2019

CHEMISTRY

(Honours)

Paper : CHE-HC-1026

(Physical Chemistry—I)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following as directed : 1×7=7

(a) From kinetic gas equation, show that PV = constant for an ideal gas at constant temperature.

(b) A gas can be liquefied, when

(i) $T > T_c$; $P = P_c$

(ii) $T < T_c$; $P < P_c$

(iii) $T < T_c$; $P > P_c$

(iv) $T = T_c$; $P < P_c$

(Choose the correct option)

(c) Define vapour pressure of a liquid.

(d) In a cubic crystal, there are _____ C_4 axes of symmetry, _____ C_3 axes of symmetry and six C_2 axes of symmetry.

(Fill in the blanks)

(e) Explain why non-stoichiometric form of NaCl is yellow in colour.

(f) Explain why pH of 1×10^{-8} mol dm^{-3} hydrochloric acid solution is not 8.

(g) An aqueous solution of Na_2CO_3 is basic. Explain.

2. Answer the following questions : 2×4=8

(a) Define mean free path of a gas. How does mean free path of a gas vary with temperature and pressure?

(b) Give a qualitative idea about the structure of water.

(c) State the symmetry elements present in the following molecules :

H_2O; C_6H_6

(d) The pH value of a solution containing equimolar concentrations of a weak acid and its salt is 5·0. Calculate the K_a value of the weak acid.

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

(a) Derive the van der Waals' equation for a gas. Explain why van der Waals' equation cannot be considered as a generalized equation of state for real gases.

(b) What is critical state of a gas? Derive the expressions for critical constants in terms of the van der Waals' constants.

(c) Derive the Bragg's equation. In an experiment on a crystal using X-rays of wavelength 10^{-10} m, the value of angle of incidence for the first-order reflection was found to be 30°. Calculate the interplanar distance of the crystal.

(d) For a weak monobasic acid, show that the degree of ionization at a given temperature is inversely proportional to the square root of the initial concentration of the acid. Give the expressions for dissociation constants of carbonic acid.

(e) Define solubility product of a sparingly soluble salt solution. Give the conditions for precipitation in terms of solubility product. 50 mL of $0{\cdot}01$ mol dm^{-3} $AgNO_3$ solution is mixed with 50 mL of $0{\cdot}001$ mol dm^{-3} aqueous NaCl solution. Predict whether AgCl will be precipitated or not. Given $K_{sp}(AgCl) = 1{\cdot}7 \times 10^{-10}$.

4. (a) Answer *either* [*(i)* and *(ii)*] *or* [*(iii)*, *(iv)* and *(v)*] :

(i) Give the postulates of kinetic molecular model of a gas. On the basis of these postulates, derive the kinetic gas equation. 3+4=7

(ii) Two flasks *A* and *B* have equal volumes. Flask *A* contain H_2 gas at 300 K, while flask *B* contains equal mass of C_2H_6 gas at 900 K. If both the gases behave ideally, answer the following : 3

In which flask the molecules will have higher average speed and how many times than the average speed of the other?

(iii) Derive an expression for root-mean-square speed of gas molecules from the expression for Maxwell distribution of molecular speeds of the gas. 3

(iv) Show that root-mean-square speed of hydrogen gas is four times that of oxygen gas at the same temperature. 3

(v) Derive an expression for reduced equation of state for any substance. State the law of corresponding states. 3+1=4

(b) Answer *either* [*(i), (ii)* and *(iii)*] *or* [*(iv), (v)* and *(vi)*] :

(i) How does viscosity of gas differ from that of liquid? 2

(ii) Describe a method with theory commonly used for the measurement of viscosity of a liquid. 4

(iii) What are liquid crystals? Give the structural difference between smectic and nematic liquid crystals. Give two applications of liquid crystals. 1+2+1=4

(iv) Define the terms—symmetry element, plane of symmetry and centre of symmetry. 3

(v) What are Bravais lattices? How can the following crystal systems be characterized?

Cubic; orthorhombic

Give one example each of these two crystal systems. 4

(vi) What are Schottky and Frenkel defects? Give example of each of these two defects. 3

(c) Answer *either* [*(i), (ii)* and *(iii)*] *or* [*(iv), (v)* and *(vi)*] :

(i) Define pH of a solution. Give the limitations of pH scale. Calculate pH of a solution obtained by mixing 50 mL 0·1 mol dm^{-3} HCl solution with 50 mL 0·2 mol dm^{-3} NaOH solution at 298 K. 1+1+3=5

(ii) Discuss briefly about the following : 2

Applications of buffers in qualitative analysis of salt sample.

(iii) Obtain an expression for hydrolysis constant for the hydrolysis of CH_3COONH_4 salt. 3

(iv) What are acid-base indicators? Give examples. Discuss briefly the Ostwald's theory of acid-base indicators. 1+1+3=5

(v) State with reasons, what indicators you would choose for the following titrations : 3

$NaOH$ vs. CH_3COOH;

Na_2CO_3 vs. HCl

(vi) Calculate the solubility of $Mg(OH)_2$ in pure water at 298 K. Given K_{sp} for $Mg(OH)_2$ at 298 K is $1{\cdot}20\times10^{-11}$. 2

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