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CHEMISTRY

( Major )

Paper : 6.2

( Physical Chemistry )

Full Marks : 60

Time : 3 hours

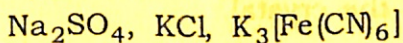
*The figures in the margin indicate full marks  
for the questions*

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

(a) The ionic radii of  $\text{Cs}^+$  and  $\text{Cl}^-$  ions are 1.69 Å and 1.81 Å respectively. Predict the coordination number of  $\text{Cs}^+$ .

(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 :



- (d) When a freshly prepared precipitate of  $\text{Fe}(\text{OH})_3$  is treated with water and a small amount of  $\text{FeCl}_3$  solution,  $\text{Fe}(\text{OH})_3$  is converted to colloidal solution. What is the role of  $\text{FeCl}_3$  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  $60000 \text{ kg mol}^{-1}$  and  $40000 \text{ kg mol}^{-1}$  respectively. What will be the polydispersity index of the polymer?

2. Answer the following :

2×4=8

- (a) Lithium borohydride,  $\text{LiBH}_4$  crystallizes in an orthorhombic system with 4 molecules per unit cell. The unit cell dimensions are  $a=6.81 \text{ \AA}$ ,  $b=4.43 \text{ \AA}$  and  $c=7.17 \text{ \AA}$ . If its molar mass is  $21.76 \text{ g mol}^{-1}$ , 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  $10.59 \text{ cm}^{-1}$ . 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  $11.2^\circ$  when  $\text{CuK}_\alpha$  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 tetrahedral void, its radius must be 0.225 times the radius of the sphere.  $4$

- (c) Non-stoichiometric cuprous oxide,  $\text{Cu}_2\text{O}$  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 :  $2 \times 2 = 4$
- (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  $217 \text{ cm}^3 \text{ g}^{-1}$ . Calculate the appropriate concentration of myosin in water if it has a relative viscosity of 1.5.  $3$

( 6 )

- (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.

( 7 )

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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