH_2 - Cl + HCl + POCl_3$ 

- Among the following, the compound that is both paramagnetic and coloured is
  - (a) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>
- (b) (NH<sub>4</sub>), (TiCl<sub>6</sub>)
- (c) CoSo<sub>4</sub>
- (d) K<sub>3</sub>[Cu(CN),]

Ans: (c) CoSo<sub>4</sub>

In  $(NH_4)_2(TiCl_6)$ ,  $Ti^{4+}(3d^04s^0)$  has no unpaired electrons.

In  $K_2Cr_2O_7$ ,  $Cr^{6+}(3p^64d^0)$  has no unpaired electrons. In  $CoSo_4$ ,  $Co^{2+}(d^7)$  has three unpaired electrons in d

-orbitals so it is both paramagnetic and coloured. In K<sub>3</sub>[Cu(CN)<sub>4</sub>], Cu<sup>+</sup>(3d<sup>10</sup>), no unpaired electron.

- 8. Which of the following compounds does not react with NaNO<sub>2</sub> and HCl?
  - (a) C<sub>6</sub>H<sub>5</sub>OH
- (b) C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>
- (c) (CH<sub>3</sub>)<sub>3</sub>CNO<sub>2</sub>
- (d) (CH<sub>3</sub>)<sub>3</sub>CNO<sub>2</sub>

Ans: (c) (CH<sub>3</sub>)<sub>2</sub>CHNO<sub>2</sub>

With nitrous acid: (i) phenol gives p-nitrosophenol, (ii) aniline gives diazonium salt, and (iii)  $2^{\circ}$  nitro compounds give pseudonitrole, while  $3^{\circ}$  nitro compounds do not react because they have no  $\alpha$ -hydrogen atom.

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- 9. Ethylene reacts with Baeyer's reagent to give
  - (a) ethane
- (b) ethyl alcohol
- (c) ethylene glycol
- (d) none

Ans: (c) ethylene glycol

This reaction is known as Baeyer's test for unsaturation.

- 10. Which one of the following esters cannot undergo Clasien self-condensation?
  - (a) CH<sub>3</sub> CH<sub>2</sub> CH<sub>2</sub> CH<sub>2</sub> COOC<sub>2</sub>H<sub>5</sub>
  - (b) C<sub>6</sub>H<sub>5</sub>COOC<sub>2</sub>H<sub>5</sub>
  - (c) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub>
  - (d) C<sub>6</sub>H<sub>11</sub>CH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub>

Ans: (b)  $C_6H_5COOC_2H_5$ 

The ester having  $\alpha$  hydrogen atom show Claisen condensation reaction. We know that ethyl benzoate ( $C_6H_5COOC_2H_5$ ) does not contain  $\alpha$ -hydrogen. Therefore  $C_6H_5COOC_2H_5$ does not undergo Claisen self-condensation.

- 11. The pyrimidine bases present in DNA are
  - (a) cytosine and thymine
  - (b) cytosine and uracil
  - (c) cytosine and adenine
  - (d) cytosine and guanine

Ans: (a) cytosine and thymine

The Pyrimidine bases present in DNA are cytosine and thymine.

- 12. If 0.1 M solution of glucose and 0.1 M solution of urea are placed on two sides of the semi-permeable membrane to equal heights, then it will be correct to say that:
  - (a) there will be no net movement across the membrane
  - (b) glucose will flow towards urea solution
  - (c) urea will flow towards glucose solution
  - (d) water will flow from urea solution to glucose

Ans: (a) there will be no net movement across the membrane

As both the solutions are isotonic hence there is no net movement of the solvent through the semi-permeable membrane between two solutions.

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

 Assertion: Hydroxyketones are not directly used in Grignard reaction.

Reason: Grignard reagents react with hydroxyl group.

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

Ans: (a) Both Assertion and Reason are correct and Reason is a correct explanation of the Assertion. Hydroxy ketones are not directly used in Grignard reagent. Grignard reagents are very reactive. Therefore, they react with hydroxyl group. Hence assertion and reason both are correct and reason is a correct explanation of the assertion

 Assertion: An ether is more volatile than an alcohol of comparable molecular mass.

Reason: Ethers are polar in nature.

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

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

As hydrogen bonding does not exist among ether molecules. It is more volatile than alcohol.

 Assertion: Magnetic moment values of actinides are lesser than the theoretically predicted values.

Reason: Actinide elements are strongly paramagnetic.

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

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

The magnetic moment is less as the 5f electrons of actinides are less effectively shielded which results in quenching of orbital contributions. They are strongly paramagnetic due to presence of unpaired electrons.

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 Assertion: Protonation of a carbonyl group increases its electrophilic character.

Reason: Protonation of a carbonyl group involves addition of an electrophile on nucleophilic oxygen.

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

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

## SECTION-B

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

 Arrange the following carbonyl compounds and nucleophilic addition-climination reaction.

Ethane, Propanal, Propanone, Butanone

#### Ans:

The increasing order of +I effect of the alkyl group is

$$CH_3$$
 $C=O < CH_3CH_2$ 
 $C=O < CH_3$ 
 $C=O <$ 

With increase in +I effect of alkyl groups electron density on the carbon atom of carboxyl group increases and hence the attack by the nucleophile becomes slower and slower. Thus the reactivity is

butanone<Propanone<Propanal<Ethanal

Discuss the factors responsible for rusting of iron.

#### Ans

- Air and moisture: These are responsible for rusting of iron.
- Presence of Impurities: Impurities in general, increase the rate of corrosion.
- Presence of electrolyte in water: Rate of corrosion is more in saline water.
- 4. Strain: Strain in metal increases the rate of corrosion.
- 19. What are the products obtained at the platinum anode and the platinum cathode respectively in the electrolysis of fused or molten NaCl?

#### Ans:

In the electrolysis of fused (or) molten NaCl with platinum anode and platinum cathode, sodium metal obtained at cathode and chlorine gas at anode

$$2 \operatorname{NaCl} \longrightarrow 2 \operatorname{Na}^+ + 2 \operatorname{Cl}^-$$
  
 $2\operatorname{Cl}^- \longrightarrow \operatorname{Cl}_2 + 2\operatorname{e}^-$  (anode)  
 $2\operatorname{Na}^+ + 2\operatorname{e}^- \longrightarrow 2 \operatorname{Na}$  (cathode)

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Every School conduct Pre-Board From These Sample Papers Explain hydrogenolysis reaction of an ester.

#### Ans:

**Hydrogenolysis**: (cleavage by hydrogen) of an ester requires high pressure, elevated temperatures and copper chromite catalyst (which is a mixture of oxides of approx composition  $CuO \cdot CuCr_2O_4$ )

For example,

 $CH_3(CH_2)_{10}COOCH_3$ 

Methyl dodecanoate

$$\xrightarrow{\text{H}_{2},\text{CuO} \cdot \text{CuCr}_{2}\text{O}_{2}} \text{CH}_{3}(\text{CH}_{2})_{10}\text{CH}_{2}\text{OH} + \text{CH}_{3}\text{OH}$$

$$\xrightarrow{\text{1-Dodecanol}}$$

or

How is chemical reduction of esters done? What are the products obtained?

#### Ans

Chemical reduction is carried out by use of sodium metal and alcohol or by use of LiAlH<sub>4</sub>.

For example,

 $CH_3(CH_2)_{14}COOC_2H_5$ 

Ethyl hexadecanoate

$$\xrightarrow{\text{LiAlH}_4}$$
 CH<sub>3</sub>(CH<sub>2</sub>)<sub>14</sub>CH<sub>2</sub>OH + C<sub>2</sub>H<sub>5</sub>OH

1-Hexadecanol

- 21. Write and IUPAC name of the following coordination compounds:
  - (a) K<sub>4</sub>[Fe(CN)<sub>6</sub>]
  - (b) Ni(CO)<sub>4</sub>
  - (c) K<sub>2</sub>[Pt(Cl)<sub>6</sub>]
  - (d) Fe<sub>4</sub>[Fe(CN)<sub>6</sub>],

#### Ans:

- (a) K<sub>4</sub>[Fe(CN)<sub>6</sub>] Potassium hexacyganoferrate (II)
- (b) Ni(CO)<sub>4</sub> tetracarbonylnickel (0)
- (c) K<sub>2</sub>[Pt(Cl), Potassium hexachlorido palatinate (IV)
- (d) Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>8</sub> iron (III) hexa cyano ferrate (II)

# SECTION-C

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

22. Predict the products of the following reactions.

$$(ii) \qquad \begin{array}{c} O \\ + NH_2 - NH \end{array} \longrightarrow \begin{array}{c} NO_2 \\ - NO_2 \end{array}$$

(iii) 
$$R-CH=CHCHO+NH_2-C-NH-NH_2 \xrightarrow{H^+}$$

(iv) 
$$CH_3 + CH_3CH_2NH_2 \xrightarrow{H^+}$$

Ans:

(ii) 
$$NNH \longrightarrow NO_2$$

(iii) R-CH=CH-CH=NNHCONH,

$$(iv) \quad \begin{array}{c} \overset{\operatorname{CH}_3}{\longleftarrow} & \overset{\operatorname{CH}_3}{\longleftarrow} \\ \overset{\operatorname{C}}{\longrightarrow} & \overset{\operatorname{CH}_2}{\longleftarrow} & \overset{\operatorname{CH}_3}{\longleftarrow} & \overset{\operatorname$$

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23. Which aqueous solution has higher concentration: 1 molar or 1 molal solution of the same solute. Give reason.

#### Ans:

1 Molar solution has higher concentration than 1 molar solution. A molar solution contains one mole of solute in one litre of solution while a one molal solution contains one mole of solute in 1000 g of solvent. If density of water is one, then one mole of solute is present in 1000 ml of water in 1 molal solution while one mole of solute is present in less than 100 ml of water in 1 molar solution (100 ml solution = amount of solute + amount of solvent). Thus, 1 molar solution is more concentrated.

24. How is molar conductivity of an aqueous electrolyte solution measured experimentally?

#### Ans:

Molar conductivity: The conductivity of a volume of solution containing one gram molecular weight of the electrolyte placed between two parallel electrodes separated by a distance of unit length of 1 meter is called molar conductivity ( $\Lambda_m$ ).

Relation between conductivity and molar conductivity:

$$\Lambda_m = \frac{\kappa}{c}$$
; Hence  $c = \text{constant}$ 

→ The conductance of a solution measured in a conductivity cell.

→ By using the conductivity cells

Resistance 
$$(R) = \frac{l}{\kappa \times A}$$

l = distance between electrodes;

A = Area of cross section

 $\kappa = \text{conductivity}$ 

$$G^* = \frac{l}{A} = \text{cell constant}$$

→ Cell constant is measured by measuring the resistance of the cell containing a solution whose conductivity is known.

→ Cell constant determined is used for measuring the resistance (or) conductivity.

Hence, Molar conductivity

$$\Lambda_{\!\scriptscriptstyle (so)} = \frac{\kappa (Scm^{-1})}{1000 \, (L.m^{-3}) \, molarity \, (moles/lit)}$$

- 25. Write IUPAC names of the following:
  - (a) [Cu(NH<sub>3</sub>),]Cl<sub>2</sub>
  - (b) K<sub>4</sub>[Fe(CN)<sub>c</sub>]

#### Ans:

(a) [Cu(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>

$$x + 0 \times 4 + (-1) \times 2 = 0$$
  
 $x = 2$ 

Tetraammine copper (II) chloride

(b) K<sub>4</sub>[Fe(CN)<sub>6</sub>]

$$1 \times 4 + x + (-1) \times 6 = 0$$
  
 $x = 6 - 4 \quad x = 2$ 

Potassium hexacyano ferrtate (II)

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- Arrange each set of compounds in order of increasing boiling points.
  - Bromomethane, bromoform, chloromethane, dibromomethane.
  - 1-Chloropropane, Isopropyl chloride, 1-chlorobutane.

#### Ans

(i) Boiling point increases with increase the size of halogen atom for the same alkyl group and the boiling points increase as the number of halogen atom increases, therefore the order is: Chloromethane < dibromomethane

<br/>bromoform.

(ii) Boiling point increases as the size of the alkyl group increases and boiling point decreases as the branching increases, therefore the order is: Isopropyl chloride<1-Chloropropane<1-Chlorobutane.</p>

27. Give important used of carboxylic acids.

#### Ans

The important uses of carboxylic acids are as follows:

- 1. In the manufacturing of soaps.
- Production of soft drinks and food products. Sodium salts of organic acids find application in preservatives.
- In the manufacturing of drugs such as aspirin, phenacetin etc.
- Acetic acids are often used as a coagulant in the manufacturing of rubber.
- In making dye stuff, perfumes and rayon.

#### 01

Explain how does -OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?

#### Ans

Due to + R effect - OH group, the electron density in the benzene ring increases, hence presence of OH group, activates the benzene ring towards electrophilic substitution reactions.

The electron density is relatively higher at ortho and para position, therefore electrophilic substitution occurs mainly at ortho and para positions.

28. Write down the electronic configuration of

Cr<sup>3+</sup>

Cu<sup>+</sup>

3.  $Co^{2+}$ 

4.  $Mn^{2+}$ 

### Ans:

1. 
$$Cr^{3+} = [Ar]^{18}3d^3$$

2. 
$$Cu^+ = [Ar]^{18} 3d^{10}$$

3. 
$$Co^{2+} = [Ar]^{18}3d^7$$

4. 
$$Mn^{2+} = [Ar]^{18}3d^5$$

## SECTION-D

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

29. The amines are basic in nature due to the presence of a lone pair of electron on N-atom of the NH<sub>2</sub> group, which it can donate to electron deficient compounds. Aliphatic amines are stronger bases than  $\mathrm{NH_3}$  because of the +I effect of the alkyl groups. Greater the number of alkyl groups attached to N-atom, higher is the electron density on it and more will be the basicity. Aniline is a weaker base compared to ammonia. This is because the lone pair of electrons on N-atom of aniline is less available for protonation due to its involvement in conjugation with the  $\pi$ -electrons of the benzene ring. Further the presence of electron withdrawing groups decreases the basicity while, the presence of electron donating groups activates the benzene ring and also increases the basicity.

Read the above passage and answer the following questions:
(a) (CH<sub>3</sub>)<sub>2</sub>NH is more basic than (CH<sub>3</sub>)<sub>3</sub>N in an aqueous

(b) Arrange the following in increasing order of basic strength: C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>,C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub>,C<sub>6</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>2</sub>

(c)

solution. Give reason

 Arrange the following compounds in an increasing order of basic strength:

 $C_6H_5NH_2$ ,  $C_6H_5N(CH_3)_2$ ,  $(C_2H_5)_2NH$  and  $CH_3NH_2$ 

 (ii) Arrange the following compounds in a decreasing order of pK<sub>b</sub> values.

 $C_2H_5NH_2$ ,  $C_6H_5NHCH_3$ ,  $(C_2H_5)_2NH$ , and  $C_6H_5NH_2$ 

or

(d) Arrange the following in increasing order of basic strength: Aniline, p-nitroaniline and p-toluidine.

#### Ans

- (a) In aqueous solution, 2° amine is more basic than 3° amine due to the combination of inductive effect, solvation effect and steric hindrance.
- (b) Increasing order of basic strength in gaseous state is as follows:

 $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5N(CH_3)_2$ 

As the number of  $-CH_3$  groups (+ I effect)

Attached to nitrogen increases, its basicity will increase.

- (c) (i) Increasing order of basic strength is C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> < C<sub>6</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>2</sub> < CH<sub>3</sub>NH<sub>2</sub> < (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH
  - (ii) Stronger the base, lower will be its pK<sub>δ</sub> value. Hence, the decreasing order of pK<sub>δ</sub> values :

or

- (d) Electron withdrawing group -(NO<sub>2</sub>) on benzene ring decreases the basicity and electron donating group -(CH<sub>3</sub>) on benzene ring increases the basicity of the compound. Increasing order of basic strength: p-nitroaniline < aniline < p-toluidine.</p>
- 30. The unique behaviour of Cu, having a positive E°, accounts for its inability to liberate H<sub>2</sub> from acids. Only oxidising acids (nitric and hot concentrated sulphuric) react with Cu, the acids being reduced. The high energy to transform Cu<sub>(s)</sub> to Cu<sup>2+</sup><sub>(aq)</sub> is not balanced by its hydration enthalpy. The general trend towards less negative E° values across the series is related to the general increase in the sum of the first and second ionisation enthalpies. It is interesting to note that the value of E° for Mn, Ni, and Zn are more negative than expected from the trend.

The stability of the half-filled d sub-shell in Mn<sup>2+</sup> and the completely filled d<sup>10</sup> configuration in Zn are related to their  $E^-$  values, whereas  $E^0$  for Ni is related to the highest negative  $\Delta$  <sub>hud</sub>  $H^0$ .

An examination of the  $E^{\circ}_{(M^{2^{\circ}}/M^{\circ})}$  values shows the varying trends. The low value for Sc reflects the stability of Sc<sup>3+</sup> which has a noble gas configuration. The highest value for Zn is due to the removal of an electron from the stable  $d^{0}$  configuration of Zn<sup>2+</sup>. The comparatively high value for Mn shows that Mn<sup>2+</sup>( $d^{\circ}$ ) is particularly stable, whereas comparatively low value for Fe shows the extra stability of Fe<sup>3+</sup>( $d^{\circ}$ ). The comparatively low value for V is related to the stability of V<sup>2+</sup> (half-filled  $t_{2g}$  level).

Read the above passage and answer the following question:

- (a) Cobalt (II) is very stable in aqueous solutions but gets easily oxidised in the presence of strong ligands.
- (b) Why are E° (M²-/M) values of Mn and Zn more negative than expected ?
- (c) Use the data to answer the following and also justify giving reasons:

	Cr	Mn	Fe	Co
$E^{\circ}_{(M^{2+}/M)}$	-0.91	-1.18	-0.44	-0.28
$E^{\circ}_{(M^{2+}/M^{2+})}$	-0.41	+1.57	+0.77	+1.97

- (i) Which is a stronger reducing agent in aqueous medium, Cr<sup>2+</sup> or Fe<sup>2+</sup> and why?
- (ii) Which is the most stable ion in +2 oxidation state and why?

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or

(d)

	Cr	Mn	Fe	Co	Ni	Cu
$E^{\circ}{}_{(M^{2^+}/M)}$	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

From the given data of  $E^{\circ}$  values, answer the following questions :

- (i) Why is E<sup>0</sup>M<sup>2</sup> value highly negative as compared to other elements?
- (ii) Which is a stronger reducing agent Cr<sup>2+</sup> or Fe<sup>2+</sup> ? Give reason.

#### Ans:

(a) The tendency to form complexes is high for Co(III) as compared to Co(II). Co<sup>2+</sup> ions are very stable and are difficult to oxidise. Co<sup>3+</sup> ions are less stable and are reduced by water. In contrast many Co(II) complexes are readily oxidised to Co(III) complexes and Co(III) complexes are very stable, e.g.,

$$\left[\operatorname{Co}\left(\operatorname{NH}_{3}\right)_{6}\right]^{2+} \xrightarrow{\operatorname{Air}} \left[\operatorname{Co}\left(\operatorname{NH}_{3}\right)_{6}\right]^{3+}$$

This happens because the crystal field stabilisation energy of Co(III) with a  $d^6(t_{2g}^6)$  configuration is higher than for Co(II) with  $d^7(t_{2g}^6e_0^1)$  arrangement.

- (b) Mn<sup>2+</sup> ion has stable half-filled (3d<sup>6</sup>) electronic configuration whereas Zn<sup>2+</sup> has completely filled d<sup>10</sup> configuration. Hence, E<sup>o</sup><sub>Mn<sup>2+</sup>/Mn</sub> and E<sup>o</sup><sub>Zn<sup>2+</sup>/Zn</sub> are more negative than expected.
- (c)

- (i) Cr<sup>2+</sup> is a stronger reducing agent than Fe<sup>2+</sup> E<sup>'</sup> Ma<sup>\*</sup>/Mn is negative (-0.41V) whereas E<sup>'</sup> Fe<sup>2+</sup>/Fe<sup>2+</sup> is positive (+0.77 V). Thus, Cr<sup>2+</sup> is easily oxidized to Cr<sup>3+</sup> but Fe<sup>2+</sup> cannot be easily oxidized to Fe<sup>3+</sup>. Hence, Cr<sup>2+</sup> is stronger reducing agent than Fe<sup>2+</sup>.
- (ii) More positive is the value of E<sup>0</sup>, reaction will be more feasible. As E<sup>0</sup><sub>Co<sup>2+</sup>/Co<sup>2+</sup></sub> is maximum, thus Co<sup>2+</sup> ion is most stable

or

(d)

- (i) Mn<sup>2+</sup> ion has stable half-filled (3d<sup>5</sup>) electronic configuration. Its ionisation enthalpy value is lower in comparison to hydration enthalpy. Hence, E<sup>°</sup><sub>Mn<sup>2+</sup>/Mn</sub> is more negative.
- (ii) Cr<sup>2+</sup> is a stronger reducing agent than Fe<sup>2+</sup>. E<sup>o</sup><sub>Cr<sup>2+</sup>/Cr<sup>2+</sup></sub> is negative (-0.41 V) whereas E<sup>c</sup><sub>Fe<sup>2+</sup>/Fe<sup>2+</sup></sub> is positive (+0.77 V). Thus Cr<sup>2+</sup> is easily oxidized to Cr<sup>3+</sup> but Fe<sup>2+</sup> cannot be easily oxidized to Fe<sup>3+</sup>. Hence, Cr<sup>2+</sup> is stronger reducing agent than Fe<sup>2+</sup>.

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## SECTION-E

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

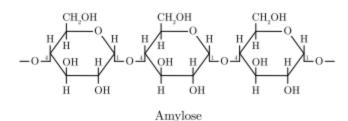
- 31. (i) What is starch?
  - (ii) Draw the structure of Amylose.
  - (iii) Draw the structure of Amylopectin.

#### Ans:

 Starch is the main storage polysaccharide of plants. It is the most important dietary source for human beings. It is a polymer α-glucose and consists of two components Amylose and Amylopectin.

Amylose is water soluble component with consitutes about 15-20% of starch. It is a long unbranched chain with 200-1000  $\alpha$ -D-(+) glucose units held by  $C_1-C_4$  glycosidic linkage.

Amylopectin is insoluble in water and constitutes about 80-85% of starch. It is a branched chain polymer of  $\alpha$ -D-glucose units in which chain is formed by  $C_1 - C_4$ glycosidic linkage whereas branching occurs by  $C_1 - C_6$ glycosidic linkage. (ii)



Amylopectin

**32.** Derive the integrated rate equation for a first order reaction.

#### Ans:

In first order reaction, the rate of the reaction is proportional to the first power of the concentration of the reactant R for example :  $R \longrightarrow P$ 

$$\mathrm{Rate} = \frac{-\,d[R]}{dt} = K[R]$$

or  $\frac{-d[R]}{R} = -Kdt$ 

Integrating this equation, we get.

$$[R] = -Kt + I$$
 ...(1)

Here, I is the constant of integration,

When t = 0,  $R = [R]_0$  Where  $[R]_0$  is initial concentration of the reactant.

Therefore equation (1) can be written as,

$$ln[R]_O = -K \times O \times I$$
  
 $ln[R]_O = I$ 

Substituting the value of I in the equation (1),

$$\ln[R] = -Kt + In[R]_O$$

Rearranging the equation,

$$\ln \frac{[R]}{[R]_o} = -Kt$$

$$K = \lim_{K \to \infty} [R]$$

or 
$$K = \frac{1}{t} \ln \frac{[R]_O}{[R]}$$

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

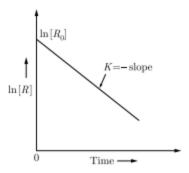


Figure : A Plot between [R] and t for a First Order Reaction.

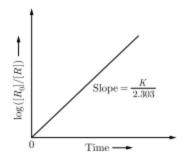


Figure : Plot of  $log[R]_0/[R]$  vs Time for a First Order Reaction.

or

Define threshold energy and activation energy. How are they related ?

#### Ans:

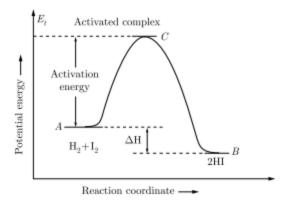
Threshold energy: It is the minimum amount of energy which the reactant molecules must possess for the effective collisions.

Activation energy: The minimum extra amount of energy required by the reactant molecules so that their energy becomes equal to threshold value is called activation energy OR the difference between the threshold energy and the average kinetic energy of the reactant molecules is called activation energy.

Average kinetic energy of the reactants.

Example :  $H_2(g) + I_2(g) \longrightarrow 2HI(g)$ 

According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate called activated complex (C). It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.



The energy required to form the activated complex is known as activation energy  $(E_a)$ .

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- Compare the chemistry of actinoids with that of lanthanoids with special reference to
  - 1. Electronic configuration
  - 2. Oxidation state
  - Atomic and ionic size
  - 4. Chemical reactivity

#### Ans:

- Electronic configuration: The general electronic configuration of lanthanoids is [Xe] 4f<sup>1-14</sup>5d<sup>0-1</sup>6s<sup>2</sup> and actinoids is [Rn] 5f<sup>1-14</sup>6d<sup>0-1</sup>7s<sup>2</sup>.
- Oxidation state: Lanthanoids show limited oxidation states +2, +3 and +4 out of which +3 is most common, because of large energy gap between 4f and 5d subshell whereas actinoids show a large number of oxidation states because of small energy gap between 5f, 6d and 7s subshell.
- Atomic and ionic size: Both show decreases in size,in lanthanoids it is called lanthanoid contraction, and in actinoids it is called actinoid contraction.
- 4. Chemical reactivity: The first few members of lanthanoids are quite reactive they react with dilute acids to liberate H<sub>2</sub> gas. They form oxides M<sub>2</sub>O<sub>3</sub> and hydroxides M(OH)<sub>3</sub> which are basic in nature. Actinoids are highly reactive metals, they react with boiling water to give a mixture of oxide and hydride, Due to the formation of a protective oxide layer on their surface they are slightly affected by nitric acid.

r

What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

#### Ans

Lanthanoid contraction: The overall decrease in atomic and ionic radii from lanthanum to leutetium is observed in the lanthanoids. This phenomenon is called lanthanoid contraction. It is due to the fact that with every additional proton in the nucleus, the corresponding electron goes into a 4f-subshell. This is too diffused to screen the nucleus as effectively as the more localised inner shell. Hence, the attraction of the nucleus for the outermost electrons increases steadily with the atomic number.

Consequences of Lanthanoid contraction: The important consequences of lanthanoid contraction are as follows:

- Basic character of oxides and hydroxides: Due to the lanthanoid contraction, the lanthanoid contraction, the covalent nature of La-OH bond increases and thus, the basic character of oxides and hydroxides decreases from La(OH)<sub>3</sub> to Lu(OH)<sub>3</sub>
- Similarity in the size of elements of second and third transition series: Because of lanthanoid contraction, elements which follow the third transition series are considerably smaller than would otherwise be expected. The normal size increases form Sc → Y → La and disappears after lanthanides. Thus, pairs of elements such as Zr/Hf, Nb/Ta and Mo/w are almost identical in size.
  - Due to almost similar size, such pairs have very similar properties which makes their separation difficult.
- Separation of lathanoids: Due to lanthanoid contraction, there is a difference in some properties of lanthanoid like solubility, degree of hydration and complex formation. These difference enable the separation of lanthanoids by ion exchange method.

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