Chemistry

Model Set - 2

Academic Year: 2020-2021 Marks: 70
Date: April 2021
Duration: 3h

1. The question paper is divided into four sections.
2. **Section A**: Q. No. 1 contains Ten multiple-choice type of questions carrying One mark each.
3. **Section A**: Q. No. 2 contains Eight very short answer type of questions carrying One mark each.
4. **Section B**: Q. No. 3 to Q. No. 14 contains Twelve short answer type of questions carrying Two marks each. **(Attempt any Eight)**.
5. **Section C**: Q. No.15 to Q. No. 26 contains Twelve short answer type of questions carrying Three marks each. **(Attempt any Eight)**.
6. **Section D**: Q.No. 27 to Q. No. 31 contains Five long answer type of questions carrying Four marks each. **(Attempt any Three)**.
7. Use of log table is allowed. Use of calculator is not allowed.
8. Figures to the right indicate full marks.
9. For each MCQ, correct answer must be written along with its alphabet.
   e.g., (a) ..... / (b) .... / (c) .... / (d) ..... Only first attempt will be considered for evaluation.
10. Draw well labeled diagrams and write balanced equations wherever necessary.
11. Given data:
    Atomic mass of C = 12, H = 1, O = 16
    Atomic number (Z): Mn = 25, Fe = 26, Ce = 58, Ar = 18,
    R = 8.314 J K^{-1} mol^{-1} or 0.083 L bar K^{-1} mol^{-1}

Q. 1 | Select and write the correct answer:

1.i Dacron is a copolymer of ethylene glycol and ______________

1. adipic acid
2. hexamethylenediamine
3. phthalic acid
4. terephthalic acid

1.ii In which of the following structure of DNA carries genetic information of the organism?

1. the primary structure of DNA

2. the double helix structure of DNA
3. complementary base pairing
4. sugar-phosphate backbone

1.iii The rate law relates to the rate of a chemical reaction in terms of ______.

1. concentration of catalyst
2. temperature
3. potential energy
4. mol/L of reactants

1.iv The following will react faster by S_N1 mechanism

1. 1-chloropropane
2. 2-chloropropane
3. 2-chloro-2-methylpropane
4. Chloroethane

1.v The change in internal energy in a reaction when 2kJ of heat is released by the system and 6 kJ of work is done on the system will be _____.

1. +4 kJ
2. 4kJ
3. +3 kJ
4. – 8 kJ

1.vi In interhalogen compounds, which of the following halogens is never the central atom?

1. I
2. Cl
3. Br
4. F

1.vii The catalyst used for decomposition of $KClO_3$ is ______.

1. ZnO
2. MnO_2
3. CuO
4. K_2O

1.viii The following ion has the maximum number of unpaired electrons.

1. Sc^{3+}
2. Ti^{3+}
3. Fe^{3+}
4. Co^{2+}

1.ix The molar conductivity and conductivity of $AgNO_3$ solution is 121.4 Ω^{-1} cm^2 mol^{-1} and 2.428×10^{-3} Ω^{-1} cm^{-1} at 25 °C. What is molar concentration of $AgNO_3$ solution?

1. 0.2 M
2. 0.02 M
3. 2.0 M
4. 2.2 M

1.x

For a reaction $HCl_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$

Which of the following is a conjugate acid-base pair?

1. HCl and H_2O
2. H_3O^+
3. H_3O^+ and H_2O
4. HCl and H_3O^+

Q. 2 | Answer the following:

2.i Which principle of green chemistry has its perspective towards carrying out reactions at room temperature and pressure?

Ans. Design for energy efficiency has its perspective towards carrying reactions at room temperature and pressure.

2.ii Write the name of the catalyst used for preparation of high density polythene polymer.

Ans. Zieglar-Natta catalyst (triethylaluminium with titanium tetrachloride)

2.iii Write the order of reactivity of alkyl halides with ammonia.

Ans. The order of reactivity of alkyl halides with ammonia is, R–I > R–Br > R–Cl.

2.iv Give SI unit of resistivity.

Ans. The SI unit of resistivity is Ω m.

2.v Give SI unit of resistivity.

Ans. The SI unit of resistivity is Ω m.

2.vi What is lanthanoid contraction?

Ans. As we move along the lanthanoid series, there is a decrease in atomic and ionic radii. This steady decrease in the atomic and ionic radii is called lanthanoid contraction.

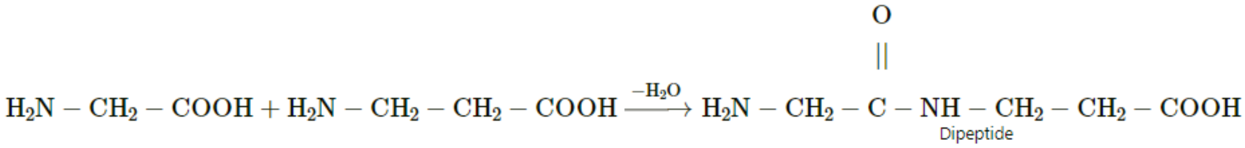
2.vii Write the name of the product when ketones react with 1,2-diol in presence of dry HCl.

Ans. The product obtained when ketones react with 1,2-diol in presence of dry HCl is known as cyclic ketal.

2.viii Complete the following reaction.

$$H_2N - CH_2 - COOH + H_2N - CH_2 - CH_2 - COOH \xrightarrow{-H_2O} ?$$

Ans.



$$H_2N - CH_2 - COOH + H_2N - CH_2 - CH_2 - COOH \xrightarrow{-H_2O} H_2N - CH_2 - \overset{\overset{\displaystyle O}{||}}{C} - NH - CH_2 - CH_2 - COOH$$

Dipeptide

Q. 3 | Attempt any Eight:

Write industrial application of enzyme catalysis.

Ans. Industrial application of enzyme catalysis:

i. Conversion of glucose to sweet-tasting fructose, using glucose isomerase.
ii. Manufacture of new antibiotics, using penicillin G acylase.
iii. Manufacture of laundry detergents, using proteases.
iv. Manufacture of esters used in cosmetics, using the genetically engineered enzyme.

Q. 4 For a very dilute solution, the osmotic pressure is given by $\pi = n_2RT/V$ where V is the volume in L containing n_2 moles of nonvolatile solute. Establish the equation for molar mass of solute.

Ans. For very dilute solutions, the osmotic pressure follows the equation,

$$\pi = \frac{n_2RT}{V} \quad ....(1)$$

If the mass of solute in V litres of solution is W2 and its molar mass is

$$M_2, \text{ then } n_2 = \frac{W_2}{M_2}$$

Substituting the value of n_2 in equation (1), we get

$$\pi = \frac{W_2}{M_2}\frac{RT}{V}$$

$$\therefore M_2 = \frac{W_2RT}{\pi V}$$

This formula can be used for the calculation of molar mass of a nonionic solute (i.e., nonelectrolyte), by osmotic pressure measurement.

Q. 5 Define molar solubility. Write it's unit.

Ans. The number of moles of a compound that dissolve to give one litre of saturated solution is called its molar solubility.

Unit of molar solubility: mol L^{-1}.

Q. 6 Distinguish between : Order and Molecularity of reaction

Ans.

ORDER OF A REACTION	**MOLECULARITY OF A REACTION**
It is sum of the concentration terms on which the rate of reaction actually depends or it is the sum of the exponents of the concentrations in the rate law equation.	It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction.
It need not be a whole number i.e. it can be fractional as well as zero.	It is always a whole number.
It can be determined experimentally only and cannot be calculated.	It can be calculated by simply adding the molecules of the slowest step.
It is for the overall reaction and no separate steps are written to obtain it.	The overall molecularity of a complex reaction has no significance. It is the only slowest step whose molecularity has significance for the overall reaction.
Even the order of a simple reaction may not be equal to the number of molecules of the reactants as seen from the unbalanced equation.	For simple reactions, the molecularity can usually be obtained from the Stoichiometry of the equation.
It may be an integer, fraction or zero	It is always an integer and never a fraction or zero.

Q. 7 What is the action of following reagents on pent-3-enal?

a. H_2/Ni
b. $LiAlH_4/H_3O^+$

Ans. Pent-3-enal contains an isolated > C = C < and an aldehyde group. H_2/Ni can reduce both these functional groups while $LiAlH_4$ can reduce only –CHO of the two.

a. **H_2/Ni:**

$$\underset{\text{Pent-3-enal}}{CH_3 - CH = CH - CH_2 - CHO} \xrightarrow{H_2/Ni} \underset{\text{Pentan-1-ol}}{CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - OH}$$

b. **$LiAlH_4/H_3O^+$:**

$$\underset{\text{Pent-3-enal}}{CH_3 - CH = CH - CH_2 - CHO} \xrightarrow[\text{(ii)}H_3O^+]{\text{(i)}LiAIH_4} \underset{\text{Pent-3-en-1-ol}}{CH_3 - CH = CH - CH_2 - CH_2 - OH}$$

Q. 8 How many moles of electrons are required for reduction of 2 moles of Zn^{2+} to Zn?

Ans. The balanced equation for the reduction of Zn^{2+} to Zn is

$$Zn^{2+}_{(aq)} + 2\,e^- \longrightarrow Zn_{(s)}$$

The equation shows that 1 mole of Zn^{2+} is reduced to Zn by 2 moles of electrons.

For reduction of 2 moles of Zn^{2+}, 4 moles of electrons will be required.

Q. 9 Explain. Aryl halides are less reactive than alkyl halides towards nucleophilic substitution reactions.

Ans.

i. The low reactivity of aryl halides is due to the resonance effect and sp^2 hybrid state of carbon to which halogen atom is attached.
ii. In aryl halides, one of the lone pairs of electrons on the halogen atom is in conjugation with π-electrons of the ring. Due to resonance, the C–X bond acquires partial double bond character. Thus, the C–X bond in aryl halides is stronger and shorter than alkyl halides. Hence, it is difficult to break C–X bond in aryl halides.
iii. Further, the phenyl cation produced due to the self-ionization of aryl halide will not be stabilised by resonance. This rules out the possibility of S_N1 mechanism. Also, the backside attack of nucleophiles is blocked by the aromatic ring. This rules out the possibility of S_N2 mechanism. As a result, nucleophilic substitution reaction involving cleavage of C–X bond in haloarenes proceeds with difficulty.
iv. Therefore, aryl halides are less reactive than alkyl halides towards nucleophilic substitution reactions.

Q. 10 Write four points of distinction between Lanthanoids and Actinoids.

Ans.

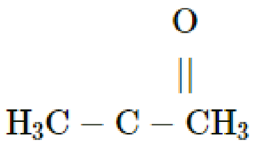
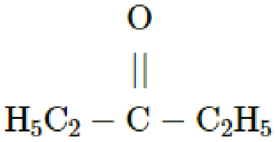
	Lanthanoids	**Actinoids**
1.	In lanthanoids, last differentiating electron occupies 4f orbital.	In actinoids, last differentiating electron occupies 5f orbital.
2.	They are the elements of first inner transition series.	They are the elements of second inner transition series
3.	They are present in period 6.	They are present in period 7.
4.	Most of lanthanoids (with exception of promethium) occur in nature.	Most of actinoids (with exception of uranium and thorium) are prepared in laboratory
5.	Most of lanthanoids (with exception of promethium) are non-radioactive.	All the actinoids are radioactive.
6.	Lanthanoids do not form oxo cation.	Actinoids form oxo cation such as 22 UOUO22+, PuO^{2+}, UO^{+}.
7.	4f orbitals in lanthanoids have higher binding energy.	5f orbitals in actinoids have lower binding energy.
8.	Contraction in atomic and ionic radii is relatively less in lanthanoids.	Contraction in atomic and ionic radii is relatively greater in actinoids due to poor shielding of 5f electrons.
9.	Lanthanoids show +2, +3 and +4 oxidation states.	Actinoids show +3, +4, +5, +6, +7 oxidation states.
10.	Lanthanoids have less tendency to form complexes.	Actinoids have greater tendency to form complexes.
11.	Some ions of lanthanoids are coloured.	Most of the ions of actinoids are deeply coloured.
12.	Lanthanoid hydroxides are less basic in nature.	Actinoid hydroxides are more basic in nature.

Q. 11 Write Classification of aliphatic ketones with suitable example

Ans. On the basis of types of alkyl groups bonded to carbonyl carbon, aliphatic ketones are further classified as simple and mixed ketones.

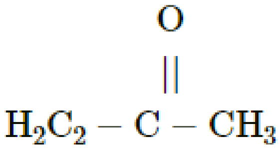
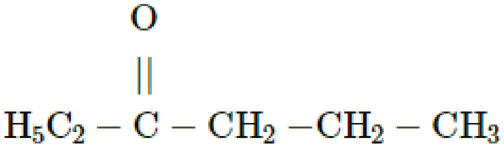
Simple or symmetrical ketones: The ketones in which both the alkyl groups bonded to carbonyl carbon are identical are called simple ketones or symmetrical ketones.

e.g.

- 
  $H_3C - \overset{\overset{O}{||}}{C} - CH_3$
  Dimethyl ketone (Acetone)
- 
  $H_5C_2 - \overset{\overset{O}{||}}{C} - C_2H_5$
  Diethyl ketone

Mixed or unsymmetrical ketones: The ketones in which two alkyl groups bonded to carbonyl carbon are different are called mixed ketones or unsymmetrical ketones.

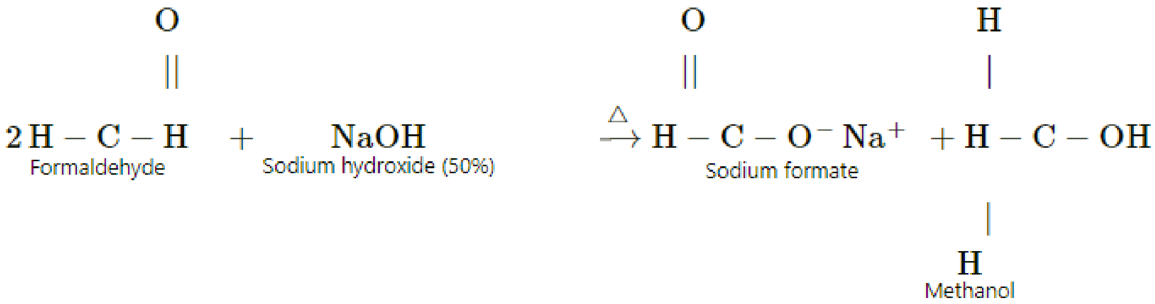
e.g.

- 
  $H_2C_2 - \overset{\overset{O}{||}}{C} - CH_3$
  Ethyl methyl ketone
- 
  $H_5C_2 - \overset{\overset{O}{||}}{C} - CH_2 - CH_2 - CH_3$
  Ethyl n-propyl ketone

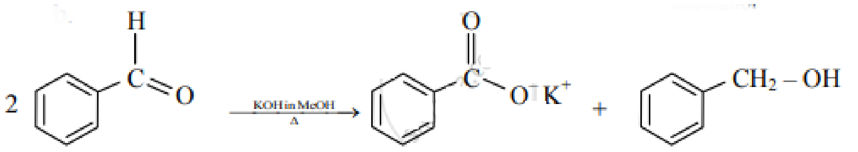
Q. 12 Describe Cannizzaro reaction

Ans.

1. This reaction is given only by aldehydes having no α-hydrogen atom.
2. Aldehydes undergo self -oxidation and reduction reaction on heating with concentrated alkali.
3. In Cannizzaro reaction, one molecule of an aldehyde is reduced to alcohol and at the same time the second molecule is oxidized to carboxylic acid salt. Thus, the reaction is an example of disproportionation reaction.

e.g. 1. 

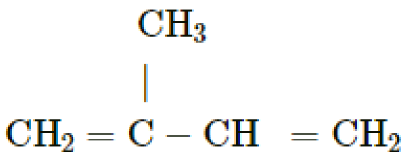
$$2\,\underset{\text{Formaldehyde}}{H-\overset{\overset{O}{\|}}{C}-H} + \underset{\text{Sodium hydroxide (50\%)}}{NaOH} \xrightarrow{\Delta} \underset{\text{Sodium formate}}{H-\overset{\overset{O}{\|}}{C}-O^-Na^+} + \underset{\text{Methanol}}{H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-OH}$$

2. 

Benzaldehyde Potassium benzoate Phenylmethanol /benzyl alcohol

Q. 13 Write the structure of the monomer used in natural rubber.

Ans.



$$\underset{\text{Isoprene}}{CH_2=\overset{\overset{CH_3}{|}}{C}-CH=CH_2}$$

Q. 14 Calculate the number of unit cells in 0.3 g of a species having density of 8.5 g/cm^3 and unit cell edge length 3.25 × 10^{-8} cm.

Ans. Given: Density (ρ) = 8.5 g/cm^3, Edge length (a) = 3.25 × 10^{-8} cm, Mass of the species (x) = 0.3 g

To find: Number of unit cells in 0.3 g of niobium

Formula: Number of unit cells in x g of species = $\frac{x}{\rho a^3}$

Calculation: Using formula,

Number of unit cells in 0.3 g of the species

$$= \frac{0.3\text{g}}{8.5\text{g cm}^{-3} \times \left(3.25 \times 10^{-8}\text{cm}\right)^3} = 1.03 \times 10^{21}$$

Number of unit cells in 0.3 g of the given species is 1.03 × 10^{21}.

Q. 15 | Attempt any Eight:

Explain any three characteristic features of nanoparticles.

Ans. Following are the characteristic features of nanoparticles:

i. **Colour:** It is an optical property that is different at nanoscale.
e.g. Elemental gold has a shining yellow colour. However, if only 100 gold atoms are arranged in a cube, its colour would be much more red.

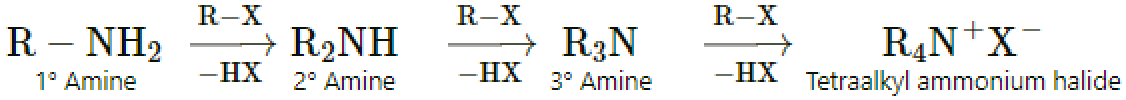
ii. **Surface area:** High surface-to-volume ratio is a very important characteristic of nanoparticles. If a bulk material is a sub divided into a group of individual nanoparticles, the total volume remains the same, but the collective surface area is largely increased. With a large surface area for the same volume, these small particles react much faster because more surface area provides more number of reaction sites, leading to more chemical reactivity.

iii. **Catalytic activity:**
a. Due to an increase in surface area with the decrease in particle size, nanomaterial-based catalysts show increased catalytic activity.
b. Usually, they are heterogeneous catalysts that mean catalysts are in solid form and the reactions occur on the surface of the catalyst.
c. Nanoparticle catalysts can be easily separated and can be recycled.
e.g. Pd, Pt metal nanoparticles used in hydrogenation reactions.
TiO_2, ZnO are used in photocatalysis.
Gold in bulk form is unreactive, but gold nanoparticles are found to be a very good catalyst for various organic reactions.

Q. 16 Explain Hoffmann's exhaustive alkylation with suitable reactions.

Ans. Hofmann's exhaustive alkylation of amines:

i. When a primary amine is heated with excess of primary alkyl halide it gives a mixture of secondary amine, tertiary amine along with tetraalkylammonium halide. This can be given as,



$$\underset{\text{1° Amine}}{R-NH_2} \xrightarrow[-HX]{R-X} \underset{\text{2° Amine}}{R_2NH} \xrightarrow[-HX]{R-X} \underset{\text{3° Amine}}{R_3N} \xrightarrow[-HX]{R-X} \underset{\text{Tetraalkyl ammonium halide}}{R_4N^+X^-}$$

i. If the excess alkyl halide is used tetraalkylammonium halide is obtained as a major product and the reaction is known as exhaustive alkylation of amines.

ii. Tetraalkylammonium halides or quaternary ammonium salts are the derivatives of ammonium salts in which all the four hydrogen atoms attached to nitrogen in N^+H_4 are replaced by four alkyl groups (same or different).

iii. Tetraalkylammonium halides are crystalline solids.

iv. Primary, secondary and tertiary amines consume three, two and one moles of alkyl halide respectively to get converted into quaternary ammonium salt.

v. The reaction is carried out in presence of mild base $NaHCO_3$, to neutralize the large quantity of HX formed.

vi. If the alkyl halide is methyl iodide, the reaction is called exhaustive methylation of amines.

e.g. When methylamine is heated with excess methyl iodide, it gives tetramethyl ammonium iodide.

$$\underset{\text{Methylamine}}{CH_3-NH_2} + \underset{\text{Methyl iodide}}{CH_3-I} \xrightarrow{\Delta} \underset{\text{Dimethylamine}}{(CH_3)_2NH} + HI$$

$$(CH_3)_2-NH + CH_3-I \xrightarrow{\Delta} \underset{\text{Trimethyl amine}}{(CH_3)_3N} + HI$$

$$(CH_3)_3N + CH_3-I \xrightarrow{\Delta} \underset{\text{Tetramethyl ammonium iodide}}{(CH_3)_4N^+I^-}$$

Q. 17. A Define buffer solution.

Ans. A Buffer solution is defined as a solution which resists drastic changes in pH when a small amount of strong acid or strong base or water is added to it.

Q. 17. B Explain the types of buffer solutions.

Ans. B There are two types of buffer solutions:

1. **Acidic buffer:**
   A solution containing a weak acid and its salts with strong base is called an acidic buffer solution. It maintains an acidic pH.
   e.g. A solution containing weak acid such as CH_3COOH and its salt such as CH_3COONa is an acidic buffer solution.
2. **Basic buffer:**
   A solution containing a weak base and its salt with strong acid is the basic buffer solution. It maintains an alkaline pH.
   e.g. A solution containing a weak base such as NH_4OH and its salt such as NH_4Cl is a basic buffer solution.

Q. 18 Why is molecularity applicable for only elementary reactions whereas order of a reaction is applicable for elementary and complex reactions? Explain with suitable examples.

Ans.

1. Reactions occuring in a single step which cannot be broken down further into simpler reactions are called elementary reactions. Molecularity refers to how many reactant molecules are involved in reactions. Hence, the molecularity of each elementary reaction is fixed.
2. A number of chemical reactions are complex. They take place as a series of elementary steps. The molecularity of each step in a complex reaction may be different. Hence, the concept of molecularity is meaningless for complex reactions.
3. The slowest step in a complex reaction determines the rate of the overall reaction. Hence, the order of the reaction is applicable for both; elementary and complex reactions.

Example:

Consider the reaction: $2\,NO_2Cl_{(g)} \longrightarrow 2\,NO_{2(g)} + Cl_{2(g)}$

The reaction takes place in two steps:

1.	$NO_2Cl_{(g)} \xrightarrow{k_1} NO_{2(g)} + Cl_{(g)}$	(slow)
2.	$NO_2Cl_{(g)} + Cl \xrightarrow{k_2} NO_{2(g)} + Cl_{2(g)}$	(fast)
	Overall: $2\,NO_2Cl_{(g)} \longrightarrow 2\,NO_{2(g)} + Cl_{2(g)}$	

The molecularity of elementary reaction (1) is 1 and that of elementary reaction (2) is 2. The first step being slower than the second and is the rate determining step. Hence, the reaction is of first order.

Q. 20. A Define coordination number.

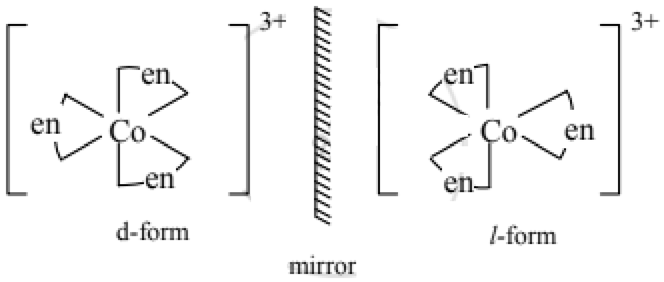
Ans. Coordination number (C.N.) of metal ion in a complex is the number of ligand donor atoms directly attached to it or the number of electron pairs involved in the coordinate bond.

Q. 20. B Define Anionic sphere complex.

Ans. A negatively charged coordination sphere or a coordination compound having a negatively charged coordination sphere is called anionic complex or anionic sphere complex.

Q. 20. C Draw optical isomers of $[Co(en)_3]^{3+}$.

Ans.



Q. 21 What is Grignard reagent? How is it prepared? Why are they prepared under anhydrous condition?

Ans.

i. **Grignard reagent:** When alkyl halide is treated with magnesium in the dry ether as the solvent, it gives alkyl magnesium halide. This is known as the Grignard reagent.

ii. The Grignard reagent can be prepared as,

$$\underset{\text{Alkyl halide}}{R - X} + Mg \xrightarrow{\text{dry ether}} \underset{\text{Alkyl magnesium halide (Grignard reagent)}}{R - Mg - X}$$

iii. Grignard reagents are highly reactive compounds.

iv. They react with water or compounds containing hydrogen attached to the electronegative element.
Hence, reactions involving Grignard reagent must be carried out under anhydrous condition.

Q. 22 Derive the expression for work done in chemical reaction. Write the relationship between ΔH and ΔU for an isochoric process.

Ans. Expression for work done in a chemical reaction:

The work done by a system at constant temperature and pressure is given by

$W = P_{ext}\, \Delta V$ .....(1)

Assuming $P_{ext} = P$,

$W = - P\Delta V$

$= - P (V_2 - V_1)$ W

$= - PV_2 + PV_1$ ......(2)

If the gases were ideal, at constant temperature and pressure.,

$PV_1 = n_1RT$ and $PV_2 = n_2RT$ ...(3)

Substitution of equation (3) into equation (2) yields

$W = - n_2RT + n_1RT$

$= - (n_2 - n_1) RT$

$= - \Delta n_g RT$ ...(4)

Equation (4) gives the work done by the system in chemical reactions.

Relationship between ΔH and ΔU for an isochoric process:

For an isochoric process, $\Delta V = 0$.

$\Delta H = \Delta U + P\Delta V = \Delta U + 0 = \Delta U$

$\therefore \Delta H = \Delta U$

Q. 23 Write three uses of sulfuric acid.

Ans. Sulfuric acid is a very important industrial chemical.
It is used:

1. in the manufacture of fertilizers. For example, ammonium sulfate, superphosphate, etc.
2. in the manufacture of pigments, paints and dyestuff intermediates.
3. in petroleum refining.
4. in detergent industry.
5. in metallurgy, for cleaning of metals electroplating and galvanising.
6. in storage batteries.
7. as a laboratory reagent.
8. in the manufacture of nitrocellulose products.

Q. 24 Discuss the position of d-block elements, lanthanoids and actinoids in the periodic table.

Ans.

- **Position of d-block elements in the modern periodic table:**

1. The transition elements are placed in the periods 4 to 7 and groups 3 to 12.
2. They constitute 3d, 4d, 5d and 6d series.
3. They are placed at the centre with s block on one side and p block on the other side.
4. The electropositivity, reactivity and other properties show a gradual change from s block to p block through those of the d block elements.

- **Position of lanthanoids and actinoids in the modern periodic table:**

1. Lanthanoids and actinoids are placed separately at the bottom of the periodic table. They are a subset of 6th and 7th periods.
2. These elements have 1 to 14 electrons in their f orbital, 0 or 1 in the penultimate energy level and 2 electrons in the outermost orbital.

Q. 25 Discuss the position of d-block elements, lanthanoids and actinoids in the periodic table.

Ans.

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1. Lanthanoids and actinoids are placed separately at the bottom of the periodic table. They are a subset of 6th and 7th periods.
2. These elements have 1 to 14 electrons in their f orbital, 0 or 1 in the penultimate energy level and 2 electrons in the outermost orbital.

Q. 26 The unit cell of Na is bcc and its density is 0.97 g/cm^3. What is the radius of a sodium atom if the molar mass of Na is 23 g/mol?

Ans. Given: Density = 0.97 g/cm^3, Molar mass (M) = 23 g/mol

To find: Radius of sodium atom (r)

Formula:

1. Density (ρ) = $\dfrac{M\ \ n}{a^3\ N_A}$

2. For bcc unit cell, r = $\dfrac{\sqrt{3}\ a}{4}$

Calculation: For a bcc lattice, number of atoms per unit cell is 2.
∴ n = 2
From formula (i),

$$a^3 = \frac{M\ \ n}{\rho\ N_A}$$

$$a^3 = \frac{23\text{g mol}^{-1} \times 2\text{ atom}}{0.97\text{g cm}^{-3} \times 6.022 \times 10^{23}\text{atom mol}^{-1}} = 7.875 \times 10^{-23}\text{cm}^3$$

$$a = \sqrt[3]{7.875 \times 10^{-23}\text{cm}^3} = 4.286 \times 10^{-8}\text{cm}$$

From formula (ii),

$$r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3} \times 4.286 \times 10^{-8}}{4} = 1.86 \times 10^{-8}\text{ cm}$$

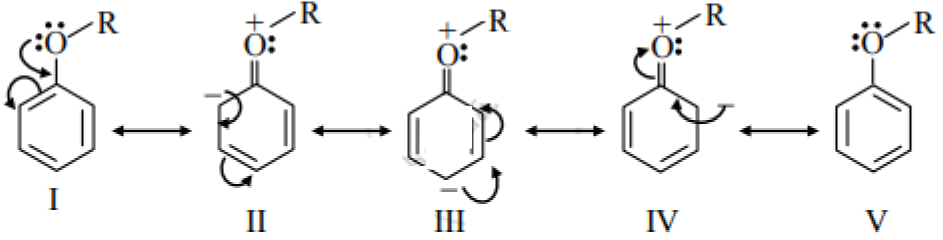
Radius of sodium atom is 1.86×10^{-8} cm.

Q. 27 | Attempt any Three:

27.i Explain the fact that in alkyl aryl ethers, the alkoxy group is ring activating and ortho/para directing towards electrophilic aromatic substitution.

Ans.

a. Resonance structures of alkyl aryl ethers are as follows:



b. The +R effect of –OR the group results in increased electron density at the para- and two ortho positions.
Hence, the alkoxy group in aromatic ether is a ring activating and ortho/para-directing group towards electrophilic aromatic substitution.

27.ii An organic compound gives hydrogen on reaction with sodium metal. It forms an aldehyde with molecular formula C_2H_4O on oxidation with pyridinium chlorochromate. Give the chemical equations in support of these observations.

Ans. Ethyl alcohol gives hydrogen on reaction with sodium metal. On oxidation with PCC ethanol will form acetaldehyde (C_2H_4O).

$$2\,\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH} \xrightarrow{2\,Na} 2\,\underset{\text{Sodium ethoxide}}{CH_3-CH_2-O^-\,Na^+} + H_{2(g)}\uparrow$$

$$\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH} \xrightarrow[PCC]{[O]} \underset{\text{Acetaldehyde}(C_2H_4O)}{CH_3-CHO} + H_2O$$

Q. 28 Calculate the standard enthalpy of formation of liquid methanol from the following data:

1. $CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} \longrightarrow CO_{2(g)} + 2\,H_2O_{(l)} \quad \Delta H° = -726\ \text{kJ mol}^{-1}$
2. $C_{(Graphite)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta_cH° = -393\ \text{kJ mol}^{-1}$
3. $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)} \quad \Delta_fH° = -286\ \text{kJ mol}^{-1}$

Ans. Given: Given equations are,

$$CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} \longrightarrow CO_{2(g)} + 2\,H_2O_{(l)} \quad \Delta H° = -726\ \text{kJ mol}^{-1} \quad \text{......(a)}$$

$$C_{(Graphite)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta_cH° = -393\ \text{kJ mol}^{-1} \quad \text{.....(b)}$$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)} \quad \Delta_fH° = -286\ \text{kJ mol}^{-1} \quad \text{.....(c)}$$

To find: The standard enthalpy of formation ($\Delta_fH°$) of $CH_3OH_{(l)}$

Calculation: Required equation is,

$$C_{(graphite)} + 2\,H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CH_3OH_{(l)}$$

Multiply equation (c) by 2 and add to equation (b),

$2\,H_{2(g)} + O_{2(g)} \longrightarrow 2\,H_2O_{(l)}$,	$\Delta_rH° = -572$ kJ mol^{-1}
$C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)}$,	$\Delta_cH° = -393$ kJ mol^{-1}
$C_{(graphite)} + 2\,H_{2(g)} + 2\,O_{2(g)} \longrightarrow CO_{2(g)} + 2\,H_2O_{(l)}$	

$\Delta_rH° = -572 - 393 = -965$ kJ mol^{-1} ….(d)

Reverse equation (a) and add to equation (d),

$CO_{2(g)} + 2\,H_2O_{(l)} \longrightarrow CH_3OH_{(l)} + \frac{3}{2}\,O_{2(g)}$,	$\Delta_rH° = 726$ kJ mol^{-1}
$C_{(graphite)} + 2\,H_{2(g)} + 2\,O_{2(g)} \longrightarrow CO_{2(g)} + 2\,H_2O_{(l)}$	$\Delta_rH° = -965$ kJ mol^{-1}
$C_{(graphite)} + 2\,H_{2(g)} + \frac{1}{2}\,O_{2(g)} \longrightarrow CH_3OH_{(l)}$	

$\Delta_fH° = \Delta_rH° = 726 - 965 =$ **– 239 kJ mol^{-1}**

The standard enthalpy of formation ($\Delta_fH°$) of $CH_3OH_{(l)}$ from the given data is **– 239 kJ mol^{-1}**

Q. 29 Describe the manufacturing of H_2SO_4 by the contact process.

Ans. Sulfuric acid is manufactured by the contact process, which involves the following three steps.

1) Roasting in air:

Sulfur or sulfide ore (iron pyrites) on burning or roasting in air produces sulfur dioxide.

i) $\underset{\text{Sulfur}}{S_{(s)}} + O_{2(g)} \xrightarrow{\Delta} \underset{\text{Sulfur dioxide}}{SO_{2(g)}}$

ii) $\underset{\text{Iron sulfide}}{4\,FeS_{2(s)}} + 11\,O_{2(g)} \xrightarrow{\Delta} 2\,Fe_2O_{3(s)} + \underset{\text{Sulfur dioxide}}{8\,SO_{2(g)}}$

2) Catalytic oxidation of sulfur dioxide:

i) Sulfur dioxide is oxidised catalytically with oxygen to sulfur trioxide, in the presence of V_2O_5 catalyst.

$$\underset{\text{Sulfur dioxide}}{2\,SO_{2(g)}} + O_{2(g)} \xrightarrow{V_2O_5} \underset{\text{Sulfur trioxide}}{2\,SO_{3(g)}}$$

ii) The reaction is exothermic and reversible and the forward reaction leads to decrease in volume. Therefore, low temperature (720K) and high pressure (2 bar) are favourable conditions for maximum yield of SO_3.

3) Absorption, followed by dilution of sulfur trioxide gas:

i) Sulfur trioxide gas (from the catalytic converter) is absorbed in concentrated H_2SO_4 to produce oleum.

$$\underset{\text{Sulfur trioxide}}{SO_3} + H_2SO_4 \longrightarrow \underset{\text{Oleum}}{H_2S_2O_7}$$

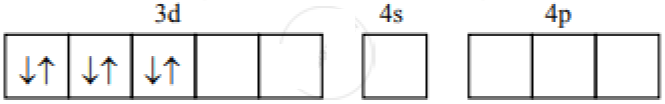
iii) The sulfuric acid obtained by contact process is 96-98 % pure.

Q. 30 Explain, why $[Co(NH_3)_6]^{3+}$ ion is low spin? Calculate number of unpaired electrons and write the geometry of $[Co(NH_3)_6]^{3+}$.

Ans. NH_3 is a strong field ligand. Strong field ligands cause larger splitting of d orbitals and pairing of electrons is favoured. Hence, $[Co(NH_3)_6]^{3+}$ is a low spin complex.

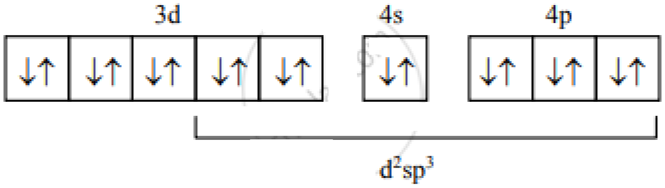
a. In $[Co(NH_3)_6]^{3+}$ ion, oxidation state of cobalt is +3.
Valence shell electronic configuration of Co^{3+} is:

b. Number of ammine ligands is 6. Therefore, the number of vacant metal ion orbitals required for bonding with ligands must be six. Complex is low spin, so the pairing of electrons will take place prior to hybridisation.
Electronic configuration after pairing would be:



c. Six orbitals available for hybridisation are two 3d, one 4s, three 4p orbitals.
The orbitals for hybridization are decided from the number of ammine ligands which is six. Here, (n−1)d orbitals participate in hybridization since it is the low spin complex.

d. Electronic configuration after complex formation is:



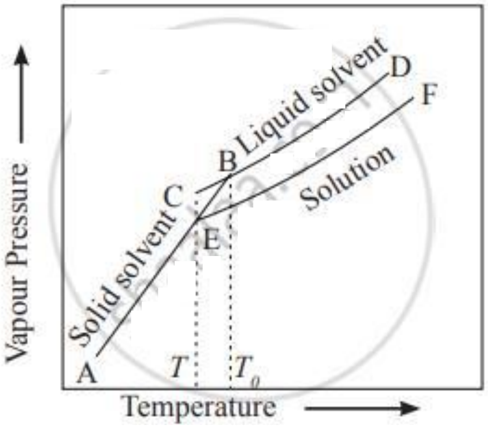
e. Number of unpaired electrons = 0

f. Geometry of the complex ion = Octahedral

Q. 31 Explain with vapour pressure-temperature curves that the freezing point of a solvent is lowered by dissolving a nonvolatile solute into it. Give reason for such lowering of freezing of solvent.

Ans.

1. The vapour pressures of solution and of pure solvent are plotted as a function of temperature in the diagram.



Variation of vapour pressure with a temperature of pure solvent, solid solvent and solution

2. The diagram consists of three curves. AB is the vapour pressure curve of solid solvent while CD is the vapour pressure curve of pure liquid solvent. EF is the vapour pressure curve of solution that always lies below the pure solvent.
3. The curves AB and CD intersect at point B where solid and liquid phases of pure solvent are in equilibrium. The two phases have the same vapour pressure at B. The temperature corresponding to B is the freezing point of a solvent Tf(Tf0).
4. Similarly at E, the point of intersection of EF and AB, the solid solvent and solution are in equilibrium. They have the same vapour pressure at E. The temperature corresponding to E is the freezing point of a solution Tf(Tf).
5. It is clear from the diagram that freezing point of solution Tf(Tf) is lower than that of pure solvent Tf(Tf0) because the vapour pressure curve of solution lies below that of solvent.
6. **Reason for lowering of freezing of the solvent:**
   At the freezing point of a pure liquid, the attractive forces among molecules are large enough to cause the change of phase from liquid to solid. In a solution, the solvent molecules are separated from each other because of solute molecules. Thus, the separation of solvent molecules in solution is more than that in pure solvent. This results in decreasing the attractive forces between solvent molecules. Consequently, the temperature of the solution is lowered below the freezing point of the solvent to cause the phase change. Hence, freezing point of solvent is lowered by dissolving a nonvolatile solute into it.