13.12.18 (M)

This question paper contains **4+2** printed pages]

Roll No. | | | | | | | | | | | |

S. No. of Question Paper : **40**

Unique Paper Code : **32171102** **I**

Name of the Paper : **Physical Chemistry–I**

Name of the Course : **B.Sc. (Hons.) Chemistry**

Semester : **I**

Duration : **3 Hours** Maximum Marks : **75**

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

Attempt *six* questions in all.

Question No. **1** is compulsory.

Use of scientific calculator and log tables is allowed.

Physical constants : $R = 8.314\ JK^{-1}\ mol^{-1}$, $N_A = 6.023 \times 10^{23}\ mol^{-1}$, $k = 1.38 \times 10^{-23}\ JK^{-1}$.

1. Attempt any *five* of the following : 5×3=15

Explain why :

(*a*) The end-centred bravais lattice is not possible for a cubic unit cell ?

P.T.O.

(*b*) The pH of water is *not* 7.0 at 60°C ? Will it remain neutral at this temperature ?

(*c*) Irrespective of their nature, drops of all the liquids falling freely in air are spherical in shape ?

(*d*) Addition of KNO_3 increases the surface tension of water but addition of detergent decreases it ?

(*e*) CO and N_2 have the same speed distribution at the same temperature ?

(*f*) The viscosity of gas increases with temperature but that of liquid decreases with temperature ?

(*g*) The initial slope of the graph of compressibility factor, Z *versus* the pressure, *p*, at constant temperature is positive for some gases and negative for others ?

2. (*a*) Write the mathematical expression for the Maxwell distribution of molecular speeds of a gas, explain briefly the terms involved. How does the change in temperature influence the distribution of molecular speeds ? 4

(*b*) Calculate the temperature at which average velocity of SO_2 equals to that of O_2 at 20 K. 4

(*c*) Derive the relations using van der Waals gas equation : $P_c = a/27b^2$ and $T_c = 8a/27Rb$. 4

3. (*a*) Explain the terms σ, λ, Z_1 and Z_{11}. Discuss the effect of temperature and pressure on these terms. 5

(*b*) Calculate λ, Z_1 and Z_{11} for oxygen at 298 K and 10^{-3} mmHg. Given $\sigma = 3.61 \times 10^{-8}$ cm. 4

(*c*) Write a note on continuity of state. 3

4. (*a*) Starting from the postulates of the kinetic theory of gases, derive the kinetic gas equation. 5

(*b*) Calculate the pressure exerted by 3.023×10^{23} molecules of CH_4 in 0.5 dm^3 at 298 K using van der Waals equation. (Given : $a = 2.253$ L^2 atm mol^{-2}, $b = 0.0428$ L mol^{-1} and R = 0.0821 L atm mol^{-1} K^{-1}). 4

(*c*) What are the units of van der Waals constants *a* and *b* ? Do these constants depend upon temperature of the gas ? 3

5. (*a*) Define the surface tension of liquid. Describe drop number method for the determination of surface tension of a liquid. 4

(*b*) With the given viscometer, the times of flow at 20°C for water and an unknown liquid ($d = 1.22$ g cm^{-3}) were found to be 155 sec and 80 sec respectively. Calculate the absolute viscosity of the unknown liquid at 20°C if viscosity and density of water are 1.005 centipoise and 1 g cm^{-3} respectively. 4

(*c*) What is capillary action ? Derive : $\gamma = \pm \frac{1}{2} h\rho g r$, where the symbols have their usual meanings. 4

6. (*a*) What are the differences between crystalline and amorphous solids ? 4

(*b*) When a certain crystal was studied by the Bragg's method using X-rays of wavelength 229 pm, first order X-ray reflection was observed at an angle of 23°20' :

(*i*) What is corresponding inter-planar spacing ?

(*ii*) When another X-ray source was used, a reflection was observed at 15°26' ? What was the wavelength of these X-rays ? 4

(*c*) Give the Miller indices of the plane which intercepts the three crystallographic axes at the multiple of unit distance at :

(*i*) 3/2, 2, 1

(*ii*) 1/2, 2/3, ∞. 4

7. (*a*) Show that the concentration of H_3O^+ in an aqueous solution of an acid HA can be computed from the expression :

$$K_a = \frac{\left[H_3O^+\right]^3 - \left[H_3O^+\right] K_w}{\left[H_3O^+\right]\left[HA\right]_0 - \left[H_3O^+\right]^2 + K_w}.$$

Under what conditions can the following expressions be used :

(*i*) $K_a = \dfrac{\left[H_3O^+\right]^2}{\left[HA\right]_0 - \left[H_3O^+\right]}$

(*ii*) $K_a = \dfrac{\left[H_3O^+\right]^2}{\left[HA\right]_0}$. 5

(*b*) What is the pH of a solution containing 10^{-8} M hydronium ion and compare it with the pH value of 10^{-8} M HCl solution ? 4

(c) What is pH of a solution obtained by mixing 50 mL, 0.1 M CH_3COOH and 50 mL, 0.1 M NaOH. Given $pK_a (CH_3COOH) = 4.74$. 3

8. (a) Show that the pH of an aqueous solution of salt formed from a weak acid and strong base is given by $pH = 7 + \frac{1}{2}(pK_a + \log c)$. 4

(b) Define different types of buffer solutions. Derive Henderson-Hasselbalch equation for pH of acidic and basic buffer. 4

(c) What is the solubility of $Ag_2(CrO_4)$ in water if the value of solubility product is $K_{sp} = 1.3 \times 10^{-11}$ M^3 ? 4

9. (a) What is an indicator and how does it work ? 3

(b) Define solubility and solubility product. Determine solubility of $Mg(OH)_2$ in pure water and 0.01 M NaOH solution. K_{sp} of $Mg(OH)_2 = 1.2 \times 10^{-11}$ M^3. 5

(c) Will a precipitate form if 20 cm^3 of 0.01 M $AgNO_3$ and 20 cm^3 of 0.0004 M NaCl are mixed ? Given K_{sp} of AgCl $= 1.7 \times 10^{-10}$ M^2. 4