FIRST B. SC. EXAMINATION, 2017

(2nd Semester)

CHEMISTRY (SUBSIDIARY)

PAPER - IIIS

Time : Two hours Full Marks : 50

Use a separate answerscript for each group.

GROUP - A

1. a) Discuss the criteria for achieving the state of *'thermodynamic equilibrium'*. 'The final pressure for an adiabatic expansion is always lower compare to that of corresponding isothermal expansion for same final volume' – Justify or criticize the statement. 2+2

   b) State and explain of 'Zeroth law of thermodynamics'. 2

   c) Explain the fact that the internal energy of a fixed mass of an ideal gas only depends on its temperature. 2

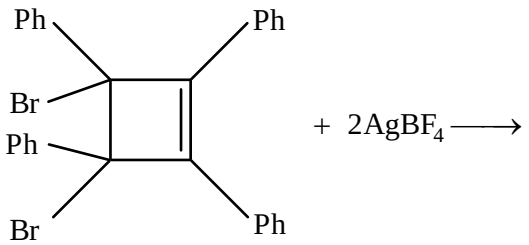
   d) Define Joule-Thomson (J-T) coefficient. Explain why the J-T coefficient is always zero for an ideal gas, whereas its value varies with initial pressure of a real gas at a particular temperature. 2+3

   e) Calculate the enthalpy of fusion of ice at $-20^{o}C$, if that at $0^{o}C$ is 1.44 kcal mol^{-1}. Given molar heat capacities of ice & water are 8·7 and 18·0 cal K^{-1} mol^{-1}, respectively and are temperature independent. 4

GROUP - B

2. a) Draw the properly labelled orbital picture of 'benzene' showing hybridization of each carbon atom. Comment on its shape. 2

   b) Predict the product of the following reaction with proper explanation. 2



$+ \ 2AgBF_4 \longrightarrow$

   c) Mention with brief explanation the basic difference(s) between bromination of cyclohexene and bromination of benzene. 2

   d) Mechanistically discuss hydrolysis of chlorobenzene in aqueous alkali under drastic condition. Draw properly labelled energy profile diagram for it. Explain on the basis of relative stability of the intermediates that the presence of nitro group at *p*-position to the chlorine atom in the benzene ring activates the displacement reaction. 2+2+2

5. The radii of Zn^{2+} and S^{2-} are $0{\cdot}74\,\mathring{A}$ and $1{\cdot}84\,\mathring{A}$, respectively. Predict the coordination number of Zn^{2+} in a ZnS crystal. What is the lattice type ? Is there any deviation of the predicted structure from the actual structure ? Explain. 3

6. a) The melting points of the Group II metal halides are as follows :

   $BeCl_2$: 400°C ; $MgCl_2$: 714°C ; $CaCl_2$: 772°C ; $SrCl_2$: 874°C ; $BaCl_2$: 962°C. Explain from the Fajan's rules, the nature of chemical bonding in each of these metal halides. $1\frac{1}{2}$

   b) Stannous chloride is a solid but stannic chloride is a liquid. Explain. $1\frac{1}{2}$

7. Explain a molecular system where the central atom has five electron pairs (three bond pairs and two lone pairs) from the concept of VSEPR. What would be the actual shape of such a molecule ? Give an example. $2\frac{1}{2}+\frac{1}{2}$

GROUP - C

Answer question No. ***3*** and ***any two*** from the rest

3. a) Mention the essential stages that lead to the formation of an ionic compound. 2

   b) Create the Born-Haber cycle for the formation of CaO from its constituent elements and write the expression for the heat of formation of CaO. 2

   c) Mention any two applications of the Born-Haber cycle. 2

   d) Cupric compounds of copper are much more stable than their cuprous counterpart in solid state. Explain. 2

   e) The toal potential energy (E) of Avogadro number of ions on an M^+ and X^- ionic crystal having the NaCl structure would be given by $E = -Z^+Z^-e^2 AN_A/r+BN_A/r^n$ where the terms have their usual meaning. Use this expression to derive the final form of the Born-Lande equation. 2

4. How are the radius ratio rules useful for predicting structures of ionic compounds ? Mentioning the necessary assumptions, derive the limiting condition for radius-ratio of a cation to anion having coordination number six in a face centred cubic lattice (fcc). 3

e) Arrange the following in order of increasing nucleophilicity and give your reason(s) :

$Br^{\ominus}$, $Cl^{\ominus}$, $F^{\ominus}$, $I^{\ominus}$ 3

f) State whether the following statement is correct or not :

"There will be an increase in crowding around the carbon atom on going from initial bromide to the transition state during the hydrolysis of bromomethane in aqueous alkali following S_N2 pathway."

Justify your answer by drawing probable structure of the transition state. 2