# M. Sc. Chemistry Examination, 2017

( 1st Semester )

## Physical Chemistry

## Paper - IV

Time : Two hours Full Marks : 50

( 25 marks for each unit )

Use a separate answerscript for each unit.

## UNIT - 1041

1. Answer any ***one*** question :

   a) Define chemical potential. Show that in a system at equilibrium, total change in chemical potential of reactants must be equal to that of products. 1+4

   b) The coefficient of thermal expansion ($\alpha$) of copper at 298K is $5.0 \times 10^{-5} K^{-1}$ and its isothermal compressibility ($\beta$) is $7.85 \times 10^{-7}$ $atm^{-1}$. Given that the density of copper is 8.92 gm $cm^{-3}$ at 298K. Calculate the value of $C_p - C_v$ for copper. 5

2. Answer any ***two*** questions :

   a) i) Considering the relation between activity of solvent in a solution with its freezing point depression, determine the activity coefficient of solute in the solution. 7

ii) Show that partial molar volume of solute in a solution is

$$\bar{V}_2 = \frac{1}{\rho}\left[ M_2 - V\frac{d\rho}{dm} \right]$$

where m moles of solute of molar mass $M_2$ are dissolved in 1000 gms solvent to make the volume of solution V and mass density $\rho$. 3

b) i) State Nerust heat theorem and limitations of 3rd law of thermodynamics. 5

ii) The constant pressure molar heat capacity of oxygen gas from 300 K to 1200 K is given by

$C_P/JK^{-1}mol^{-1} = 25.72 + 12.98 \times 10^{-3}T - 38.62 \times 10^{-7}T^2$.

Calculate the value of $\Delta S$ when one mole of oxygen gas is heated at constant pressure from 300K to 1200K. 3

iii) Find the variation of chemical potential with temperature. 2

c) i) Using the expression for the compressibility factor, Z of a van der Waals gas, Calculate the fugacity of the gas at 50 bar and 298 K.

$$Z = 1 + \left[ b - \left( \frac{a}{RT} \right) \right] \frac{P}{RT}$$



c) Calculate the difference in the values of Gibbs energy of solvation of $Cl^-$ and $I^-$ in water for which dielectric constant = 78.54 at 25°C using Born model, given their radii are 181 pm and 220 pm respectively and unit of charge = $4.802 \times 10^{-10}$ esu. $2\frac{1}{2} \times 2$

and a=1.408 $L^2$ bar $mol^{-1}$ and b=0.03913 L $mol^{-1}$. 5

ii) From Debye Huckel theory calculate the radius of ion atmosphere for a 0.1 mol $L^{-1}$ aqueous solution of KCl at 25°C. The dielectric constant of the aqueous solution is 78 at 25°C. 3

d) Calculate the mean ionic activity coefficient in $10^{-4}$molal $Al_2(SO_4)_3$ solution at 25°C. 2

**UNIT - 1042**

3. Answer ***any two*** questions :

a) i) Why does Born model usually give an overestimate of the ion solvent interaction ?

ii) Distinguish between primary and secondary solvation.

iii) Describe the principle of any method of determination of primary solvation number.

iv) What are the merits and demerits of the method ?

$2\frac{1}{2}+2\frac{1}{2}+3+2$

b) i) Describe qualitatively the role of relaxation and electrophoretic effects on the conductance of ions in solution.





ii) Derive the electrophoretic component of velocity of an ion moving under the action of an electric field.

iii) Describe the variation of transport number of cations in solution of HCl, KCl and LiCl with square root of concentration. Derive the necessary relation to explain. 3+3+4

c) i) Deduce the expression for 'Bjerrum critical distance' for ion pair formation and thereby obtain the condition for ion pair formation.

ii) Give a brief account of Debye Falkenhagen effect on conductance. 5+5

4. Answer ***any two*** questions :

a) Find out the radius of $ClO_4^-$ ion from the following data : $\lambda 0\left(ClO_4^-\right) = 54$mho $cm^2$ / g.equiv. Viscosity co-efficient of water=0.893 cP at 20°C.

b) Association constant of MCl is 200 in acetonitrile $(\epsilon = 40)$ at 25°C. What will be association constant of MCl in aqueous solution $(\epsilon = 80)$ at the same temperature by using Bjerrum equation for ion-pair formation ? Take $\lambda^3 Q(b) = a^3 e^b / b$. Given also $a = 4\,\mathring{A}$ in both the solvents, $e = 4.802 \times 10^{-10}$ esu,

$k = 1.34 \times 10^{-16}$ erg $K^{-1}$ molecule$^{-1}$. .