2018

CHEMISTRY

(Major)

Paper : 6.2

(Physical Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following in brief : 1×7=7

(a) The ionic radii of Cs^+ and Cl^- ions are 1·69 Å and 1·81 Å respectively. Predict the coordination number of Cs^+.

(b) Yttrium barium copper oxide superconductor is often referred to as the 123 superconductor. Why?

(c) Arrange the following in increasing order of their effectiveness in coagulating ferric hydroxide sol :

Na_2SO_4, KCl, $K_3[Fe(CN)_6]$

(d) When a freshly prepared precipitate of $Fe(OH)_3$ is treated with water and a small amount of $FeCl_3$ solution, $Fe(OH)_3$ is converted to colloidal solution. What is the role of $FeCl_3$ in this process?

(e) Why should one always use purest monomer in free-radical polymerization?

(f) What do you mean by dominant configuration?

(g) The weight average and number average molecular weight of a polymer is 60000 kg mol^{-1} and 40000 kg mol^{-1} respectively. What will be the poly-dispersity index of the polymer?

2. Answer the following : 2×4=8

(a) Lithium borohydride, $LiBH_4$ crystallizes in an orthorhombic system with 4 molecules per unit cell. The unit cell dimensions are $a = 6{\cdot}81$ Å, $b = 4{\cdot}43$ Å and $c = 7{\cdot}17$ Å. If its molar mass is $21{\cdot}76$ g mol^{-1}, calculate the density of the crystal.

(b) Give the physical significance of molecular partition function.

(c) Explain the difference between accuracy and precision with examples.

(d) 100 ml of a colloidal solution is completely precipitated by addition of 5 ml of 1 *M* NaCl solution. Calculate the coagulation value of NaCl.

3. (a) How does electrical conductivity of a metal and a semiconductor vary with temperature? What do you mean by *n*-type and *p*-type semiconductors? Explain with appropriate diagram and example. 1+4=5

Or

What are Schottky and Frenkel defects? Derive an expression for the number of Schottky defects in a crystal. 2+3=5

(b) Deduce an expression for the entropy of monoatomic perfect gas in terms of partition function. 5

Or

Derive an expression for rotational partition function. The rotational constant of gaseous HCl, determined from microwave spectroscopy is $10{\cdot}59\ cm^{-1}$. Calculate the rotational partition function of HCl at 100 K. 3+2=5

(c) Distinguish between repeatable and reproducible results. Analyzing of a sample of iron ore gave the following percentage values for the iron content :

7·08, 7·21, 7·12, 7·09, 7·16, 7·14, 7·07, 7·14, 7·18, 7·11

Calculate the mean, standard deviation and coefficient of variations for the values. 1+4=5

4. Answer *either (a), (b)* and *(c) or (d), (e)* and *(f)* :

(a) A reflection from the (111) planes of a cubic crystal was observed at a glancing angle of 11·2° when CuK_α X-rays of wavelength 154 pm were used. What is the length of the side of the unit cell? 3

(b) Show that for an atom to occupy a tatrahedral void, its radius must be 0·225 times the radius of the sphere. 4

(c) Non-stoichiometric cuprous oxide, Cu_2O can be prepared in laboratory. In this oxide, copper to oxygen ratio is slightly less than 2 : 1. How will you account for the fact that this substance is a *p*-type semiconductor on the basis of the above stated information? 3

(d) What is radius-ratio? How does radius-ratio help in determining the structure of ionic solids and coordination number of ions? Explain. 1+3=4

(e) Why does zinc oxide exhibit enhanced electrical conductivity on heating? 2

(f) Explain the following terms with examples : 2×2=4

(i) Ferrimagnetism

(ii) Piezoelectricity

5. Answer *either (a), (b)* and *(c) or (d), (e)* and *(f)* :

(a) Discuss the osmotic pressure method for determination of molar mass of polymers. Why does this method give number average molar mass only? 4+1=5

(b) The intrinsic viscosity of myosin is 217 $cm^3 g^{-1}$. Calculate the appropriate concentration of myosin in water if it has a relative viscosity of 1·5. 3

(c) What are lyophilic and lyophobic sols? Give one example of each. 1+1=2

(d) Discuss the kinetics of condensation polymerization. Give an example of a polymer produced by this method. 3+1=4

(e) In a polymer sample, 30% molecules have a molar mass 20000, 40% have molar mass 60000 and the rest have 30000. Calculate weight average and number average molar mass of the polymer. 3

(f) Account for the origin of charge on colloidal particles in detail. 3

6. Answer *either (a)* and *(b) or (c)* and *(d)* :

(a) Derive the Boltzmann distribution law. Give its physical significance. 5+1=6

(b) Distribute three energy quanta among three particles. Calculate the probability of each distribution. 4

(c) Using the concept of partition function, deduce an expression for the internal energy of a monoatomic perfect gas.

Hence find an expression for the heat capacity at constant volume. Graphically show how heat capacity of diatomic molecules varies with temperature. 3+2+1=6

(d) For a diatomic molecule vibrating as a simple harmonic oscillator, obtain an expression for vibrational partition function. 4

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