2011

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 only one part each from Question Nos.* **1** *and* **2** *along with the rest of the questions* (*Marks* : 65)

Candidates ***not eligible*** *for Internal Assessment shall answer only two parts each from Question Nos.* **1** *and* **2** *along with the rest of the questions* (*Marks* : 75)

1. *(a)* Why was van der Waals' equation of state necessary? Describe the corrections introduced for 'pressure' and 'volume' of an ideal gas. 5

(b) Define mean, r.m.s. and most probable speed of the molecules of an ideal gas and arrange them in order of

magnitude. Verify your results with respect to any ideal gas chosen by you at ambient temperature. 5

(c) How do molecular collisions alter the physical properties of a gas? Draw a diagram to explain the collision cross-section of an ideal gas. How does the mean free path of ideal gas molecules change with temperature and pressure? 5

(d) When an ideal gas flows through a long tube, show how the velocity of each layer of gas varies in a direction perpendicular to the direction of flow. What is drift velocity and how is it affected? 5

2. (a) Discuss the basis of the equation $\Delta E = q + w$ and explain the sign convention. In reversible melting of ice at 1 atm and 0 °C, find out whether q, w, ΔU and ΔH will be positive, zero or negative. 5

(b) Give examples to explain the concepts of closed, isolated and open thermodynamic systems. Find an expression for the work done in reversible expansion of a gas in a closed system. 5

(c) What do you mean by a state function? Give examples. For air at temperatures near 298 K and pressures in the range 0 to 50 bar, the Joule-Thomson coefficient is close to $0 \cdot 2$ °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. 5

(d) Discuss how you can determine the heat of reaction. The combustion of ethanol in a constant volume calorimeter produces $1364 \cdot 34$ kJ mol^{-1} at 25 °C. Find $\Delta H°$ for the reaction

$$C_2H_5OH\ (l) + 3O_2\ (g) = 2CO_2\ (g) + 3H_2O\ (l)$$ 5

3. Answer any *three* of the following : 5×3=15

(a) Show how the Clausius inequality could be described as the mathematical statement of the second law of thermodynamics. Explain that for an infinitesimal irreversible process, the entropy change is greater than the differential of the heat divided by the temperature.

(b) Explain why molar entropy of a vapour is greater than that of the liquid with which it is in equilibrium. Oxygen gas is heated from 300 K to 500 K. What is the increase in molar entropy?

(c) Discuss the differences in the change in entropy for a system and its surroundings for *(i)* a reversible process and *(ii)* an irreversible process.

(d) A change can take place spontaneously at constant temperature, pressure and amounts of species if the Gibbs energy decreases. Elucidate.

(e) Obtain Gibbs-Duhem equation and show that the intensive variables of a system are not independent.

(f) Toluene is vapourized at its boiling point (111 °C). The heat of vaporization at this temperature is 361·9 J/g. Calculate the changes in molar enthalpy, entropy and Gibbs energy.

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

(a) Some properties of ideal solutions are grouped together as colligative properties. What are these properties and why are they colligative? Discuss at least one colligative property to bring out the differences between an ideal solution and a real solution.

(b) State and explain Raoult's law and Henry's law. When are these laws applicable to non-ideal solutions?

(c) Calculate the osmotic pressure of a 1 mol L^{-1} sucrose solution in water if the vapour pressure of the solution is 4·1606 kPa at 30 °C, the vapour pressure and the density of water at the same temperature are 4·2429 kPa and 0·99564 g cm^{-3} respectively.

(d) Define 'activity' and 'activity coefficients'. State how these quantities depend on *(i)* concentration, *(ii)* temperature and *(iii)* pressure.

5. Answer any *three* of the following : 5×3=15

(a) The reaction, $H_2 + Br_2 = 2HBr$ is carried out in a 0·250 L reaction vessel. The change in amount of Br_2 in 0·01 s is −0·001 mol. Find *(i)* the rate of conversion, *(ii)* the rate of reaction and *(iii)* the values of $d[Br_2]/dt$, $d[H_2]/dt$ and $d[HBr]/dt$.

(b) Under what conditions, a reaction is zero order? Give a few examples.

(c) For a reversible first-order reaction, show how the concentrations of the reactant and the product will change with time. Draw a diagram when the rates of the forward and the backward reactions are respectively 3 s^{-1} and 1 s^{-1}.

(d) Describe a consecutive first-order reaction and show how the expressions for concentrations of the reactants can be obtained. For the reaction, $A_1 \rightarrow A_2 \rightarrow A_3$, draw plots of concentrations of reactants with time.

(e) How does the reaction rate depend on temperature? Show how Arrhenius plot of a reaction can be obtained. What is the significance of the pre-exponential factor?

(f) Discuss the kinetics of enzyme-catalyzed reactions with reference to Michaelis-Menten equation. What do you mean by turnover number?

6. Answer any *three* of the following : 5×3=15

(a) The mobility of an ion can be defined as its drift velocity in the direction of the applied electric field. Explain. Why do the protons have the highest mobility?

(b) Draw a plot to show how the molar conductivity of a strong electrolyte solution changes with concentration. Discuss the significance of the results. State why the molar conductivity becomes largest at infinite dilution.

(c) Obtain the Henderson-Hasselbalch equation for the dissociation of a weak acid. Show, with a diagram, how the pH of a dilute aqueous solution of acetic acid varies when titrated with a concentrated aqueous solution of sodium hydroxide.

(d) Give an expression for the ionic strength of an electrolyte solution. Calculate the ionic strength of 0·01 molar solutions of NaCl, $Zn(NO_3)_2$ and $Al(NO_3)_3$.

(e) Write short notes on :

(i) Corrosion and its prevention

(ii) Calomel electrode

(iii) Buffer solution

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