

4/CHE-252 Syllabus-2023

2026

(May-June)

FYUP : 4th Semester Examination

CHEMISTRY

(Physical Chemistry—I)

(CHE-252)

Marks : 75

Time : 3 hours

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

1. (a) Describe the Andrews experiment on critical phenomenon. Support with the isotherm of pressure vs. volume of CO_2 . 5
- (b) What is Boyle's temperature? How can we obtain it from van der Waals' equation? 2+3=5
- (c) Derive the relationship between C_{mp} , C_{av} and C_{rms} . 3
- (d) Calculate the root mean square velocity and most probable velocity of SO_2 molecules at 427°C . $1\frac{1}{2}+1\frac{1}{2}=3$
- (e) What is continuity of state? Explain. 3

OR

2. (a) Derive the Maxwell's distribution of molecular velocities in three dimensions. 5
- (b) Explain graphically how the molecular velocities change with temperature. 3
- (c) Starting from van der Waals' equation, obtain an expression for critical constants in terms of van der Waals' constants a and b . 5
- (d) The reduced volume and temperature of a gas are 10.2 and 0.6. What will be its pressure if its critical pressure is 42 atm? 3
- (e) Explain the principle of equipartition of energy. 3
3. (a) What is Carnot's cycle? Derive the efficiency of a Carnot engine working between two temperatures T_1 and T_2 . 1+5=6
- (b) What are the limitations of the first law of thermodynamics? 2
- (c) Define Gibbs' free energy and derive its variation with temperature and pressure. 1+2+2=5

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- (d) Calculate the maximum efficiency of a steam engine operating between 100 °C and 20 °C. What would be the efficiency of the engine if boiler temperature is raised to 150 °C? 3
- (e) State and explain Trouton's rule. 3
- OR**
4. (a) Prove that in an irreversible process, the net entropy change for the system and surrounding is greater than zero. 4

(b) Show that

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad 4$$

- (c) Derive the integrated form of the Clausius-Clapeyron equation. 5
- (d) Calculate the entropy change involved in the isothermal reversible expansion of 5 moles of an ideal gas from a volume of 12 litres to 24 litres. 3
- (e) Establish the criteria for thermodynamic equilibrium and spontaneity in terms of ΔG . 3
5. (a) Explain the following terms : 2+2=4
- (i) Electrolytic conductor
 - (ii) Specific conductance

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- (b) Derive Ostwald's dilution law. How will you test its validity? 4+2=6
- (c) What is transport number of ions? Mention the factors affecting transport number of ions. 2+3=5
- (d) Calculate the hydrogen ion concentration of a solution of formic acid containing 0.092 g of acid per litre. The dissociation constant of formic acid at 25 °C is 2.1×10^{-4} . 3

OR

6. (a) State and explain Kohlrausch law and mention its applications. 3+3=6
- (b) Discuss the Debye-Hückel theory for strong electrolytes. 6
- (c) Discuss the curve obtained by conductometric titration of a strong acid with a strong base. What are the advantages of conductometric titrations over conventional titrations? 3+1=4
- (d) Calculate the ionic strength of 0.2 molal K_2SO_4 solution. 2
7. (a) What is a galvanic cell? Explain its working. 2+3=5
- (b) Derive Nernst equation showing the effect of electrolyte concentration on the potential of calomel electrode. 6

(5)

(c) Calculate the EMF of a zinc-silver cell at 30 °C when activity of Zn^{2+} ions is 0.5 and the activity of Ag^+ ions is 10. Standard reduction potentials at 30 °C are—

(i) Ag^+ , Ag electrode = + 0.799 volt;

(ii) Zn^{2+} , Zn electrode = - 0.760 volt. 4

(d) Write short notes on the following : 2+2=4

(i) Concentration cells with transport

(ii) Overpotential

OR

8. (a) Discuss the potentiometric titrations involving redox reactions. 3

(b) Derive expressions for ΔG , ΔH and ΔS in terms of EMF of the cell and the temperature coefficient of the EMF. 6

(c) Write notes on the following : 2+2=4

(i) Glass electrode

(ii) Quinhydrone electrode

(d) A zinc electrode is placed in 0.1 M solution of zinc sulphate at 25 °C. If the degree of dissociation of salt at this concentration is found to be 0.95, calculate the electrode potential of the electrode at 25 °C. Given that $E_{\text{Zn}^{2+}, \text{Zn}}^\circ = -0.76$ volt. 4

- (e) Predict the feasibility of the oxidation of Fe^{2+} to Fe^{3+} by iodine (I_2) under standard conditions. Given :

$$E_{\text{I}_2/\text{I}^-}^\circ = +0.54 \text{ V}$$

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = +0.77 \text{ V}$$

2

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