[This question paper contains 4 printed pages.]

4602 *Your Roll No.* .....

B.Sc. Prog./II **AS**

CH–203 : PHYSICAL CHEMISTRY

Time : 2 Hours *Maximum Marks : 50*

(Write your Roll No. on the top immediately on receipt of this question paper.)

Use of scientific calculators is allowed.

Attempt **Four** *questions in all.*
At least **two** *questions from each section.*

SECTION A

1. (a) Draw the Andrews isotherms of CO_2 gas and explain the phenomenon of continuity of state. (6)

   (b) Define the term critical temperature and derive the expression of van der Waals constants 'a and b' in terms of critical constants P_C, V_C and T_C and gas constant R. (6½)

2. (a) Calculate the temperature at which the rootmean square velocity of N_2 gas will be 1500 ms^{-1}. (3)

   (b) Define the term mean free path. How it can be calculated. What is the effect of pressure on mean free path. (3½)

P.T.O.

(c) How will you determine viscosity of a liquid using Ostwald viscometer. Compare the effect of temperature on coefficient of viscosity of a liquid and a gas. (6)

3. (a) Explain the term partial molar free energy and show that

$$\left(\frac{\partial \mu_i}{\partial \rho}\right)_{T,N} = \overline{V}_i \qquad (4)$$

(b) In a surface tension experiment using stalgmometer equal volumes of liquid gave 58 drops and water 24 drops. The densities of water and liquid is 9968 and 8204 kg m^{-3}, respectively and surface tension of water is 0.072 Nm^{-1}. Calculate the surface tension of liquid. (4)

(c) Draw the three types of boiling point – composition curves of completely miscible binary solutions and explain the term azeotropic mixture. (4½)

4. (a) Derive a relation between depression in freezing point and cryscopic constant using chemical potential concept and prove that

$$\Delta T_f = K_f.m$$

where m is the molality of the solution. (4)

(b) The vapour pressire of a solution containing 2.5×10^{-3} kg of a solute in 80×10^{-3} kg of water at 299 K is 3321 Pa. If the vapour pressure of

water at this temperature is 3361 Pa and the solution is assumed to be very dilute. Calculate the molar mass of solute. (4)

(c) Draw the temperature - composition diagram for phenol-water system and label it. Why it does not show lower consolute temperature. How does impurities influence the CST of this system. (4½)

SECTION B

5. (a) Derive the integrated form of Clausius-Clayperon equation for a liquid-vapour equilibria. (5)

(b) Explain the conductometric curve obtained when a strong acid is titrated against a strong base and compare it with the conductometric titration curve of weak acid and strong base. (4½)

(c) How salt bridge reduces liquid junction potential ? (3)

6. (a) Define the term 'Transport Number' and describe the moving boundary method to determine it. (6½)

(b) Draw the phase diagram of water and label it. (6)

7. (a) Calculate E^0_{cell} and equilibrium constant for the cell reaction

$$2\,Fe^{3+}_{(aq)} + S_n^{2+}{}_{(aq)} = 2\,Fe^{2+}_{(aq)} + S_n^{4+}{}_{(aq)}$$

if $E^0_{Fe^{2+},Fe^{3+}}|Pt = 0.77\,V$ and $E^0_{S_n^{4+},S_n^{2+}}|Pt = 0.15\,V$ (5)

P.T.O.

(b) For the formation of ammonia the equilibrium constant at 673 K is 1.64×10^{-4} and at 773 K it is 1.44×10^{-5}. Calculate the heat of reaction. (4½)

(c) Calculate K_c at 300 K and 1.01×10^5 Pa pressure for the reaction $N_2O_4(g) = 2NO_2(g)$ when $K_p = 0.1825 \times 10^5$ Pa. (3)

8. (a) A silver nitrate solution was electrolysed between platinum electrodes. After passing current concentration fall in anodic compartment was 0.005124 g eq. The mass of copper deposited in the coulometer was found to be 0.03879 g. Calculate the transport number of silver and nitrate ion in $AgNO_3$ (Eg. mass of Cu = 31.8) (3½)

(b) The emf of the cell

$Cd(s) | CdCl_2\,2H_2O$ sat solu $| AgCl(s) | Ag(s)$

at 298 K is 0.6753 V and $\left(\frac{\partial E}{\partial T}\right)_p = -6.5\times10^{-4} V\,K^{-1}$

(a) Write the reaction taking place in the cell.

(b) Calculate ΔG, ΔH and ΔS at 298 K. (6)

(c) Discuss briefly various potentiometric titration curves. (3)