KNT/KW/16/5143

Bachelor of Science (B.Sc.) Semester—IV (C.B.S.) Examination

CHEMISTRY (Physical Chemistry)

Paper—II

Time : Three Hours] [Maximum Marks : 50

N.B. :— (1) All **FIVE** questions are compulsory and carry equal marks.

(2) Give diagrams and chemical equations wherever necessary.

1. (A) Derive an expression for entropy change of an ideal gas when it expands reversibly and isothermally.

Calculate the entropy change when 2 moles of an ideal gas is allowed to expand at 300 K from a pressure of 10 atm to 2 atm. 5

(B) Derive Van't-Hoff reaction isotherm. Calculate K_p for the following reaction :

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Given that the standard free energy change for the reaction is $-29.7\ kJmol^{-1}$ 5

OR

(C) Explain the physical significance of Gibb's free energy. 2½

(D) Derive Gibbs-Helmholtz equation. 2½

(E) Give any five statements of second law of thermodynamics. 2½

(F) Define efficiency of a heat engine. Calculate the maximum efficiency of an engine operating between 25ºC and 135ºC. 2½

2. (A) Derive the relationship between emf of the cell and enthalpy change of the cell reaction. Calculate the emf of the cell at 298 K.

The half cell reactions are

$$Pb(s) + SO_4^{2-} \longrightarrow PbSO_4(s) + 2e^-$$

$$Hg_2SO_4(s) + 2e^- \longrightarrow 2Hg_{(l)} + SO_4^{2-}$$

Given :

$$\left(\frac{\partial E}{\partial T}\right)_P = 1.85\times10^{-4}\,VK^{-1},\ \Delta H^o = -176.11\,kJmol^{-1}.$$ 5

(B) What are concentration cells ? Derive an expression for the emf of the concentration cell without transference. 5

OR

(C) How pH of the solution can be determined by using glass electrode ? 2½

(D) Write the cell reaction :

$$Zn(s) + Cu^{2+}(aq.) \rightleftharpoons Zn^{2+}(aq.) + Cu(s)$$

and derive Nernst's equation for this reaction. 2½

(E) What are reversible and irreversible cells ? Give a suitable example of each. 2½

(F) Emf of the cell,

$$Ag \mid AgCl(s), KCl(Sat.) \mid NH_4NO_3, AgNO_{3(0.01\ N)} \mid Ag$$

is 0.578 V at 25ºC. Find the solubility product of AgCl. 2½

3\. (A) Define :

(i) Mass defect and

(ii) Binding energy.

Calculate the binding energy per nucleon of oxygen atom $^{16}_{8}O$ which has a mass of 15.995 amu. (Mass of neutron = 1.0086 amu. Mass of Proton = 1.0072 amu and mass of electron = 0.00054 amu). 5

(B) What is dipole moment ? How is dipole moment used to distinguish ortho, meta and para isomers of dichlorobenzene ? Calculate dipole moment of m-dichlorobenzene if bond moment of the C–Cl bond is 1.59 D. 5

OR

(C) How is the radioisotopes used in the study of reaction mechanism ? 2½

(D) Explain nuclear fusion with example. 2½

(E) What is induced polarization ? At NTP the dielectric constant and density of nitrogen are 1.00485 and 0.00125 g cm^{-3} respectively. Calculate induced molar polarization. 2½

(F) Explain why CO_2 have zero dipole moment, while H_2O have positive dipole moment ? 2½

4\. (A) Derive an expression for the rotational energy of a diatomic molecule taking it as a rigid rotator. Draw the rotational energy level diagram for such a molecule. 5

(B) What do you understand by normal modes of vibration of a polyatomic molecule ? Show diagrammatically the different normal modes of vibration of CO_2 and H_2O molecules. 5

OR

(C) Explain the potential energy curve obtained for a simple harmonic oscillator. 2½

(D) Explain, why do molecules behave as a non-rigid rotors. 2½

(E) The rotational spectrum of CO shows a series of equidistant lines spaced 3.84 cm^{-1}. Calculate moment of inertia and bond length of C=O bond, if its reduced mass is 1.1365×10^{-26} kg. 2½

(F) What is force constant ? How is it related to reduced mass ? 2½

5. Attempt any **TEN** questions of the following :

(i) Give any two limitations of first law of thermodynamics.

(ii) Define partial molar free energy.

(iii) What is the criteria for spontaneity and equilibrium in terms of free energy change ?

(iv) What do you know about standard electrode potential ?

(v) What are the advantages of potentiometric titration over ordinary titrations ?

(vi) What is Salt bridge ?

(vii) What is nuclear fission ?

(viii) Calculate the dipole moment of HCl molecule, if equilibrium bond length is 1.2746Å. (Charge on electron = 1.602×10^{-19}C)

(ix) How % age ionic character of a polar diatomic molecule can be calculated from dipole moment measurement ?

(x) Which of the following molecules will show rotational spectra ?

HCl, NH_3, CO_2 and N_2O

(xi) What are the selection rules for harmonic and anharmonic oscillators ?

(xii) What is fundamental band ? 1×10=10