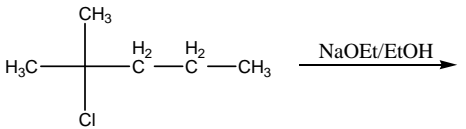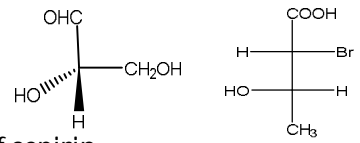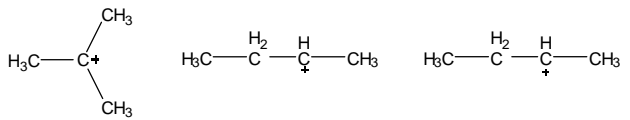7. (a) Write down the Arrhenius equation for the temperature dependence of specific rate and explain the terms used. Plot logK vs 1/T and explain the significance of the slope of the plot.

    (b) Why does the H^+ ion show abnormally high conductance compared to the other cations?

    (c) The specific conductance of 0.02(N) weak acid solution is 3.2×10^{-4} ohm^{-1}cm^{-1}. Calculate the equivalent conductance at infinite dilution. (Given the degree of dissociation of this acid is 0.045).

    (d) Calculate the equilibrium constant at 298 K of the following cell reaction:
    $Fe^{2+} + Ag^+ \longrightarrow Fe^{3+} + Ag(s)$
    (Given $E°(Fe^{3+}/Fe^{2+}) = 0.77V$ and $E°(Ag^+/Ag) = 0.80V$).

    (e) A galvanic cell is represented as: $Ni(s)INi^{2+}(aq)IICu^{2+}(aq)ICu(s)$
    Write down the half cell reactions and comment on the spontaneity of the overall cell reaction. (Given $E°(Ni^{2+}/Ni) = -0.25V$ and $E°(Cu^{2+}/Cu) = 0.34V$.)

    3 + 2 + 2 + 2 + 3 = 12

Group – E

8. (a) Identify the product with mechanism.
    H_3C—HC=CH_2 $\xrightarrow{HBr/H_2O_2}$

    (b) Why phenol is acidic?

    (c) Which is a stronger base CH_3NH_2 or $C_6H_5NH_2$ and why?

    (d) What are the essential conditions for aromaticity?

    (e) Predict the elimination products for the following reaction. Identify the major product.

    H_3C—C(CH_3)(Cl)—$C H_2$—$C H_2$—CH_3 $\xrightarrow{NaOEt/EtOH}$

    3 + 2 + 2 + 2 + 3 = 12

9. (a) Draw the eclipsed and staggered forms of ethane molecule.

    (b) Identify the R/S configuration of the each stereocentre of the following compounds.

    (c) Write the molecular structure and use of aspirin.

    (d) Arrange the order of stability of the following carbocations.

    (e) Write the differences between S_N1 and S_N2 reactions.

    2 + 3 + 2 + 3 + 2 = 12

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) For an endothermic process S is positive. The reaction is feasible when
    (a) $\Delta H < T\Delta S$ (b) $\Delta H > T\Delta S$
    (c) $\Delta H = \Delta S$ (d) $\Delta H = T\Delta S$.

    (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) The Heisenberg uncertainty principle is concerned with the following two properties
    (a) mass and velocity   (b) mass and momentum
    (c) mass and position   (d) position and momentum.

    (iv) A salt derived from a strong base and a weak acid will be
    (a) acidic   (b) basic
    (c) neutral   (d) volatile.

    (v) The hybridization of the central atom in XeF_4 molecule is
    (a) sp^2 (b) sp^3 (c) sp^3d (d) sp^3d^2.

    (vi) The frequency of a wave of light is 12×10^{14} s^{-1}. 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}.

    (vii) For a reaction $A + B \rightarrow C + D$ if the concentration of A is doubled without altering the concentration of B, the rate gets doubled. If the concentration of B is increased by nine times without altering the concentration of A, the rate gets tripled. The order of the reaction is
    (a) 2   (b) 4/3   (c) 3/2   (d) 1.

(viii) The intermolecular force(s) responsible for the fact that CH_4 has the lowest boiling point in the set CH_4, SiH_4, GeH_4, SnH_4 us/are
    (a) hydrogen bonding
    (b) dipole dipole interactions
    (c) London dispersion forces
    (d) mainly London dispersion forces but also dipole dipole interactions.

(ix) Which of the following compounds will undergo S_N1 reaction most readily?
    (a) $H_3C\text{-}Br$ (b) $CH_3CH_2\text{-}Br$
    (c) $(CH_3)_2CH\text{-}Br$ (d) $(CH_3)_3C\text{-}Br$.

(x) The K_{SP} of AgI is 1.5×10^{-16}. On mixing equal volumes of the following solutions, precipitation will occur only with
    (a) 10^{-7} M Ag^+ and 10^{-19} M I^- (b) 10^{-8} M Ag^+ and 10^{-8} M I^-
    (c) 10^{-16} M Ag^+ and 10^{-16}M I^- (d) 10^{-9} M Ag^+ and 10^{-9} M I^-.

Group – B

2. (a) Derive the expression for the total work produced in the Carnot cycle.

(b) Determine the wavelength for the transition from $n_1 = 6$ to $n_2 = 3$ in a hydrogen atom (the value of Rydberg constant is 109677.57 cm^{-1}).

(c) Derive Gibbs Duhem Equations.

(d) Write the basic principle and the usefulness of IR spectroscopy.

4 + 2 + 3 + 3 = 12

3. (a) Derive the expression for the change in entropy for the isothermal expansion of one mole of an ideal gas.

(b) Write the Clapeyron-Clausius equation. The vapour pressure of water is 1.0 atm at 373 K, and the enthalpy of vaporization is 40.7 kJ mol^{-1}. Estimate the vapour pressure at 383 K (Assuming water vapour as ideal gas).

(c) Write the wave function and the total energy of a particle in a one dimensional box for ground state.

(d) On passing monochromatic light through a 0.01 (M) solution in a cell of 2 cm thickness, the intensity of the transmitted light was reduced to 10%. Calculate the molar extinction coefficient.

(e) Define Helmholtz free energy.

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

Group – C

4. (a) Using VSEPR theory, predict the structure of BrF_3 and also mention its hybridization.

(b) Using Slater's rule, calculate the shielding constant and therefore find out the effective nuclear charge experienced by the first valence electron in Ca (Z = 20).

(c) Why phenolphthalein is not a suitable indicator for the titration of ammonium hydroxide with HCl? Explain with the help of a pH curve for titration.

(d) What is buffer solution? Calculate the pH of a buffer solution of 0.25 M formic acid and 0.10 M sodium formate. (K_a of formic acid = 1.8×10^{-4}).

(e) Why B_2 is paramagnetic while C_2 is not?

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

5. (a) Draw the MO energy level diagram of HF molecule. Mention the HOMO and LUMO from the diagram.

(b) Electronegativity of Ga(31) is greater than Al(13), though the reverse is expected — explain.

(c) Derive the expression for pH of a solution containing salts of strong acid and weak base.

(d) The first ionization energy of elements increases from left to right in a given period of the periodic table but Be (IE = 899KJ mol^{-1}) has higher ionization energy than B (IE = 801KJ mol^{-1}) — Explain.

(e) Melting point of maleic acid is lower than that of fumaric acid though they have same molecular formula ($HO_2CCH = CHCO_2H$) justify.

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

Group – D

6. (a) A first order reaction has rate constant equal to 1.25×10^{-4} sec^{-1} at 298 K and 8.5×10^{-4} sec^{-1} at 318 K. Calculate the activation energy of the reaction.

(b) Depict, with explanation the nature of the conductometric titration curve for the titration of a strong acid with a strong base.

(c) Express the configuration of the galvanic cell that operates with the reaction,
$2Ag + (aq) + Ni(s) \rightarrow 2Ag(s) + Ni2 + (aq)$
Also write down the Nernst equation for the above reaction.

(d) The ion conductances of Ag^+ and NO_3^- ions are 54.2 and 61.6 ohm^{-1}cm^{2}eqv^{-1} respectively. What will be the values of transport numbers of Ag^+ and NO_3^- ions in a solution of $AgNO_3$?

(e) Give a schematic of a H_2-O_2 fuel cell operating at ambient temperature. Write the half cell reactions for the fuel cell.

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