2009

CHEMISTRY

(Major)

Paper : 1.1

(Physical Chemistry)

Time : 3 hours

The figures in the margin indicate full marks for the questions

Candidates ***eligible*** *for Internal Assessment shall answer from PART—I only* (*Marks* : 65)

Candidates ***not eligible*** *for Internal Assessment shall answer both from PART—I and PART—II* (*Marks* : 75)

PART—I

(*Marks* : 65)

1. Answer any *three* of the following : 3×3=9

(a) Assuming ideal behaviour, calculate the density of ammonia gas in g/L at 1 atm and 300 K.

(b) What are the factors on which the speeds of ideal gas molecules depend? Show the difference between mean speed, r.m.s. speed and most probable speed of oxygen molecules at 300 K. Assume ideal behaviour.

(c) State and explain the laws of diffusion. How can you calculate the rate of diffusion of an ideal gas through a small orifice?

(d) Obtain an expression for the collision frequency in a gas mixture consisting of two gases.

(e) When does a real gas behave ideally? Give all the necessary conditions and explain the consequences.

2. Answer any *three* of the following : 3×3=9

(a) Define the internal energy of a system. Explain the sign convention in the equation $\Delta U = q + w$.

(b) Explain what is meant by a state function. Give examples of one state function and one that is not. If a sample of gas is allowed to expand at constant temperature against atmospheric

pressure, state *(i)* does the gas do work on its surroundings; *(ii)* is there heat transfer between the system and the surrounding; *(iii)* what is ΔE for the process?

(c) A non-ideal gas is heated slowly and the gas expands reversibly at a constant pressure of 275 mm from a volume of 385 cm^3 to 875 cm^3. Find the work done in joules.

(d) What state function must remain constant in the Joule-Thomson experiment? For air at temperatures near 298 K and pressures in the range 0 to 50 bar, the Joule-Thomson coefficient is close to 0·2 °C/bar. Estimate the final temperature of air if 58 g of it at 298 K and 50 bar undergoes Joule-Thomson effect to a final pressure of 1 bar.

(e) For each of the following processes, deduce whether each of the quantities q, w, ΔU and ΔH is positive, zero or negative :

(i) Reversible melting of ice at 1 atm and 0 °C

(ii) Reversible adiabatic expansion of an ideal gas

(iii) Adiabatic expansion of an ideal gas into vacuum

3. Answer any *four* of the following : 3×4=12

(a) State how the entropy will change for the following processes *(i)* freezing of ethanol, *(ii)* dissolving glucose in water, *(iii)* evaporation of bromine from a bromine solution at room temperature and *(iv)* cooling nitrogen gas from 373 K to 273 K. What are the characteristics of a spontaneous process?

(b) In the relation $\Delta G = \Delta H - T\Delta S$, state the conditions when ΔG can be positive or negative. Obtain the relation between the equilibrium constant and the standard Gibbs free energy change.

(c) Of the following pairs, which has higher chemical potential?

(i) H_2O (l) at 298 K, 1 atm and H_2O (g) at 298 K, 1 atm

(ii) H_2O (s) at 273 K, 1 atm and H_2O (l) at 273 K, 1 atm

(iii) H_2O (s) at 268 K, 1 atm and supercooled H_2O (l) at 268 K, 1 atm

(iv) Glucose (s) at 298 K, 1 atm and glucose (aq.) at 298 K, 1 atm

Give brief reason in each case.

(Continued)

(d) Give the physical interpretation of the entropy function. State the third law of thermodynamics and its usefulness in obtaining absolute entropies.

(e) Calculate ΔG for the isothermal compression of 30·0 g of water from 1·0 atm to 100·0 atm at 298 K (ignore variations in V with P).

4. Answer any *three* of the following : 3×3=9

(a) Obtain a general formula for measuring the molar mass of non-electrolytes from changes in colligative properties.

(b) What are abnormal colligative properties? Give examples. Find the osmotic pressure of an aqueous glucose solution of concentration 0·010 mol/kg at 298 K and 1 atm.

(c) The vapour pressure of water at 110 °C is 1074·6 mm. Find the vapour pressure at the same temperature for a 2·00 wt% sucrose solution in water. State any approximation you have to make.

(d) How can you distinguish a 'real' solution from an 'ideal' solution?

(e) Discuss qualitatively the differences between the structure of ice and liquid water. What are the significances of these differences?

5. Answer any *four* of the following : 3×4=12

(a) Distinguish between order and molecularity of a reaction. Deduce the integrated rate expression for a second-order reaction.

(b) For a homogeneous reaction $aA + bB + cC + ... = eE + fF + ...$, obtain the complete rate expression. Show that the rate is an intensive property that depends on T, p and concentration.

(c) Show, indicating the principle involved, how an expression for the concentration of the final product can be obtained for a consecutive reaction of the type $A \rightarrow B \rightarrow C$. How do the concentrations of A, B and C change with time?

(d) For the reaction, $2HI = H_2 + I_2$, the rate coefficient is $1 \cdot 2 \times 10^{-3}$ and $3 \cdot 0 \times 10^{-5}$ $dm^3\ mol^{-1}\ s^{-1}$ at 700 K and 629 K respectively. Estimate the activation energy and the pre-exponential factor for the reaction.

(e) Discuss the kinetics of H_2-Br_2 chain reaction.

(f) Describe enzyme catalysis. Discuss the application of Michaelis-Menten equation.

6. Answer any *three* of the following : 3×3=9

(a) How does molar conductivity depend on the mobilities of ions? What is the reason behind hydrogen ions having highest mobility?

(b) What are the factors that determine the e.m.f. of a galvanic cell? Predict whether the following reaction would proceed spontaneously at 298 K :

$$Co(s) + Fe^{2+}(aq.) \rightarrow Co^{2+}(aq.) + Fe(s)$$

Given that $[Co^{2+}] = 0{\cdot}15$ m and $[Fe^{2+}] = 0{\cdot}68$ m, $E^{\circ}_{Fe^{2+}/Fe} = -0{\cdot}44$ V and $E^{\circ}_{Co^{2+}/Co} = -0{\cdot}28$ V.

(c) What do you mean by 'liquid junction potential'? Show how this potential can be eliminated in a cell.

(d) How many different types of electrodes exist? Describe the working of any standard electrode.

(e) Write short notes on :

(i) Corrosion and its prevention

(ii) Applications of Debye-Hückel-Onsager equation

7. Answer either *(a)* or *(b)* : 5

(a) Define pK of acids and bases. How can you arrange a number of acids in respect of their pK values? Give examples.

(b) Discuss the construction and working of the calomel electrode. Use a diagram.

PART—II

(*Marks* : 10)

(In lieu of Internal Assessment)

8. Answer any *two* of the following : 5×2=10

(a) Obtain the expression for the work done in adiabatic expansion and isothermal expansion.

(b) Describe how the refractive index of liquids can be determined.

(c) Write a short note on synthetic zeolites and their utilization.

★★★