M.Sc. Sem I April 2017

Chemistry I

(2½ Hours)

[Total Marks : 60

N.B. :   (1) **All** questions are **compulsory**.
(2) **Figures** to the **right** indicate **full** marks.
(3) Use of **non-programmable calculator is allowed.**

Useful constants :

$c = 2.998 \times 10^8 ms^{-1}$ $R = 8.314 JK^{-1}mol^{-1}$
$h = 6.626 \times 10^{-34} Js$ $N_A = 6.022 \times 10^{23} mol^{-1}$
$e = 1.602 \times 10^{-19} C$ $k = 1.381 \times 10^{-23} Jk^{-1}$
$1J = 6.24 \times 10^{18} eV$ $1\ atm = 1.013 \times 10^5\ Nm^{-2}$
$1eV = 8.06 \times 10^3 cm^{-1}$
Atomic mass of N=14, H=1

1. (a) Attempt **ANY TWO** of the following :-
    i) State the third law of thermodynamics. Show that dU is an exact differential whereas   4
    dq and dw are not.
    ii) Derive an expression to show how entropy varies with temperature at constant pressure.   4
    iii) What is Joule -Thomson effect? Show that the enthalpy of the system remains constant   4
    in an adiabatic expansion.
    iv) Explain the term 'Gibbs free energy'. How does it vary with respect to temperature at   4
    constant pressure?

   (b) Attempt **ANY ONE** of the following :-
    i) Calculate the standard free energy change (ΔG^0) for the following reaction   4

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}I_{2(g)} \rightarrow HI_{(g)}$$
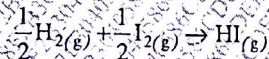
   where S^0 of H_2, I_2 and HI are 130.146 $JK^{-1}mol^{-1}$, 116.622 $JK^{-1}mol^{-1}$ and 206.074 $JK^{-1}mol^{-1}$
   respectively. The standard enthalpy change for the reaction is 25.916 $kJmol^{-1}$

    ii) If Cv for Uranium metal is 3.04 $JK^{-1}mol^{-1}$ at 20K, then calculate the absolute entropy   4
    of the metal at that temperature.

2. (a) Attempt **ANY TWO** of the following:-
    i) Explain the terms 'partial molal volume' and 'partial molal enthalpy'.
    ii) Define fugacity. Give its unit. How is it graphically determined?   4
    iii) Derive Gibbs-Duhem-Margules equation.   4
    iv) Explain with reference to free energy change, the role of ATP in biological systems.   4
                                                                                              4

   (b) Attempt **ANY ONE** of the following:-
    i) Calculate the entropy of mixing when 56g of nitrogen gas, 6g of hydrogen gas and 34g   4
    of ammonia gas are mixed at constant temperature, assuming no chemical reaction
    occurs.
    ii) The partial molal volumes of two liquids P and Q in a mixture in which the mole fraction   4
    of P is 0.3713 are 188.2cm³ and 176.14cm³ respectively. The molar masses of A and
    B are 241.4.gmol⁻¹ and 198.2gmol⁻¹ What is the volume of solution of mass 1.000kg?

[TURN OVER]

3. (a) Attempt **ANY TWO** of the following:-
     i) Derive thermodynamically the Gibbs adsorption isotherm for the adsorption of a solute 4
       on the surface of a liquid.
     ii) Derive thermodynamically the Kelvin equation of the vapour pressure of droplets.   4
     iii) Explain the phase diagram of a two component system of solid-gas involving formation 4
       of hydrates of copper sulphate.
     iv) Draw and discuss the phase diagram of a two component system forming a stable 4
       compound with incongruent melting point.

   (b) Attempt **ANY ONE** of the following :-
     i) Draw and discuss the phase diagram of a three component system consisting of three 4
       pairs of partially miscible lliquids.
     ii) Draw and discuss the phase diagram of double salt decomposed by water with a suitable example. 4

4. (a) Attempt **ANY TWO** of the following:-
     i) Explain the term activity coefficient and the mean ionic activity coefficent. State the 4
       Debye-Huckel's limiting law of mean ionic activity coefficients and explain the terms
       involved.
     ii) Explain the Debye-Falkenhagen effect for the conductance of strong electrolytes.   4
     iii) Discuss in brief the solid oxide fuel cell.   4
     iv) Explain the structure and function of cell membrane.   4

   (b) Attempt **ANY ONE** of the following :-
     i) Calculate the value of the resting membrane potential for the following :-   4

Ion species	Intra cellular concentration (mM)	Extra cellular concentration (mM)
Na^+	150	5
Cl^-	4	120

       given that $\dfrac{2.303RT}{F}$ at 298K = 60.

     ii) Calculate the mean activity coefficient of $ZnCl_2$ in a solution containing 1×10^{-3} m $ZnCl_2$ 4
       and 5×10^{-3} m $ZnSO_4$ solution (A = 0509 for water at 298K).

5. Attempt **ANY FOUR** of the following :-   12
     a) What are exact and inexact differentials? Draw' the Maxwell's thermodynamic square.
     b) Derive the relation

$$\left[\frac{\partial T}{\partial P}\right]_s = \left[\frac{\partial V}{\partial S}\right]_p$$

       from the definition of enthalpy.
     c) Give the physical significance of partial molal free energy.
     d) Obtain an expression for the following thermodynamic excess functions
         i) Excess entropy   ii) Excess enthalpy
     e) What is condensed phase rule? Sketch a labelled phase diagram of ternary system in
       which the hydrate is dehydrated by a second salt.
     f) Draw and discuss the phase diagram of a hydrated double salt decomposed by water.
     g) State the Debye-Huckel-Onsager's equation and explain the terms involved.
     h) What are fuel cells and explain how they play an important role in the space programme.