2019

CHEMISTRY

(Honours)

Paper : CHE-HC-1016

(Inorganic Chemistry—I)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Choose the correct answer from the following : 1×7=7

(a) Maximum number of electron possible in *N* shell of an atom of an element is

(i) 18 *(ii)* 8

(iii) 28 *(iv)* 32

(b) Physically meaningful quantity is given by

(i) only ψ

(ii) only ψ^2

(iii) both ψ and ψ^2

(iv) none of ψ and ψ^2

(c) In the long form of modern periodic table, element 49 has the position at

(i) group 12 of 4th period

(ii) group 13 of 5th period

(iii) group 13 of 4th period

(iv) group 15 of 4th period

(d) The radii of Mg^{2+} and O^{2-} ions are 0·66 Å and 1·40 Å, and that of B^{3+} and O^{2-} ions are 0·23 Å and 1·40 Å respectively. The crystals formed by MgO and B_2O_3 have shapes respectively

(i) octahedral and trigonal planar

(ii) tetrahedral and octahedral

(iii) octahedral and cubic

(iv) trigonal planar and octahedral

(e) The van der Waals' forces active in solid I_2 are

(i) ion-dipole forces

(ii) dipole-dipole interactions

(iii) induced dipole interactions

(iv) zero

(f) The half-cell reaction of two redox systems are as follows :

$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$, $E^\circ_{el} = +0{\cdot}92$

$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$, $E^\circ_{el} = +0{\cdot}15$

If the two half cells are linked to give a cell, then

(i) Hg_2^{2+} will be oxidized and Sn^{4+} will be reduced

(ii) Hg^{2+} will be reduced and Sn^{2+} will be oxidized

(iii) both Hg^{2+} and Sn^{2+} will be oxidized

(iv) both Hg^{2+} and Sn^{2+} will be reduced

(g) When you prepare $KMnO_4$ and $H_2C_2O_4 \cdot 2H_2O$ solution by transferring a measured amount of these from chemical balance, then it is necessary to standardize

(i) both $KMnO_4$ and $H_2C_2O_4 \cdot 2H_2O$ solution

(ii) only $H_2C_2O_4 \cdot 2H_2O$ solution, but not $KMnO_4$

(iii) only $KMnO_4$, but not $H_2C_2O_4 \cdot 2H_2O$ solution

(iv) none of $KMnO_4$ and $H_2C_2O_4 \cdot 2H_2O$ solution

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

(a) Deduce de Broglie equation of wave-particle duality.

(b) Write Born-Landé equation with meaning of all the terms involved. From this equation, predict which of CaO and $Al_2(SO_4)_3$ has higher lattice energy.

(c) Define the terms 'bond moment' and 'dipole moment'. Taking an example, explain that bond moment in a molecule does not lead to a non-zero dipole moment in the molecule.

(d) Isolate the equation in acidic medium $MnO_4^- + I^- \rightarrow I_2 + Mn^{2+}$ into oxidized half reaction and reduced half reaction and balance the two parts separately and write down the overall balanced reaction.

3. Answer the following questions : 5×3=15

(a) Find an expression for energy of hydrogen atom. Write the Schrödinger's wave equation for the electron in hydrogen atom. 4+1=5

Or

Draw the proper diagram of *p*-orbitals and *d*-orbitals of an atom. Write the values of all the quantum numbers for an atom when $n = 3$. 3+2=5

(b) Define electronegativity and deduce the expression for Pauling electronegativity scale. Calculate the electronegativity of carbon atom following Allred-Rochow's approach. (Covalent radius of carbon atom is 0·77 Å) 1+2+2=5

(c) Discuss Heitler-London approach of valence bond theory. 5

Or

(i) What is solvation energy? Discuss the mechanism of dissolution of an ionic solute in a polar solvent. 3

(ii) Calculate the formal charge of P and H in PH_3. 2

4. Answer the following questions (any *three*) : 10×3=30

(a) *(i)* What are the factors that affect ionization energy? Discuss its periodic trend. Why does successive ionization enthalpy of atom of an element increase immensely? 1+2+2=5

(ii) State Slater's rule. Calculate the effective nuclear charge at the periphery of chromium atom. 3+2=5

(b) (i) Draw Lewis dot picture for NO and CO_3^{2-}. 2

(ii) Give a neat molecular orbital diagram of N_2. Identify HOMO and LUMO in this diagram. Is it possible to obtain an N_2^+ molecular ion? Justify it. 3+1+1=5

(iii) What is non-bonding molecular orbital? Explain it with appropriate example. 1+2=3

(c) (i) Explain the terms 'radial' and 'angular' wave functions for hydrogen atom. Draw radial probability distribution curve for hydrogen atom when $n = 2$. 3+2=5

(ii) What are the two basic postulates of VSEPR theory? Is it possible to give suitable explanation for the shape of PCl_3F_2 molecule by VSEPR theory? Elaborate your answer. 2+3=5

(d) (i) State and explain Hund's rule of maximum multiplicity. 2

(ii) How does electronegativity change in sp, sp^2 and sp^3 hybridization? 2

(iii) Apply molecular orbital theory to CO molecule. 3

(iv) Describe the theory involved in estimation of Fe^{2+} ion in a given solution of unknown strength. 3

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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 0·01 mol dm^{-3} $AgNO_3$ solution is mixed with 50 mL of 0·001 mol dm^{-3} aqueous NaCl solution. Predict whether AgCl will be precipitated or not. Given $K_{sp}(AgCl) = 1·7 \times 10^{-10}$.

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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