CBSE Board
Class XII Chemistry

Time: 3 Hrs Total Marks: 70

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1. All questions are compulsory.
2. Question nos. **1 to 8** are very short answer questions and carry 1 mark each
3. Question nos. **9 to 18** are short answer questions and carry 2 marks each. Use of calculator is not permitted.
4. Question nos. **19 to 27** are also short answer questions and carry 3 marks each
5. Question nos**. 28 to 30** are long answer questions and carry 5 marks each
6. Use log tables if necessary, use of calculators is not allowed.

Q.1 The rate law for a reaction is: Rate = k [A] $[B]^{3/2}$
Can the reaction be an elementary process? Explain.

Q.2 Why is silica gel is used as a dehumidizer?

Q.3 What is the shape of chlorate ion?

Q.4 Name the type of isomerism exhibited by $[Cr(en)_3]^{3+}$.

Q.5 Which isomer viz., 1, 2- and 1, 4-dichlorobenzenes, has the larger value of dipole moment?

Q.6 The boiling point of ethers are lower than the corresponding isomeric alcohols. Explain.

Q.7 Suggest a suitable reagent to convert:
$(CH_3)_2C{=}CH\text{-}CO\text{-}CH_3$ to $(CH_3)_2C{=}CHCOOH$.

Q.8 What are the components of a nucleoside?

Q.9

(a) Au having atomic radius 144 pm crystallises in a fcc structure. Find the edge length of the cell.

(b) Give the significance of a lattice point.

Q.10 A compound is formed by two elements X and Y. Atoms of the element Y (as anions) make *ccp* and those of the element X (as cations) occupy all the octahedral voids. What is the formula of the compound?

Q.11 Which of the following will have a greater conduction?

(a) 0.1 M acetic acid solution or 1 M acetic acid solution.

(b) 0.1 M NaCl solution at 25°C or 0.1 M NaCl solution at 50°C.

Q.12 The reaction between H_2 and O_2 yielding H_2O is exothermic. Then why the reaction does not proceed under ordinary conditions?

Q.13 The activation energy of a reaction is of 50 kJ/mol. If temperature increases from 300 to 310 K, what will be the change in reaction rate of the reaction?

Q.14

(a) Give the reason for bleaching action of chlorine molecule.

(b) PH3 has lower boiling point than NH3. Why?

Q.15

(a) Why is the second ionisation constant of sulphuric acid in water much less than the first ionisation constant?

(b) Give the product in the following reactions:
(i) $NH_4Cl(aq) + NaNO_2(aq) \rightarrow$ Product/s
(ii)

$$Ba(N_3)_2 \xrightarrow{\text{thermal decomposition}} \text{Product/s}$$

Q.16

(a) Specify the oxidation number of the metal in the following complex compounds:
(i) $K_3[Fe(CN)_6]$
(ii) $[Cr(NH_3)_3Cl_3]$
(iii) $[Co(H_2O(CN)(en)_2]^{2+}$
(iv) $Ni(CO)_4$

(b) Write the formulas for the following coordination compounds:

(i) Potassium trioxalatoaluminate(III)
(ii) Dichloridobis (ethane-1,2-diamine)cobalt(III)

Q.17 A mixture of two compounds, A and B, was dissolved in HCl and filtered off.The residue, on chemical analysis, was found to be a ketone, which on vigorous oxidation gave benzoic acid and butyric acid. The HCl-soluble portion, upon neutralisation with sodium carbonate, gave a nitrogen containing compound A. Diazotisation of compound A followed by heating with water gave alpha naphthol. Identify compounds A and B.

OR

What are lyophilic and lyophobic colloids? Which of these sols can be easily coagulated on the addition of small amounts of electrolytes?

Q.18 Suggest one method each for the following conversions:

(i) Nitrobenzene into aniline,
(ii) Nitrobenzene into azobenzene,
(iii) Nitrobenzene into phenylhydroxyl amine and
(iv) Nitrobenzene into p-aminophenol.

Q.19

(a) How long would it take to deposit 60.8 g of Ag from a solution of silver(I) nitrate by a current of 5.036 ampere?
(b) Write the cathode and anode half-cell reactions for the following reaction:

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

Q.20

(a) What happens when a colloidal sol of $Fe(OH)_3$ and As_2O_3 are mixed?
(b) Explain the Bredig's Arc method for the preparation of colloids. Give one example of a colloid which can be prepared by this method.

Q.21

(a) How is nickel refined to get it in pure form?
(b) Which method of refining is generally used when a metal of high degree of purity is needed?

Q.22 Complete and balance the following reactions:

(i) $PbO_2 \xrightarrow{\text{Heat}}$
(ii) ($Li + N_2 \xrightarrow{\text{Heat}}$
(iii) $P_4 + NaOH + H_2O \rightarrow$

Q.23 Explain why in the presence of peroxide, hydrogen chloride and hydrogen iodide don't give anti-Markovnikov's addition to propene whereas hydrogen bromide does?

Q.24

(i) Arrange the following in increasing order of basicity:
H_2O, HO^-, CH_3O^-, CH_3OH

(ii) Which of these is the strongest nucleophile? Give the weakest nucleophile among these?

(iii) What is the name of reaction in which CS_2 and $HgCl_2$ are used?

OR

Gold crystallizes in face-centred cubic unit cell. Each side of this unit cell has a length of 407 pm. Calculate the radius of the gold atom. (Assume the atoms just touch each other on the diagonal across the face of the unit cell. That is each face atom is touching the four corner atoms.)

Q.25

(a) Give two salient features of amino acids.

(b) Give a succinct definition of carbohydrates and their classification, too.

(c) Write the chemical formulas of sucrose and cellulose.

Q.26

(a) What is nylon-6, 6? How is it prepared?

(b) What are elastomers?

Q.27 Give a brief account of medicinal products.

Q.28

(a) What are ideal and non-ideal solutions?

(b) Why do we get abnormal molar masses from colligative property measurements?

(c) How can we come to know the cause of abnormal behaviour – association or dissociation of molecules?

(d) 200 cm^3 of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be 2.57×10^{-3} bar.
Calculate the molar mass of the protein.

OR

Q.28

(a) In what different ways the concentrations of solutions are expressed?
(b) Explain any one of them.
(c) Calculate molality of 2.5 g of ethanoic acid (CH_3COOH) in 75 g of benzene.

Q.29

(a) Explain the magnetic behaviour of copper in +1 and+2 oxidation states.
(b) Which will have intense colour, a Cr(II) salt or a Mn(II) salt? Give reason?
(c) Explain why Mn and Cr show several oxidation states?

OR

Q.29

(a) Describe the magnetic behaviour of Eu(II) and Eu(III) salts.
(b) Why only transition elements form carbonyl compounds? Explain.
(c) Which 4f element has half-filled f-orbital in its +3 oxidation state?

Q.30

(a) Give three methods to convert methylbenzene into benzaldehyde.
(b) Write the product obtained when ethylbenzene is treated with hot alkaline potassium permanganate.
(c) Complete the following reactions:

(i) Phthalic acid and thionyl chloride /heat;
(ii) 2,2,6-Trimethylcyclohexanone is treated with H-CN;
(iii) Nitrobenzene is heated with benzoyl chloride in the presence of $AlCl_3$.

OR

Q.30 Write names and structures of the missing reactants (R, R', R'' etc.), reagents (r, r', r'' etc.), Products (P, P', X, Y) and reactions (N, N' etc.) in the following schemes:

(i) Ethanoic acid + r →Ammonium ethanoate (=B);
B +heat →P + water;
P + Br_2/NaOH/N → CH_6N
(ii) R' + NaOH/water/heat → amide of hexano ic acid
(iii) R'' (an alkanone) + KOH + I_2 →P' (a bright yellow solid) + butanoic acid(N')
(iv) R''' + Mg /ether/heat→X ;
X + O=C=O →Y;
Y + H_2O →C_6H_5-COOH

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Solution

Ans.1 No the reaction cannot be an elementary process because an elementary process would have the rate law equal to its molecularity and therefore must be integers. (1)

Ans.2 Silica gel has strong adsorbing capability for humidity. Hence, it is used as a dehumidizer for protecting important but humidity sensitive materials. The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel. (1)

Ans.3 Triangular pyramidal. (1)

Ans.4 Optical isomerism (1)

Ans.5 The 1, 2-dichlorobenzene has the larger value of dipole moment. (1)

Ans. 6 Ethers have low polarity and therefore, do not show any association by intermolecular hydrogen bonding. On the other hand, their isomeric alcohols have strong intermolecular hydrogen bonding and therefore, their boiling points are high. (1)

Ans.7 A good, mild reagent is NaOI. Strong oxidants are unsuitable for this case.

$(CH_3)_2C = CO - CH_3 \xrightarrow{NaOI} (CH_3)_2C = CHCOOH$ (1)

Ans.8 A pentose sugar and a nitrogen containing heterocyclic base. (1)

Ans.9 (a) For an fcc cubic unit cell, the edge length ‘a’ is given by

$a = 2 \times \sqrt{2} \times \text{radius of atom}$. (1/2)

Therefore, the edge length

$a = 2 \times \sqrt{2} \times 144\,\text{pm} = 407\,\text{pm} = 4.07 \times 10^{-10}\,\text{m}$ (1/2)

(b)Lattice points represent the positions of the constituent particles (atoms, molecules or ions) in a crystal lattice. (1)

Ans.10 The *ccp* lattice is formed by the element Y. The number of octahedral voids generated would be equal to the number of atoms of Y present in it. (1/2)
Since all the octahedral voids are occupied by the atoms of X, their number would also be equal to that of the element Y. (1/2)
Thus, the atoms of elements X and Y are present in equal numbers or 1:1 ratio.
Therefore, the formula of the compound is XY. (1)

Ans.11 (a) 0.1 M acetic acid because with dilution dissociation increases and therefore, conduction increases. (1)

(b) 0.1 M NaCl solution at 50oC because with increase in temperature, ionic mobility of strong electrolytes increase. (1)

Ans.12 Firstly, cleavage of the H-H and O-O bonds requires vigorous conditions in the form of large activation energy. This is a must for the reaction to start. (1)
Secondly, two moles of hydrogen and one mole of oxygen gases react to yield two moles of liquid water. This results in a large decrease of entropy – an unfavourable change. This needs to be compensated by a large decrease in enthalpy of the system. Therefore, the reaction becomes exothermic. (1)

Ans.13 According to Arrhenius equation,

$$\log\frac{k_{310}}{k_{300}} = -\left(\frac{50000\,\mathrm{J}}{2.303\times 8.314\,\mathrm{J/mol\,K}}\right)\left(\frac{1}{310}-\frac{1}{300}\right) \qquad 1$$

$$\log\frac{k_{310}}{k_{300}} = 0.2809 \qquad 1/2$$

$$\frac{k_{310}}{k_{300}} = 1.90 \approx 2 \qquad 1/2$$

Ans.14 (a) When chlorine gas is brought in contact with moisture, it decomposes water to yield HCl and HOCl, which react together giving nascent oxygen. The latter oxidizes colouring matter to form colourless compounds or breaks them down to simpler, water soluble compounds. (1/2)
$Cl_2 + H_2O \rightarrow HCl + HOCl$;
$HOCl \rightarrow HCl + [O]$ (nascent oxygen);
Coloured matter + [O] → Colourless matter (1/2)

(b) Unlike NH_3, PH_3 molecules are not associated through hydrogen bonding in liquid state. That is why the boiling point of PH_3 is lower than NH_3.

(1)

Ans.15

(a) Sulphuric acid is a very strong protonic acid in water largely because of its first ionisation giving H_3O^+ and HSO_4^- ions. Further ionisation of HSO_4^- ion is less effective on account of two reasons: (i) This anion is highly hydrated and stabilised; (ii) The separation of H^+ from a negatively charged ion is unfavourable kinetically as well as thermodynamically. Thus, Ka(II) << Ka(I). (1)

(b)

(i)

$NH_4Cl(aq) + NaNO_2(aq) \rightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$ (1/2)

(ii) $Ba(N_3)_2 \xrightarrow{\text{thermal decomposition}} Ba + 3N_2$ (1/2)

Ans.16 The oxidation states of metal atom /ion are as follows:-

(i)+3

(ii)+3

(iii) +3

(iv) 0 (1)

(b) (i) $K_3[Al(C_2O_4)_3]$ (1/2)

(ii)

$[CoCl_2(en)_2]^+$ (1/2)

Ans.17 Compound A = 1-aminonaphthalene, $C_6H_7NH_2$, and (1)

compound B = phenyl n-propyl ketone or 1-phenylbutanone

B= C_6H_5-CO-$CH_2CH_2CH_3$ (1)

Or

Lyophillic colloids: The colloidal solutions in which the particles of the dispersed phase have a great affinity for the dispersion medium are called lypophilic colloids. These are reversible in nautre. These are quite stable and cannot be easily coagulated by small amounts of electrolytes. (1)

Lyophobic colloids: The colloidal solutions in which there is no affinity between particles of dispersed phase and the dispersion medium are called lyophobic colloids. These are irreversible in nature. These are unstable and can be easily coagulated on addition of small amount of electrolyte due to lack of protecting layer around charged colloidal particles. (1)

Ans.18

(i)

$C_6H_5NO_2$ (nitrobenzene) $+H_2$/weak acid medium→ $C_6H_5NH_2$ (1/2)

(ii)

$C_6H_5NO_2$ (nitrobenzene) +Zn /NaOH/CH_3OH/heat → $C_6H_5N{=}NC_6H_5$ (azobenzene) (1/2)

(iii)

$C_6H_5NO_2$ (nitrobenzene) +Zn /NH_4Cl/H_2O/heat → C_6H_5NHOH (phenyl hydroxyl amine) (1/2)

(iv)

$C_6H_5NO_2$ (nitrobenzene) $\xrightarrow{\text{electrolytic reduction}}$ p-$HOC_6H_4NH_2$ (phenyl hydroxylamine) (1/2)

Ans.19

(a) Q = nF = 1 x 96485 = 96485 C

Q = It = 5.036 x t

108 g of Ag require current = 96485 C (1)

60.8 g of Ag require current = (96485/ 108) * 60.8 C

(96485/ 108) * 60.8 C = 5.036 x t

T = (96485/ 108) * (60.8) / 5.036 = 10785.8 s = 2.99 hours (1)

(b) Half-cell reactions:

Cathode (reduction): $2Ag^+ (aq) + 2e^- \rightarrow 2Ag(s)$

Anode (oxidation): $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ (1)

Ans.20

(a) Their mutual precipitation takes place. (1)

(b) This process involves dispersion as well as condensation method. In this method, electric arc is struck between electrodes of the metal immersed in the dispersion medium. The intense heat produced vapourises the metal, which then condenses to form particles of colloidal size.

(1)

The colloidal sols of metals such as gold, silver, platinum, etc., can be prepared using this method. (1)

Ans.21

(a) Nickel is refined by Mond process. When impure nickel is heated in the presence of CO gas at 330-350K, volatile nickel tetracarbonyl is formed.

$Ni(impure) + 4CO \xrightarrow{330\text{-}350\,K} Ni(CO)_4$ (1)

It is separated, condensed and reheated at 450 – 470K whereupon it decomposes giving CO gas and pure nickel metal. The reactions are as follows:

$Ni(CO)_4 \xrightarrow{450\text{-}470\,K} Ni(impure) + 4CO(g)$ (1)

(b) Zone refining method (1)

Ans.22

(i) $2PbO_2 \xrightarrow{heat} 2PbO + O_2$ (1)

(ii) $6Li + N_2 \xrightarrow{heat} 2Li_3N$ (1)

(iii) $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$ (1)

Ans. 23

In the presence of a free radical initiator, R-O-O-R, the addition of HBr to propene produces 1-bromopropane – an anti Markovnikov addition product, because homolytic cleavage of HBr giving H and Br radicals takes place rather easily. Then a 2° radical intermediate is formed which abstracts H atom from HBr molecule forming 1-bromopropane. (1)

Initiation step:

R-O-O-R +heat →2RO• ;

Propagation steps:

H-Br + RO• → ROH + Br• ;

$Br^{\bullet} + CH_3CH{=}CH_2 \rightarrow CH_3C^{\bullet}HCH_2Br$

(a 2• radical)

$CH_3C^{\bullet}HCH_2Br + HBr \rightarrow CH_3CH_2CH_2Br$ (1-bromopropane) + Br• (1)

On the other hand, homolytic cleavage of H-Cl is an endothermic step and does not take place easily. Therefore, addition of HCl goes the normal way giving Markovnikov' addition product, that is, 2-chloropropane. Regarding addition of H-I, it is a stronger acid than HBr or HCl. The generation of free radicals H and I atoms is not a difficult step but the ionisation step is equally easy. Secondly, the reversibility of the propagation step involving C-I bond formation also accounts for a difference. Thirdly, the overall reaction of HI gas with propene in the presence of R-O-O-R is exothermic. (1)

Ans. 24(i) Increasing basicity: H_2O, CH_3OH, HO^-, CH_3O^- (1)

(ii) Strongest nucleophile: CH_3O^- ; weakest nucleophile: H_2O (1)

(iii) Hoffman's mustard oil reaction. (1)

or

Given , gold crystallizes in face-centered cubic unit cell.

So, $r = \frac{a}{2\sqrt{2}}$ (1)

Where r is the radius of the gold atom and a is the edge length

Now, edge length = 407 pm = 407×10^{-10} cm (1)

Thus,

$$r = \frac{407 \times 10^{-10}\,\text{cm}}{2 \times 1.414}$$

$= 143.92 \times 10^{-10}$ cm (1)

$= 143.9\,\text{pm}$

Thus, the radius of the gold atom was found to be 143.9 pm.

Ans. 25

(a) Salient features of amino acids are:

(i)

They are bi-functional molecules having a COOH and a NH_2 group attached to the C-2 position;

(ii)

Except for two amino acids, all other natural ones are optically active, L-enantiomers; (1)

(b) Carbohydrates are defined as polyhydroxy alkanals or their 2 –keto analogues, existing either as water soluble sweet monomers, di- or trimers, or as water insoluble, tasteless polymers like cellulose, glycogen and starch. They are classified as aldoses and ketoses, like aldotrioses, aldotetroses, aldopentoses and aldohexoses, and their keto analogues. (1)

(c) Sucrose is a disaccharide, $C_{12}H_{22}O_{11}$, and cellulose is a polysaccharide, $(C_6H_{10}O_5)_x$. (1)

Ans.26

(a) Nylon 6, 6 is formed by the condensation of hexamethylene diamine with adipic acid. Nylon 6, 6 is used in making sheets, bristles for brushes and in textile industry.

$nHOOC\text{-}(CH_2)_4\text{-}COOH + n\ H_2N\text{-}(CH_2)_6\text{-}NH_2 \rightarrow [\text{-}OC\text{-}(CH_2)_4\text{-}CO\text{-}NH\text{-}(CH_2)_6\text{-}NH\text{-}]_n + 2nH_2$

(2)

(b) These are rubber – like solids with elastic properties. In these elastomeric polymers, the weakest intermolecular forces hold the polymer chains together. These weak binding forces permit the polymer to be stretched. A few 'cross links' are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanized rubber. The examples are Buna-S, Buna-N, neoprene, etc.

(1)

Ans.27 A number of organic compounds are used as medicinal ingredients. Some examples are:

i) Antipyretic and analgesic compounds, like acetyl salicylate, paracetamol etc.;

ii) Pain-relievers and anti-inflammatory compounds like phenacetin, acetyl morphine etc.

iii) Tranquillizers like LSD;

iv) Antibiotics like penicillins, chloramphenicol, ampicillin, amoxicillin, tetracycline etc.;
v) Antiseptics and disinfectants like phenol;
vi) Antifertility compound like norethindrone. (3)

Ans.28 (a) **Ideal and Non-ideal Solutions**:

The solutions which obey Raoult's law over the entire range of concentration are known as *ideal solutions*. The ideal solutions have two other important properties. The enthalpy of mixing of the pure components to form the solution is zero and the volume of mixing is also zero, i.e.,

$\Delta_{mix}H = 0, \ \Delta_{mix}V = 0$ (1)

It means that no heat is absorbed or evolved when the components are mixed and the volume of solution would be equal to the sum of volumes of the two components.
No truly ideal solutions are known. When a solution does not obey Raoult's law over the entire range of concentration, then it is called *non-ideal solution*. (1)

(b) The abnormal masses are found due to any of the following reasons: (a) Degree of association; (b) Degree of dissociation /ionisation etc.
In most cases deviations from ideal behaviour arise due to either of two main causes: **Dissociation or association**. For example, the measured value of freezing point depression data reveal that the molar mass of benzoic acid is twice that of actual value due to dimer formation between the two Ph-C(=O)-OH molecules via H-bonding. Likewise, for an aqueous solution of $CaCl_2$, colligative properties (e.g. osmotic pressure) reveal partial dissociation.

(1/2)

(c) **Van't Hoff's Factor i**: In order to find the extent of deviation, van't Hoff defined a factor i as follows:

$$i = \frac{\text{(observed value of colligative property)}}{\text{(theoratically calculated value of that property)}} \quad (1/2)$$

(d)

The various quantities known to us are as follows: $P = 2.57 \times 10^{-3}$ bar,
$V = 200 \text{ cm}^3 = 0.200$ litre
$T = 300$ K
$R = 0.083$ L bar $mol^{-1}K^{-1}$
Substituting these values in equation

$$M_2 = \frac{1.26\,\text{g} \times 0.083\,\text{L bar K}^{-1}\text{mol}^{-1} \times 300\,\text{K}}{2.57 \times 10^{-3}\,\text{bar} \times 0.200\,\text{L}} \quad 1$$

$$= 61{,}038 \text{ g mol}^{-1} \quad (1)$$

Or

Ans.28

(a)**Expressing Concentrations of Solutions:** There are several ways to express concentrations of solutions. The choice depends on the type of experiment, type of chemicals to be used, and degree of precision required. Whereas the mass –to-mass units like molality and mass percentage, are the most accurate, they are less popular still today. The mass-to-volume units like normality and molarity despite being a bit less accurate owing to temperaturevolume variations, are the most used. A brief summary of all these units is presented below.

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1. Mass percentage (w/w); 2. Volume percentage (v/v); 3. Parts per million (ppm); 4. Mole fractions; 5. Molality(m); 6. Normality(N) and 7. Molarity(M).

(b)

Molar mass of $C_2H_4O_2$: 12 × 2 + 1 × 4 + 16 × 2 = 60 g mol

$$\text{Moles of } C_2H_4O_2 = \frac{2.5\,\text{g}}{60\,\text{g mol}^{-1}} = 0.0417\,\text{mol}$$

$$\text{Mass of benzene in kg} = \frac{75\,\text{g}}{1000\,\text{g kg}^{-1}} = 75\times10^{-3}\,\text{kg}$$

$$\text{Molality of C2H4O2} = \frac{\text{Moles of } C_2H_4O_2}{\text{kg of benzene}} = \frac{0.0417\,\text{mol}}{75\,\text{g}} \times 1000\,\text{g kg}^{-1}$$

$$= 0.556\,\text{mol kg}^{-1}$$

2

Ans.29

(a) Copper (Z=29, [Ar]$3d^{10}4s^1$) in +1 oxidation is diamagnetic because all its electron spins are paired and its d-orbital is filled. But copper in +2 oxidation state ($3d^9$) has one unpaired 3d electron and is therefore paramagnetic. (2)

(b) A Cr(II) ion has $3d^9$ configuration and is intensely coloured due to its unsymmetrically filled 3d orbital and therefore symmetrically allowed d-d electron transitions consequent upon absorption in the visible region of electromagnetic spectrum. In this case, before and after d-d electron excitation, total spin remains the same, that is, 4 x 1/2 = 2. (1)

On the other hand, for a Mn(II) ion ($3d^5$) with the symmetrically filled 3d orbital, d-d electron transitions are symmetry forbidden. For example, before electron transition, total spin S = 5/2. If an electron is excited to one of the d -orbitals, there will be 3 unpaired and 2 paired spins in the 3d sub-level. Obviously, this is in clear violation of the quantum mechanical principle of conservation of orbital symmetry. Therefore, Mn(II) salts are generally colourless or only faintly coloured.

(1)

(c) Mn and Cr show several oxidation states because they contain highest number of unpaired electron. (1)

or

Ans.29

(a) Europium (Z = 63) is a 4f element. Eu(II) has $4f^7$ configuration and its magnetic moment is given by the simple formula, viz.,
Magnetic moment $=\{ n(n+2)\}^{(1/2)}$ Bohr Magneton.
But For Eu(III) with unsymmetrically filled (n-2)f sub-level(it has $4f^6$ configuration) a modified formula is required.
Magnetic moment $= \{4S (S +1) +L(L+1)\}^{(1/2)}$ Bohr Magneton, where S = total electronic spin,
L = directional quantum number component. (2)

(b) The availability of vacant d-orbitals for pi-back bonding between the CO ligand and the Lewis acid (metal ion or atom) is necessary for stabilisation of carbonyl complexes. This condition is fulfilled by the transition metals but not by the normal metals. Hence, only transition metals form carbonyl complexes. (2)

(c) Gadolinium, Z = 64, Electron configuration = $[Xe]4f^7 5d^1 6s^2$ configuration. Hence, Gd(III) has half filled 4f orbital by the loss of 1 d electron and 2 s electrons. (1)

Ans.30

(a) Methylbenzene (toluene) can be converted into benzaldehyde in many ways, viz.,
(i) By Etard's reaction using chromyl chloride in CS_2 solvent followed by hydrolysis of the adduct formed,
$PhCH_3 + CrO_2Cl_2 /CS_2 \rightarrow Ph\text{-}CH(OCr(OH)Cl_2)_2$ (adduct);
$Ph\text{-}CH(OCr(OH)Cl_2)_2 \xrightarrow{\text{acidic hydrolysis}} PhCH = O$ (1)
(ii) By oxidation with chromic acid in boiling acetic anhydride,
$Ph\text{-}CH_3 + CrO_3/(CH_3CO)_2 \xrightarrow{\text{273-283 K}} Ph\text{-}CH(OCOCH_3)_2$ (adduct)
$Ph\text{-}CH(OCOCH_3)_2 \xrightarrow{\text{acidic hydrolysis}} PhCH = O$ (1)
(iii) By side-chain chlorination followed by alkaline hydrolysis of benzal chloride intermediate
$PhCH_3 + Cl_2 /hv \rightarrow HCl(g) + Ph\text{-}CHCl_2$
$Ph\text{-}CHCl_2 + H_2O/373K \rightarrow PhCH{=}O + 2NaCl + H_2O$ (1)

(b)
$PhCH_2CH_3 + KMnO_4/KOH \xrightarrow{\text{heat}} Ph\text{-}COOH$ (1/2)

(c) (i) On reaction with thionyl chloride, phthalic acid forms phthaloyl chloride.
$(1,2\text{-})\text{-}HOOC\text{-}C_6H_4\text{-}COOH + SO_2Cl_2 \rightarrow 2HCl + o\text{-}(Cl\text{-}C{=}O)\text{-}C_6H_4\text{-}(O{=}C\text{-}Cl) + SO_2$ (1/2)

(ii) The C=O group in 2,2,6-trimethylcyclohexanone is sterically hindered. Thus no addition of H-CN takes place across the >C=O group in the reactant molecule.

(1/2)

(iii) Nitrobenzene does not undergo electrophilic aromatic substitution in presence of mild Lewis acid catalyst like $AlCl_3$. (1/2)

Or

Ans.30

(i) r = ammonia, NH_3 ; P = ethanamide, CH_3 -CO-NH_2 ; N = Hoffman hypobromite degradation reaction.

$CH_3COOH + NH_3 \rightarrow CH_3\text{-}COONH_4^+$ (Ammonium ethanoate)

$CH_3\text{-}COO\text{-}NH_4^+ \xrightarrow{\text{heat}} CH_3CO\text{-}NH_2 + H_2O$ (1)

(ii) R’ = Hexanenitrile, n- $C_5H_{11}CN$

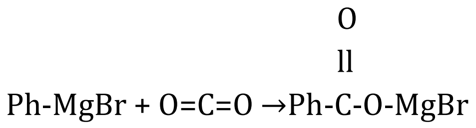
$n\text{-}C_5H_{11}CN \xrightarrow{\text{NaOH/H2O}} n\text{-}C_5H_{11}CONH_2 \xrightarrow[\text{heat}]{\text{OH-}} n\text{-}C_5H_{11}COOH$ (1)

(iii) R’’ = 2-Pentanone, n-C_3H_7-CO-CH_3 ; P’ = iodoform, CHI_3

$n\text{-}C_3H_7CO\text{-}CH_3 \xrightarrow{\text{KOH}/I_2} CH_3I + n\text{-}C_3H_7COOH$ (1)

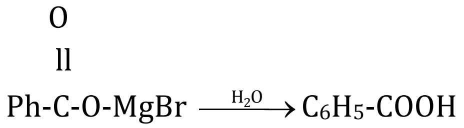
(iv) R’’’ = Bromobenzene; PhBr ; X = phenyl magnesium bromide, Ph-MgBr ;
Y = Bromomagnesium benzoate, Ph-C(=O)-O-MgBr

$PhBr \xrightarrow[\text{heat}]{\text{Mg/ether}} Ph\text{-}MgBr$ (1)



$$\text{Ph-MgBr} + \text{O=C=O} \rightarrow \text{Ph-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-O-MgBr}$$

(1)



$$\text{Ph-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-O-MgBr} \xrightarrow{H_2O} C_6H_5\text{-COOH}$$