CHEMISTRY

Time : 3 hrs.   **M. Marks : 70**

General Instructions
   (a)   All questions are compulsory.
   (b)   Section A: Q.no. 1 to 20 are very short answer questions (objective type) and carry 1 mark each.
   (c)   Section B: Q.no. 21 to 27 are short answer questions and carry 2 marks each.
   (d)   Section C: Q.no. 28 to 34 are long answer questions and carry 3 marks each.
   (e)   Section D: Q.no. 35 to 37 are also long answer questions and carry 5 marks each.
   (f)   There is no overall choice. However an internal choice has been provided in two questions of one mark, two questions of two marks, four questions of three marks and all the three questions of five marks weightage. You have to attempt only one of the choices in such questions.
   (g)   Use log tables if necessary, use of calculators is not allowed.

SECTION - A

Read the given passage and answer the questions 1 to 5 that follow:

A Lead storage battery is the most important type of secondary cell having a lead anode and a grid of lead packed with PbO_2 as cathode. A 38% solution of sulphuric acid is used as electrolyte. (Density=1.294 g mL^{-1}) The battery holds 3.5 L of the acid. During the discharge of the battery, the density of H_2SO_4 falls to 1.139 g mL^{-1}. (20% H_2SO_4 by mass)

   (1) Write the reaction taking place at the cathode when the battery is in use.
   (2) How much electricity (in Coulombs) is required to carry out the reduction of one mole of PbO_2?
   (3) What is the molarity of sulphuric acid before discharge?
   (4) What is the mass of sulphuric acid in the solution after discharge?
   (5) Write the products of electrolysis when dilute sulphuric acid is electrolysed using Platinum electrodes.

Questions 6 to 10 are one word answers:

   (6) Name the substance used as depressant in the separation of two sulphide ores in Froth floatation method.
   (7) Name the unit formed by the attachment of a base to 1′ position of sugar in a nucleoside.
                     OR

   What happens to the optical rotation for sucrose, when it is subjected to hydrolysis?

(8) Name the species formed when an amino acid is dissolved in water?

(9) What type of reaction occurs in the formation of Nylon 6,6 polymer?

(10) Which of the following compounds would undergo cannizzaro reaction:

Benzaldehyde, Cyclohexanone, 2- Methylpentanal.

Questions 11 to 15 are multiple choice questions:

(11)   The IUPAC name of the compound shown below is:
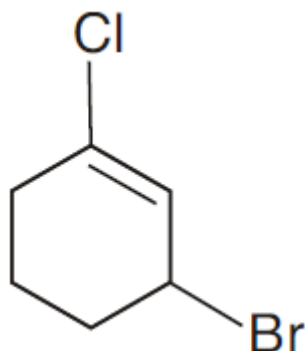
(a)   2-bromo-6-chlorocyclohex-1-ene
(b)   6-bromo-2-chlorocyclohexene
(c)   3-bromo-1-chlorocyclohexene
(d)   1-bromo-3-chlorocyclohexene

(12)   When one mole of $CoCl_3.5NH_3$ was treated with excess of silver nitrate solution, 2 mol of AgCl was precipitated. The formula of the compound is:

(a) $[Co(NH_3)_5Cl_2]Cl$

(b) $[Co(NH_3)_5Cl]Cl_2$

(c) $[Co(NH_3)_4Cl_2] (NH_3)Cl$

(d) $[Co(NH_3)_3Cl_3] (NH_3)_2$

(13)   The absorption maxima of several octahedral complex ions are as follows:

S.No	Compound	λ_{max} nm
1	$[Co(NH_3)_6]^{3+}$	475
2	$[Co(CN)_6]^{3-}$	310
3	$[Co(H_2O)_6]^{3+}$	490

The correct order of Δ_o for the ions is:

(a) $[Co(H_2O)_6]^{3+} < [Co(CN)_6]^{3-} < [Co(NH_3)_6]^{3+}$

(b) $[Co(CN)_6]^{3-} < [Co(NH_3)_6]^{3+} < [Co(H_2O)_6]^{3+}$

(c) $[Co(H_2O)_6]^{3+} < [Co(NH_3)_6]^{3+} < [Co(CN)_6]^{3-}$

(d) $[Co(NH_3)_6]^{3+} < [Co(CN)_6]^{3-} < [Co(H_2O)_6]^{3+}$

(14)   Predict the number of ions produced per formula unit in an aqueous solution

of $[Co(en)_3]Cl_3$

(a)   4

(b)   3

(c)   6

(d)   2
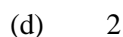
(15)   The co-polymer formed by addition polymerization of Buta-1,3-diene and styrene in presence of peroxide is:

a)   -[-CH₂- CH-CH₂ –CH=CH –CH₂-]-
             |
             C₆H₅

b)   –[-CH-CH=CH-CH₂ -CH=CH-]-
             |
             C₆H₅

c)   –[-CH₂-CH-CH-CH=CH-]-
             |
             C₆H₅
           CH₃ (above)

d)   –[CH₂-CH-CH₂ –CH=CH-]-
             | |
             C₆H₅   CH₃
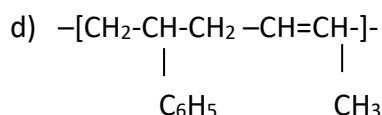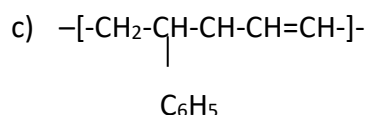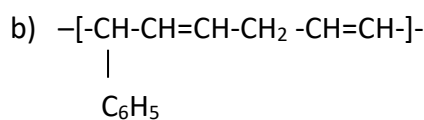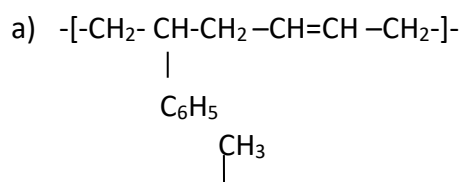
OR

The incorrect statement about LDP is:

(a) It is obtained through the free radical addition of ethene.
(b) It consists of linear molecules.
(c) It is obtained by the H-atom abstraction.
(d) Peroxide is used as an initiator.

Questions 16 to 20 :

(A) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.
(B) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

(C) Assertion is correct, but reason is wrong statement.

(D) Assertion is wrong, but reason is correct statement.

16. Assertion: The two strands in double strand helix structure of DNA are complementary to each other

Reason: Disulphide bonds are formed between specific pairs of bases

17. **Assertion**: Glucose reacts with hydroxylamine to form an oxime and also adds a molecule of hydrogen cyanide to give cyanohydrin.

    Reason: The carbonyl group present in the open chain structure of glucose is an aldehydic group.

18. **Assertion**: The acidic strength of halogen acids varies in the order HF>HCl>HBr>HI

    Reason: The bond dissociation enthalpy of halogen acids decreases in the

order   HF>HCl>HBr>HI

19. **Assertion**:   **C_2H_5OH is a weaker base than phenol but is a stronger nucleophile than phenol. (1)**

    Reason: **In phenol the lone pair of electrons on oxygen is withdrawn towards the ring due to resonance.**

20. **Assertion**: **Aryl halides undergo nucleophilic substitution reactions with ease.**

    Reason:The carbon halogen bond in aryl halides has partial double bonds character.

SECTION : B

21.   Calculate the number of lone pairs on central atom in the XeF_4

molecule and predict the geometry on the basis of VSEPR Theory:

22. The rate of a reaction depends upon the temperature and is quantitatively expressed as

$$k = A\,e^{-E_a/RT}$$

i)   If a graph is plotted between log k and 1/T, write the expression for the slope of the reaction?

ii)   If at under different conditions E_{a1} and E_{a2} are the activation energy of two reactions If $E_{a1} = 40$ J / mol and $E_{a2} = 80$ J / mol. Which of the two has a larger value of the rate constant?

23.   The experimentally determined molar mass for what type of substances is always lower than the true value when water is used as solvent. Explain. Give one example of such a substance and one example of a substance which does not show a large variation from the true value.

24.   **Write structure of the products formed:**

    (a) $CH_3CH_2COOH \xrightarrow{\;cl_2,red\,P_4\;}{\Delta}$

(b) $C_6H_5COC\ell \xrightarrow[\Delta]{H_2, Pd-BaSO_4}$
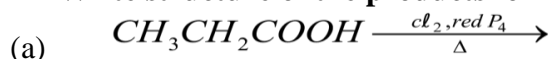
25. Draw one of the geometrical isomers of the complex $[Pt(en)_2Cl_2]^{2+}$ which is optically inactive. Also write the name of this entity according to the IUPAC nomenclature.

OR

Discuss the bonding in the coordination entity $[CO(NH_3)_6]^{3+}$ on the basis of valence bond theory. Also, comment on the geometry and spin of the given entity. (Atomic no. of Co= 27)

26. What is meant by Vapour phase refining? Write any one example of the process which illustrates this technique, giving the chemical equations involved.

OR

Write and explain the reactions involved in the extraction of gold.

27. Which one of the following compounds will undergo hydrolysis at a faster rate by S$_N$1 mechanism? Justify.
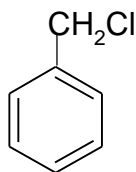
CH$_2$Cl

or $CH_3CH_2CH_2Cl$

SECTION: C

28. Calculate the freezing point of a solution containing 0.5 g KCl (Molar mass = 74.5 g/mol) dissolved in 100 g water, assuming KCl to be 92% ionized.

K$_f$ of water = 1.86 K kg / mol.

OR

A solution is having two components A and B. if vapour pressure of pure A and B are 105.2 kPa and 46.8 kPa respectively and the mole fraction of B in liquid phase is 0.6. Calculate the mole fraction of A and B in the vapour phase.

29. For the reaction A + B → products, the following initial rates were obtained at various given initial concentrations

S.No.	[A] mol / L	[B] mol / L	Initial rate M/s
1.	0.1	0.1	0.05
2.	0.2	0.1	0.10
3.	0.1	0.2	0.05

Determine the half-life period.

OR

A first order reaction is 50 % complete in 50 minutes at 300 K and the same reaction is again 50 % complete in 25 minutes at 350 K. Calculate activation energy of the reaction.

30. Answer the following questions:

(a) Which of the following electrolytes is most effective for the coagulation of AgI/Ag^+ sol?

   a. $MgCl_2$, K_2SO_4, $K_4[Fe(CN)_6]$

(b) What happens when a freshly precipitated $Fe(OH)_3$ is shaken with a little amount of dilute solution of $FeCl_3$.

(c) Out of sulphur sol and proteins, which one forms macromolecular colloids?

31. Account for the following:

a) Moist SO_2 decolourises $KMnO_4$ solution.

b) In general interhalogen compounds are more reactive than halogens (except fluorine).

c) Ozone acts as a powerful oxidizing agent

OR

Discuss the following briefly:

a) The stronger oxidising power of fluorine than chlorine.
b) The slow depletion of ozone layer by the exhaust systems of supersonic jet airplanes.

c) The effort made by Neil Bartlett that led to the discovery of xenon compounds.

32. Identify the product formed when propan-1-ol is treated with Conc. H_2SO_4 at 413 K . Write the mechanism involved for the above reaction.

33. (a) Give chemical tests to distinguish between the following pairs of compounds:

   (i) Ethanal and Propanone.
   (ii) Pentan-2-one and Pentan-3-one.

(b) Arrange the following compounds in increasing order of their acid strength:

Benzoic acid, 4- Nitrobenzoic acid, 3,4-Dinitrobenzoic acid,

4- Methoxybenzoic acid.
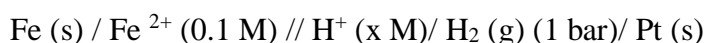
<div align="center">OR</div>

Compare the reactivity of benzaldehyde and ethanal towards nucleophilic addition reactions. Write the cross aldol condensation product between benzaldehyde and ethanal.

34. Define and write an example for the following :

(a) Broad spectrum antibiotics.

(b) Analgesics

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SECTION: D

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35. (a) The e.m.f. of the following cell at 298 K is 0.1745 V

Fe (s) / Fe $^{2+}$ (0.1 M) // H$^+$ (x M)/ H$_2$ (g) (1 bar)/ Pt (s)

Given : $E^0_{Fe^{2+}/Fe} = -0.44V$

Calculate the pH of the solution at the electrode where hydrogen is being produced.

(b) Aqueous solution of copper sulphate and silver nitrate are electrolysed by 1 ampere current for 10 minutes in separate electrolytic cells. Will the mass of copper and silver deposited on the cathode be same or different? Explain your answer.

<div align="center">OR</div>

(a) Calculate the degree of dissociation of 0.00241 M acetic acid if conductivity of this solution is 7.896×10^{-5} S cm^{-1}.

Given $\lambda^o_{H^+} = 349.6\,S\,cm^2\,mol^{-1}$; $\lambda^o_{CH_3COO^-} = 40.9\,S\,cm^2\,mol^{-1}$

(b) Solutions of two electrolytes 'A' and 'B' are diluted. The limiting molar conductivity of 'B' increases to a smaller extent while that of 'A' increases to a much larger extent comparatively. Which of the two is a strong electrolyte? Justify your answer.

36. An organic compound A' with molecular formula C$_7$H$_7$NO reacts with Br$_2$/ aq KOH to give compound B', which upon reaction with NaNO$_2$ & HCl at 0°C gives C'. Compound C' on heating with CH$_3$CH$_2$OH gives a hydrocarbon D'. Compound B' on further reaction with Br$_2$ water gives white precipitate of compound E'. Identify the

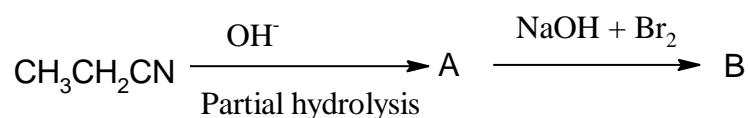compound A, B, C, D&E; also justify your answer by giving relevant chemical equations.
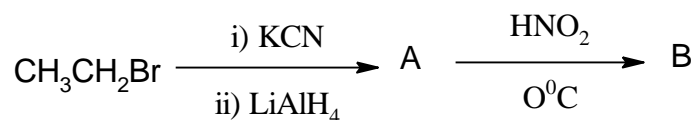

OR

(a) How will you convert:

  (i) Aniline into Fluorobenzene.
  (ii) Benzamide into Benzylamine.

  (iii) Ethanamine to N,N-Diethylethanamine.

(b) Write the structures of A and B in the following:

  i)

$$CH_3CH_2CN \xrightarrow[\text{Partial hydrolysis}]{OH^-} A \xrightarrow{NaOH + Br_2} B$$

  ii)

$$CH_3CH_2Br \xrightarrow[\text{ii) LiAlH}_4]{\text{i) KCN}} A \xrightarrow[O^0C]{HNO_2} B$$

37. (a) When a chromite ore (A) is fused with an aqueous solution of sodium carbonate in free excess of air, a yellow solution of compound (B) is obtained. This solution is filtered and acidified with sulphuric acid to form compound (C). Compound (C) on treatment with solution of KCl gives orange crystals of compound (D). Write the chemical formulae of compounds A to D.

(b) Describe the cause of the following variations with respect to lanthanoids and actinoids:
  (i) Greater range of oxidation states of actinoids as compared to lanthanoids.
  (ii) Greater actinoid contraction as compared to lanthanoid contraction.
  (iii) Lower ionisation enthalpy of early actinoids as compared to the early lanthanoids.

OR

(a) What happens when
  (i) Manganate ions (MnO_4^{2-}) undergoes disproportionation reaction in acidic medium?
  (ii) Lanthanum is heated with Sulphur?

(b) Explain the following trends in the properties of the members of the First series of transition elements:

(i) $E^o(M^{2+}/M)$ value for copper is positive(+0.34 V) in contrast to the other members of the series.

(ii) Cr^{2+} is reducing while Mn^{3+} is oxidising, though both have d^4 configuration.

(iii) The oxidising power in the series increases in the order $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$.