CHEMISTRY-I
(CHEM 1001)

Time Allotted : 3 hrs **Full Marks : 70**

Figures out of the right margin indicate full marks.

Candidates are required to answer Group A and any 5 (five) from Group B to E, taking at least one from each group.

Candidates are required to give answer in their own words as far as practicable.

Group – A
(Multiple Choice Type Questions)

1. Choose the correct alternative for the following: **10 × 1 = 10**

(i) A reaction has $\Delta H = -33$kJ and $\Delta S = 58$ kJ. This reaction would be
(a) Spontaneous below a certain temperature
(b) Non spontaneous at all temperature
(c) Spontaneous above a certain temperature
(d) Spontaneous at all temperature.

(ii) Which statement is not correct regarding reversible process?
(a) It is imaginary process. (b) It takes infinite time.
(c) Work obtained is maximum (d) It is spontaneous.

(iii) If the frequency of a wave of light is 12×10^{14} s^{-1} then the wave number associated with this light is
(a) 5×10^{-7} m (b) 4×10^{-8} cm^{-1}
(c) 2×10^{-7} m^{-1} (d) 4×10^{4} cm^{-1}.

(iv) Which one of the following is the correct electronic configuration of Lanthanum (57La)
(a) $[Rn]4f^15d^16s^1$ (b)$[Xe]4f^15d^16s^1$
(c) $[Rn]5d^16s^2$ (d)$[Xe]5d^16s^2$.

(v) The bond order and magnetic property of B2 molecule are respectively
(a) 1 and diamagnetic (b) 2 and paramagnetic
(c) 1 and paramagnetic (d) 2 and diamagnetic.

(vi) ThePb-acid storage cell consists of
(a) PbO_2 anode and Pbcathode
(b) Pb anode and PbO_2 cathode
(c) Pb anode and $PbSO_4$ cathode
(d) PbO anode and Pb cathode.

(vii) Order of the reaction $H_2 + C_2 \xrightarrow{h\upsilon} H$ is
(a)1 (b)0 (c) ½ (d) 2.

(viii) In the linear plot of equation $\lambda = \lambda_0 - b\sqrt{c}$ the slope 'b' changes at very high concentration for $CuSO_4$, but not for HCl, although both are strong electrolytes. This is due to
(a) Difference in size of the ions (b) Difference in ionic mobility
(c) Ion-pair formation (d) Ion-solvent interaction.

(ix) Identify the chiral molecule among the following
(a) Ethanol (b) 1-pentanol
(c) 2-pentanol (d) 3-pentanol.

(x) 2-fold alternating axis of symmetry is equivalent to which of the following?
(a) Plane of symmetry
(b) Centre of symmetry
(c) Both plane of symmetry and centre of symmetry
(d) None of these.

Group – B

2. (a) Write the two statements of the Second law of thermodynamics
(b) Derive Clapeyron-Clausius equation and mention its applications.
(c) Calculate (i) the de Broglie wavelength of an electron moving with a velocity of 5.0×105 ms^{-1} and (ii) relative de Broglie wavelength of an hydrogen atom and an oxygen atom moving with the same velocity ($h = 6.63 \times 10^{-34}$ kg m^2 s^{-1}).
(d) Write down the important applications of ultra-violet spectroscopy?

2 + 4 + (2 + 2) + 2 = 12

3. (a) Derive the equation to find the efficiency of Carnot cycle.
(b) Write the wave function and the total energy of a particle in a one dimensional box for its ground state.
(c) Calculate the vapour pressure of water at 90°C taking the heat of vaporization in the temperature range 90-100°C as 542 Cal/gm.
(d) What is chemical shift in NMR spectroscopy? Why ^{13}C is NMR active but ^{12}C not?

4 + 2 + 3 + (2+1) = 12

Group – C

4. (a) Carbon monoxide (CO) is a sigma donor and pi-acceptor ligand - explain with the help of Molecular Orbital energy level diagram of CO molecule.

(b) Arrange the electronegativity sequence of carbon atom in C_2H_6, C_2H_4 and C_2H_2 and justify your answer.

(c) Explain why the most common oxidation state for the heaviest element (Pb) in Group 14, is +2 rather than +4.

(d) Why the solubility of AgCl is reduced in a 0.1(M) HCl solution?

(e) Calculate pH of a mixture of 164 ml (N/5) acetic acid and 36 ml of (N/5) sodium acetate. The dissociation constant of acetic acid is 1.8×10^{-5}.

4+ 2 + 2 + 2 +2 = 12

5. (a) Why PCl_3F_2 molecule has zero dipole moment?

(b) Using VSEPR theory, draw and explain the structure of I_3^- and indicate the state of hybridization of the central atom.

(c) Using Slater's rule, calculate the shielding constant and therefore find out the effective nuclear charge experienced by the first valence electron in Ga (Z= 31).

(d) Why is the first ionization potential value of Cu higher than that of K although both K and Cu have their valence electron in 4s orbital?

(e) Derive an expression for pH of aqueous solution containing salt of weak acid and strong base. Calculate the hydrolysis constant of 0.625 M solution of CH_3COONa. ($K_a=1.754\times10^{-5}$)

2+ 2 +2 + 2 +(3+1) = 12

Group – D

6. (a) What are the typical factors affecting the chemical reaction rates?

(b) What is the significance of 'probability' or 'steric factor' in the modified 'Collision Theory' of reaction rates?

(c) At 13°C the equivalent conductance (λ^0) for NH_4Cl, NaOH and NaCl are 129.8, 217.4 and 108.9 mho cm^2 respectively. Find out the equivalent conductance of NH_4OH solution.

(d) Show how hydrogen bonding accounts for faster transport of H+ than Na+ in aqueous electrolytes.

(e) What is the physical significance of relaxation effect (Debye-Onsager constant, B) in ion conductance?

(f) Consider the cell Cd | Cd++ ‖ KCl | Hg_2Cl_2 (s)-Hg
Write the cell reaction and find out the free energy change in the reaction under standard conditions. Given the oxidation potentials, $E^0_{C/C^{++}}$ = +0.402V and E^0_{ca} = –0.268 V

2 + 2 + 2 + 2 + 2 + 2 = 12

7.(a) In a KCl solution how Cl^- ion can be estimated conductometrically?

(b) Describe standard hydrogen electrode and express the corresponding half cell reaction.

(c) What are the electrodes (anode and cathode) used in a dry Leclanche cell? Which type of cell is this, primary or secondary?

(d) Consider the following electrochemical cell configurations:
(i) Zn (s) | Zn SO_4 (solution) ‖ $CuSO_4$ (solution) | Cu (s)
(ii) Zn (s) | H_2SO_4 (aqueous) | Cu (s)
Which one is reversible and the other irreversible cell and why?

(e) Show that the reaction time for a 1st order reaction for 75% conversion is twice the time for 50% conversion.

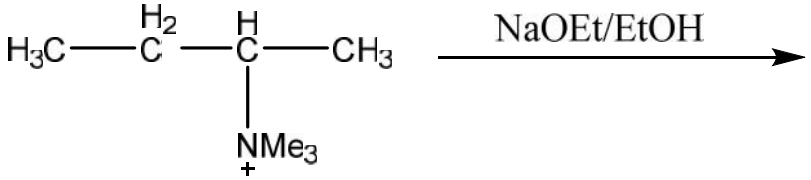
2 + 2 + 3 + 3 + 2 = 12

Group – E

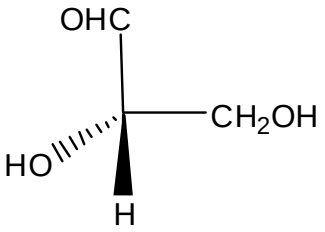
8. (a) Explain alternating axis of symmetry with suitable example.

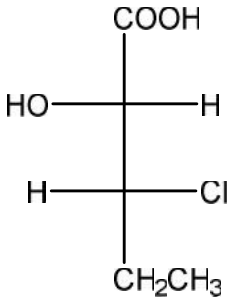
(b) Why propynoic acid (CH≡CCOOH) is stronger than propenoic acid (CH_2=CHCOOH)? Explain the fact.

(c) Identify the elimination products. Which product should be major and why?



(d) Find out the absolute configuration of the each stereocentre of the following molecules.





(2+1) + 2 + (2+1+1) + (2+1)= 12

9.(a) Briefly write down the synthetic route and uses of Aspirin.

(b) Differentiate between enantiomer and diastereomer.

(c) Predict the major and minor products obtained when HBr is added to 2-methylpropene. Explain why the reaction is taking place in such fashion.

(d) Explain the nature of inductive effect shown by phenyl ring in the compounds Ph-CH_3 and Ph-CN respectively.

(2+1) + 3 + (2+2) + 2 = 12

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