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

CHEMISTRY

(Physical Chemistry)

Compulsory Paper—2

(New Course)

Time : Three Hours] [Maximum Marks : 50

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

(2) Draw diagrams and give chemical equations wherever necessary.

1. (A) Derive an integrated form of van't Hoff equation. The equilibrium constant Kp for a reaction is 3.0 at 673 K and 4.0 at 773 K. Calculate the value of ΔH for the reaction. 5

(B) Derive Gibb's-Helmoltz equation. The Gibb's free energy of a reaction at 300 K and 310 K are –241.1 kJ and –245.263 kJ respectively. Determine its ΔH and ΔS at 300 K. 5

OR

(C) For an ideal gas derive the relation :

$$\Delta S = C_v \ell n \frac{T_2}{T_1} + R \ell n \frac{V_2}{V_1}.$$ 2½

(D) For the equilibrium :

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

$K_c = 3.75 \times 10^{-6}$ at 796°C.

Calculate Kp for this reaction at this temperature. 2½

(E) An engine that has an efficiency of 25% takes in 200 J of heat during each cycle. Calculate the amount of work this engine performs. 2½

(F) Give the physical significance of Helmoltz free energy. 2½

2. (A) Draw phase diagram of Lead-Silver system and discuss it. 5

(B) State and explain Nernst distribution law. An aqueous solution of succinic acid at 25°C containing 0.07 g in 10 cm^3 is in equilibrium with an etheral solution containing 0.013 g in 10 cm^3 succinic acid has its normal molecular weight in both the solvents. What will be the concentration of an etheral solution in equilibrium with aqueous solution containing 0.024 g in 10 cm^3 ? 5

OR

(C) Give the phase rule and define the terms :

(i) No. of components

(ii) Degree of freedom. 2½

(D) Draw well labelled diagram of sulphur system. 2½

(E) State Raoult's Law of ideal solutions. Calculate the V.P. of solution containing 1 mole of benzene and 3 moles of toluene at 320 K, if the V.P. of pure benzene and toluene at this temperature are 3.2×10^4 Nm^{-2} and 1.02×10^4 Nm^{-2} respectively. 2½

(F) Explain with diagram the critical solution temperature of Phenol-Water system. 2½

3\. (A) Explain nuclear fission and nuclear fusion in terms of binding energy per nucleon. Illustrate your answer with the help of curve of binding energy per nucleon plotted against mass number. 5

(B) What is the origin of dipole moment of a compound ? Explain the use of dipole moment to calculate the percentage ionic character. The bond length of Li-H bond is 1.595Å and has a dipole moment of 1.963×10^{-29} cm. Calculate the percentage ionic character of Li-H bond. 5

OR

(C) What are the evidences in the favour of liquid drop model ? 2½

(D) Calculate the binding energy per nucleon for $_5B^{11}$ nucleus, if its isotopic mass is 10.81 a.m.u.

(Given : Mass of proton = 1.007277 amu

Mass of neutron = 1.008665 amu

Mass of electron = 0.00054862 amu) 2½

(E) How is dipole moment measurement used to distinguish ortho, meta and para isomers of dichlorobenzene ? 2½

(F) The dipole moments of CO_2 and SO_2 are zero and 5.46×10^{-30} cm respectively. Predict the shapes of these molecules from the dipole moment. 2½

4\. (A) Derive an expression for the rate constant of second order reaction (a = b). A second order reaction is 25% complete in 10 minutes. Determine the time for 80% of the reaction to complete. 5

(B) Give the brief discussion of hard sphere collision theory of bimolecular reactions. 5

OR

(C) Explain with suitable example the pseudo-unimolecular reactions. 2½

(D) Methyl acetate was subjected to the hydrolysis in 1N HCl solution at 298 K. 10 ml of the reaction mixture was withdrawn and titrated with 0.1N NaOH at different intervals of time to get following results :

Time (min.)	:	0	10	38	∞
Vol. of NaOH (ml)	:	18.5	19.0	20.3	34.5

Show that the reaction is of first order. 2½

(E) What is energy of activation of a chemical reaction ? How can it be calculated with the help of Arrhenius equation ? 2½

(F) Discuss briefly Lindemann theory of unimolecular reactions. 2½

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

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

(ii) For the following processes predict the values of change in entropy (ΔS) :

(a) Condensation of water vapours

(b) Melting of solid.

(iii) Give the relationship between Gibb's free energy change and Helmoltz free energy change at constant temperature and pressure.

(iv) What are Azeotropic mixtures ?

(v) What is metastable state ?

(vi) Give the effect of addition of solute on consolute temperature.

(vii) What are intermolecular forces ?

(viii) Write Clausius-Mossoti equation.

(ix) What is induced polarization ?

(x) Define rate constant of a reaction.

(xi) Give the example of zero order reaction.

(xii) For the reaction, $A + B \rightarrow$ product, $r = K[A]\,[B]^{3/2}$. What is the order of reaction ?

1×10=10

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1. (A) Derive the relationship $q_p = q_v + \Delta nRT$. Calculate the heat of reaction at constant volume for the following reaction :

$$CH_3COOH_{(\ell)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(\ell)}$$

q_p for the above reaction is –490.8 kJ at 25ºC. 5

(B) Derive an expression of work-done in reversible and isothermal expansion. 22.0×10^{-3} kg of CO_2 was expanded from 11.2 dm^3 to 16.8 dm^3 isothermally and reversibly at 303 K. Calculate the work of expansion. 5

OR

(C) Derive the relationship between C_p and C_v. 2½

(D) Enthalpy change is an extensive property but molar enthalpy change is an intensive property. Why ? 2½

(E) Differentiate between reversible and irreversible processes. 2½

(F) Calculate the heat of combustion of ethane gas from the following data :

(i) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)} \quad \Delta H = -272$ kJ

(ii) $C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O \quad \Delta H = 1400$ kJ

(iii) $C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)} \quad \Delta H = -135$ kJ. 2½

2. (A) Draw phase diagram of lead-silver system and discuss it. 5

(B) State and explain Nernst distribution law. An aqueous solution of succinic acid at 25ºC containing 0.07 g in 10 cm^3 is in equilibrium with an etheral solution containing 0.013 g in 10 cm^3 succinic acid has its normal molecular weight in both the solvents. What will be the concentration of an etheral solution in equilibrium with aqueous solution containing 0.024 g in 10 cm^3 ? 5

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(C) Give the phase rule and define the terms :

(i) No. of components

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(D) Draw well labelled diagram of sulphur system. 2½

(E) State Raoult's Law of ideal solutions. Calculate the V.P. of solution containing 1 mole of benzene and 3 moles of toluene at 320 K, if the V.P. of pure benzene and toluene at this temperature are 3.2×10^4 Nm^{-2} and 1.02×10^4 Nm^{-2} respectively. 2½

(F) Explain with diagram the critical solution temperature of Phenol-Water system. 2½

3. (A) State the postulates of Arrhenius theory of electrolytic dissociation. What are its limitations ? 5

(B) What is transport number of ions ? Discuss Hittorf's method of determination of transport number. 5

OR

(C) What are the limitations of Arrhenius theory of electrolytic dissociation ? 2½

(D) Write a note on electrophoretic effect. 2½

(E) Calculate equivalent conductivity of Ammonium hydroxide at infinite dilution, if the λ_∞ values of $Ba(OH)_2$, $BaCl_2$ and NH_4Cl are 457.6 s $cm^2\,mol^{-1}$, 240.6 s $cm^2\,mol^{-1}$ and 129.8 s $cm^2\,mol^{-1}$ respectively. 2½

(F) Discuss the graph of conductometric titration of strong acid against weak base. 2½

4. (A) Derive an expression for the specific reaction rate of second order reaction (a = b). A second order reaction is 25% completed in 60 seconds. Determine the time for 80% of the reaction to complete. 5

(B) Give the brief discussion of hard sphere collision theory of bimolecular reactions. 5

OR

(C) Explain with suitable example the pseudo-unimolecular reactions. 2½

(D) Methyl acetate was subjected to the hydrolysis in 1N HCl solution at 298 K. 10 ml of the reaction mixture was withdrawn and titrated with 0.1N NaOH at different intervals of time to get following results :

Time (min.)	:	0	10	38	∞
Vol. of NaOH (ml)	:	18.5	19.0	20.3	34.5

Show that the reaction is of first order. 2½

(E) What is energy of activation of a chemical reaction ? How can it be calculated with the help of Arrhenius equation ? 2½

(F) Discuss briefly Lindemann theory of unimolecular reactions. 2½

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

(i) What do you know about Joule-Thomson effect ?

(ii) Define bond dissociation energy.

(iii) Define adiabatic process.

(iv) What are azeotropic mixtures ?

(v) What is metastable state ?

(vi) Give the effect of addition of solute on consolute temperature.

(vii) Define specific conductivity.

(viii) Why D.C. can not be used for the measurement of electrolytic conductance ?

(ix) Give the relationship between equivalent conductance of solution, equivalent conductivity at infinite dilution and degree of dissociation of electrolyte.

(x) Define rate constant of a reaction.

(xi) Give the example of zero order reaction.

(xii) For the reaction, $A + B \rightarrow$ product, $r = K[A]\,[B]^{3/2}$. What is the order of reaction ?

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