[This question paper contains 5 printed pages.]

1247 *Your Roll No. .....*

B.Sc. (Hons.)/I **A**

CHEMISTRY – Paper III

(Physical Chemistry – I)

Time : 3 Hours *Maximum Marks : 38*

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

Attempt **six** *questions in all, selecting at least* **two** *questions from each Section. Question No.* **1** *is compulsory.*

Use of scientific calculator is allowed but can't be exchanged among themselves.

($R = 8{\cdot}314\ JK^{-1}\ mol^{-1}$; $N = 6{\cdot}022 \times 10^{23}\ mol^{-1}$, $k = 1{\cdot}38 \times 10^{-23}\ JK^{-1}$)

1. Explain briefly giving reasons (any **four**) :

   (a) X-ray diffraction pattern for solids show relatively sharper peaks as compared to those for liquids.

   (b) The amount of work done, when one mole of an ideal gas contained in a bulb of 10 L capacity at 1 atm, is allowed to enter an evacuated bulb of 100 L capacity, is zero.

P.T.O.

(c) Trouton's rule.

(d) p-dichlorobenzene has zero dipole moment whereas the o- and m- isomers have non-zero dipole moments.

(e) Viscosity of gases increases whereas that of liquids decreases on increasing the temperature.

(f) The speed distribution of $O_2(g)$ at T Kelvin is the same as that of $SO_2(g)$ at 2T Kelvin.

(g) The deviations from ideal gas behaviour are most pronounced at low temperature and high pressure.

(2×4=8)

SECTION – A

2. (a) Explain the factors which led van der Waals to modify the ideal gas equation $pV = nRT$, and hence derive the van der Waals equation of state. (3)

(b) What are the units of van der Waals constants a and b ? Do they have the same value for all real gases ? (2)

(c) What is the law of corresponding states ? (1)

3. (a) What is capillary action ? Derive the formula

$$r = \frac{1}{2} h \rho g r \qquad (3)$$

(b) A steel ball of density 7.9 $g\,cm^{-3}$ and 4 mm diameter takes 55 seconds to fall through a distance of one metre through a liquid of density 1.10 $g\,cm^{-3}$. Calculate the viscosity of the liquid. (2)

(c) How will the addition of ethanol change the surface tension of water ? (1)

4. (a) Calculate the energy per mole of SO_2 gas at 300 K as predicted by law of equipartition of energy. (2)

(b) Show that the height at which the atmosphere pressure is reduced to one half of its value(p), is given by

$$x = \frac{0.6909\ RT}{Mg} \qquad (2)$$

(c) The mean free path of a gas at 300 K is 2.6×10^{-5} m. The collision diameter of the molecule is 0.26 nm. Calculate

(i) pressure of the gas

(ii) number of molecules per unit volume of the gas (2)

5. (a) Calculate the ratio of root mean square speed, average and most probable speeds. (2)

(b) Show that formation and maintenance of smaller bubbles will need a greater excess pressure than the larger ones. (2)

(c) Calculate the molar heat of vaporisation for a liquid with vapour pressure of 135 MPa and 542 MPa at 30°C and 70°C respectively. (2)

SECTION – B

6. (a) For isothermal reversible expansion of a van der Waals gas, show that work done is given by :

$$W = -nRT \ell n \frac{V_2 - nb}{V_1 - nb} - an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right) \quad (3)$$

(b) Enthalpy of neutralization of HCl by NaOH is -57.32 kJ mol^{-1} and by NH_4OH is -51.34 kJ mol^{-1}. Calculate the enthalpy of dissociation of NH_4OH. Writing the relevant equations. (3)

7. (a) State and explain the third law of thermodynamics. How is it useful in calculating the absolute entropy of a substance ? (2)

(b) Define differential enthalpy of solution. How is this different from integral enthalpy of solution ? (2)

(c) Show that for an ideal gas undergoing isothermal reversible expansion

$$\Delta G = \Delta A \quad (2)$$

8. (a) Starting with the definitions of $C_{p,m}$ and $C_{v,m}$, derive the relation between them for n moles of an ideal gas. (3)

(b) Discuss the temperature dependence of Gibbs Energy (G) and show that

$$\left[\frac{\partial(\Delta G/T)}{\partial(1/T)}\right]_P = \Delta H \qquad (3)$$

9. (a) What are intensive and extensive variables ? Pressure is an intensive property then why do we add partial pressures in Dalton's law of partial pressures ? (3)

(b) What is Hess's law of constant heat summation ? Is it possible to apply this law to other thermodynamic functions ? Explain. (2)

(c) What is adiabatic flame temperature ? (1)