(b) For a van der Waals gas, express fugacity (f) as a function of V, T, R and the vander Waals constant. 5

(c) Derive the Clausius-Clapeyron equation. 4

UNIT-V

9. (a) Derive the expression of the entropy production in a chemical reaction. 8

(b) Derive the relationship between the reaction affinity and

(i) the equilibrium constant

(ii) the Gibbs free energy and

(iii) the rate of the reaction

$H_2(g) + I_2(g) \leftrightarrow 2HI(g)$, assuming that the system behaves ideally. 6

10. (a) Derive the expression for entropy production and entropy flow in an open system. 8

(b) Discuss the transformation properties of fluxes and forces in a chemical reaction. 6

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PG Even Semester Examination, May 2025

CHEMISTRY

(2nd Semester)

Course No.: CHM-553

(Physical Chemistry-II)

Full Marks: 70

Pass Marks: 28

Time: 3 hours

The figures in the right margin indicate full marks for the question.
Answer any five questions selecting one from each unit.

UNIT-I

1. (a) Discuss the postulates of the Debye-Hückel theory. Derive an expression of the Debye-Hückel theory. 10

(b) Calculate the change in the potential difference between the anode and thesolution when the concentration of Zinc ion in the solution increases from 1.00 x10^{-3} M to 5.00 x10^{-3}M at 21.0 ^{o}C. 4

2. (a) Discuss the assumption of the Born model and obtain an expression for the free energy of the ion-solventinteraction. 6

(b) By considering the electrochemical cell reaction, derive an expression for the Nernst equation. 5

(c) From the reduction potential of Fe^{2+}, Fe^{3+}% Pt and Fe^{2+}%Fe. Calculate the reduction potential for electrode Fe^{3+}% Fe.

[E^o/V for Fe^{3+}, Fe^{2+}%Pt = 0.771and E^o/V for Fe^{2+}% Fe= -0.440] 3

UNIIT-II

3. (a) Compare the characteristics ofa fuel cell and a battery. 3

(b) What is corrosion of metal?What are the consequences of corrosion? 1+2=3

(c) Discuss the thermodynamic treatment of electrified interfaces leading to the derivation of the Lippmann equation. 4

(d) Write the expression of the Tafel equation for large overpotential. What is the significance of Tafel plots? 2+2=4

4. (a) Derive the Butler-Volmer equation forthe non-polarizable electrode. Show the variation of the net current density with overpotential obtained from the Butler-Volmer equation. 5+2=7

(b) At 25^0C the exchange current density of a $Pt \mid H_2(g) \mid H^+(aq)$ electrode is 0.79 $mAcm^{-1}$, Calculate the current flowing through a standard electrode of area 5.0 cm^2 when the overpotential is +5.0 mV. 4

(c) Distinguish between chemical corrosion and electrochemical corrosion. 3

UNIT-III

5. (a) What is the cyclic rule? Verify the cyclic rule for one mole of an ideal gas. 1+2=3

(b) What is the Joule-Thomson effect? Show that the Joule-Thomson effect is an isenthalpic process. 2+2=4

(c) Deduce the Gibbs-Helmholtz equation. 4

(d) Show the variation of work function with temperature and volume. 3

6. (a) What is Euler's reciprocal relation? Taking V as a function of T and P, show that for an ideal gas $dV$is an exact differential. 2+2=4

(b) Show that a decrease in free energy at constant temperature and pressure is equivalent to maximum available work. 3

(c) Describe in detail the Carnot cycle and hence, calculate the efficiency. 7

UNIT-IV

7. (a) What do you mean by a non-ideal solution? Derive the expression of the Gibbs-Gibbs-Duhem-Margules equation for a binary solution. Discuss the positive and negative deviations of components in the real solution using this equation. 1+4+3=8

(b) Deduce the expression of ΔG, ΔS, and ΔH of mixing for a non-ideal solution. 6

8. (a) What do you mean by chemical potentials? Derive the expression for the Gibbs-Duhem equation. 1+4=5