[This question paper contains 4 printed pages.]

Sr. No. of Question Paper : 8458 **C** **Roll No.....**

Unique Paper Code : 217305

Name of the Paper : CHHT-307 : Physical Chemistry II

Name of the Course : B.Sc. (Hons.) Chemistry, Part II

Semester : III

Duration : 3 Hours

Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. This question paper comprises of two sections, each containing 4 questions.
3. Answer **six** questions in all, selecting **3** questions from each Section.
4. Draw the graphs on your answer sheet. Graph paper is not required.
5. Use of scientific calculator is permitted.
6. $R = 8.314\ J\ K^{-1}\ mol^{-1}$; $N_A = 6.022 \times 10^{23}\ mol^{-1}$.

SECTION A

1. (a) To predict the spontaneity of a process, both ΔS_{sys} and ΔS_{surr} are considered but ΔG alone is sufficient for the same.

   (b) Starting from the definition of G and the relation $dG = -SdT + Vdp$, derive the following relation :

$$\left[\frac{\partial(\Delta G/T)}{\partial(1/T)}\right]_P = \Delta H$$

   (c) What is Hess's law of constant heat summation ? Explain with the help of an example. Is it possible to apply this law to other thermodynamic functions ? Justify your answer.

   (d) Enthalpy of neutralization of HCl with NaOH is $-57.3\ kJ\ mol^{-1}$ and by NH_4OH it is $-51.3\ kJ\ mol^{-1}$. Calculate the enthalpy of ionization of NH_4OH and write the relevant equations. (2½,4,3,3)

P.T.O.

2. (a) Enthalpy of neutralization of MgO(s) with HCl(aq) is very much higher than the accepted value –57.3 kJ mol^{-1}. Explain ?

(b) Differentiate between the following pairs giving at least one example in each case :

(i) Differential and Integral enthalpy of solution.

(ii) Bond enthalpy and Bond dissociation enthalpy.

(iii) Enthalpy of solvation and enthalpy of solution.

(c) Neatly draw the Born-Haber cycle for the formation of KCl(s) and calculate its lattice energy using the data given below.

$\Delta_{sub}H(K,s) = 89$, $\Delta_{diss}H(Cl_2,g) = 244$, $\Delta_{ion}H(K,g) = 418$,

$\Delta_{eg}H(Cl,g) = -349$ and $\Delta_f H^0$ (KCl,s) = 437 (all values in kJ mol^{-1}).

(2½,6,4)

3. (a) Entropy of O_2 at absolute zero of temperature is zero while that of CO is not. Explain.

(b) Show with the help of a diagram that $w_{rev} > w_{irr}$ when n moles of an ideal gas undergo an isothermal expansion.

(c) Starting from the definitions of G and H derive the following relation :

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

(d) Consider a dry cell of 1.5 volts, large enough to deliver a constant current of exactly 1.0 ampere for 1.0 hour. If this cell is used to power an electrical machine that is able to lift a box weighing 90 kg, how far above the ground would the box be at the end of an hour. (2½,3,4,3)

4. (a) One feels cold when the snow starts melting but not during the snowfall. Explain.

(b) The molar heat capacity of a certain metal at 20K is b J $K^{-1}mol^{-1}$. Show that the absolute entropy of this metal at 20 K is equal to b/3.

(c) A certain substance has a molar heat capacity $C_{p,m}$ given (in J $K^{-1}mol^{-1}$) by the following equations :

$C_{p,m}(s) = 16.8 \times 10^{-5}\ T^3$; $0 < T < 50K$

$C_{p,m}(s) = 21$; $50 \leq T \leq 150K$

$C_{p,m}(liq) = 25.2$; $50 < T < 400K$

At the melting point, 150 K, $\Delta H_{fusion} = 1.26$ kJ mol^{-1}.

Calculate the third- law molar entropy of this substance in the liquid state at 300 K. (2½,4,6)

SECTION B

5. (a) Osmotic pressure measurements are preferred over other colligative properties to determine the molar mass of macromolecules.

(b) Starting with the equation, $\Delta G^0 = -RT \ln K$, derive the equation :

$\ln K = -\Delta H^0/(RT) + I$

where I is an integration constant.

(c) Calculate $\Delta_{mix}G$ and $\Delta_{mix}S$ at 300 K and 10 bar pressure when :

(i) 20 mol of gas A are mixed with 20 mol of gas B.

(ii) 35 mol of gas A are mixed with 20 mol of gas B

(iii) 15 mol of A are mixed with 40 mol of equimolar mixture of A and B. (2½,4,6)

6. (a) Explain why a salt solution fails to quench thirst.

(b) Derive an expression relating depression in freezing point with molality of a dilute solution of a non volatile solute starting from the concept of chemical potential.

(c) For the reaction :

$$3Fe_2O_3(s) \rightleftharpoons 2Fe_3O_4(s) + \frac{1}{2}O_2(g)$$

$\Delta G^0_{298} = 193.3$ kJ and $\Delta H^0_{298} = 230.7$ kJ

(i) Calculate the equilibrium constant K_p at 25°C for this reaction.

(ii) Calculate the equilibrium constant K_p at 125°C.

(iii) Point out if any approximation is made in the calculation in (ii).

(2½,6,4)

7. (a) In its aqueous solutions, the molar mass of sodium chloride is found to be about one-half of its normal value when measured with the help of a colligative property while that of sucrose is found to have its normal value. Explain.

(b) Derive additivity rule for chemical potential.

(c) A 10 m solution of urea is cooled to −14.88°C. What mass of urea will separate out if 100 g of solution is taken ? K_f for water = 1.86 K kg mol^{-1}.

(2½,4,6)

8. (a) While the equilibrium constant K_p of a gaseous reaction is independent of pressure, K_x is not.

(b) Derive relations for $\Delta_{mix}G$ and $\Delta_{mix}S$, for mixing of ideal gases at constant temperature and pressure.

(c) A metal M (atomic mass 96) reacts with fluorine (atomic mass 19) to form a compound MF_x. When 9.18 g sample of the salt was dissolved in 100 g water the boiling point of the solution was 374.38 K. What is the formula of the salt ? K_b = 0.512 K kg mol^{-1} and normal boiling point = 373.15 K for water.

(2½,4,6)

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