

2025/FYUG/EVEN/SEM/
CHMDSC-251/140

FYUG Even Semester Exam., 2025

CHEMISTRY
(4th Semester)

Course No. : CHMDSC-251

[Physical Chemistry—II
(Chemical Thermodynamics of Equilibrium)]

Full Marks : 70

Pass Marks : 28

Time : 3 hours

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

UNIT—I

1. Answer any *two* questions : 2×2=4
- (a) Define state and path functions, and give one example of each.
- (b) State and explain the zeroth law of thermodynamics.
- (c) What are exact and inexact differentials?

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2. Answer any *one* question :

10

(a) (i) Distinguish between isothermal and adiabatic process. Derive a relation between temperature and volume in reversible adiabatic expression. 1+2=3

(ii) One mole of an ideal gas expands against a constant external pressure of 1 atm from a volume of 10 dm^3 to a volume of 30 dm^3 . Calculate the work done by the gas in joules. 3

(iii) Derive the expression for the work done in reversible isothermal work. 4

(b) (i) The enthalpy of combustion of glucose $\text{C}_6\text{H}_{12}\text{O}_6$ (s) is $-2816 \text{ kJ mol}^{-1}$ at 25°C . Calculate ΔH_f° ($\text{C}_6\text{H}_{12}\text{O}_6$). The ΔH_f° values for CO_2 (g) and H_2O (l) are $-393.5 \text{ kJ mol}^{-1}$ and $-285.9 \text{ kJ mol}^{-1}$ respectively. 2

(ii) Deduce Kirchhoff's equation. 3

(iii) Prove thermodynamically $C_p - C_v = R$ for 1 mol of an ideal gas. 3

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(3)

(iv) Calculate the bond enthalpy of C—H bond in methane from the following data : 2

- Heat of formation of $\text{CH}_4 = -75 \text{ kJ}$
- Heat of sublimation of carbon = 720 kJ
- Bond enthalpy of $\text{H}_2 \text{ gas} = 435 \text{ kJ}$

UNIT—II

3. Answer any *two* questions : 2×2=4

- (a) Give the statement of second law of thermodynamics in terms of entropy.
- (b) Define Helmholtz free energy.
- (c) What is Clausius inequality?

4. Answer any *one* question : 10

- (a) (i) Show that Joule-Thomson effect is isoenthalpic. 3
- (ii) Derive Gibbs-Helmholtz equation for a process at constant pressure. 3
- (iii) Discuss the variation of free energy change with temperature and pressure. 4

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- (b) (i) Derive the first thermodynamic equation of state using Maxwell relations. 2
- (ii) Show that, $-\Delta A_T = w_{\max}$, where the terms have their usual meanings. 2
- (iii) What is Gibbs free energy? 2
- (iv) Show that
- $$\left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V$$
- 2
- (v) Deduce an expression for change in entropy of an ideal gas with change in pressure and temperature. 2

UNIT—III

5. Answer any *two* questions : 2×2=4

- (a) What is triple point?
- (b) Explain the term 'eutectic mixture' with a suitable example.
- (c) Define the term 'phase' with a suitable example.

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6. Answer any one question : 10

(a) (i) Draw and discuss the phase diagram for a three-component system consisting of water, chloroform and acetic acid. 4

(ii) Deduce Gibbs' phase rule. 3

(iii) Calculate the number of components in the following systems : $1\frac{1}{2} \times 2 = 3$

(1) NaCl, KCl, Na^+ (aq), K^+ (aq), Cl^- (aq), H_2O (l)

(2) $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, Ca^{2+} (aq), Cl^- (aq), H_2O (l)

(b) (i) Explain the effect of pressure on the melting point of ice with the help of Clapeyron-Clausius equation. 2

(ii) Explain congruent melting point with the help of phase diagram of Zn-Mg system. 3

(iii) Explain the phase diagram of CO_2 in detail. 3

(iv) Calculate the number of components, number of phases and degrees of freedom in pure partly frozen acetic acid. 2

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UNIT—IV

7. Answer any *two* questions : 2×2=4

- (a) State and explain Le Chatelier's principle.
- (b) Explain the term 'partial molar quantities'.
- (c) Write the law of mass action and its mathematical form.

8. Answer any *one* question : 10

- (a)
 - (i) Deduce Gibbs-Duhem equation. 2
 - (ii) Mention the various factors affecting equilibrium constant. 2
 - (iii) For a mixture of ideal gases, show that $\Delta G_{\text{mix}} = RT \sum n_i \ln x_i$, where the terms have their usual meanings. 3
 - (iv) Calculate the entropy of ideal gas mixing, when 2 mol N_2 , 3 mol H_2 and 2 mol NH_3 are mixed at constant temperature, assuming no chemical reactions. 3
- (b)
 - (i) Explain the term 'chemical potential'. 2

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(ii) Deduce the integrated form expression for the variation of chemical potential with pressure. 4

(iii) What do you mean by exo-ergic and endo-ergic reactions? Also elaborate the phenomena of 'coupled reaction' with a suitable example. 2+2=4

UNIT—V

9. Answer any *two* questions : 2×2=4

(a) Define pH. Calculate pH of 10^{-9} M HCl.

(b) What is common-ion effect?

(c) Define buffer capacity and buffer range.

10. Answer any *one* question : 10

(a) (i) Aqueous solution of Na_2CO_3 is alkaline in nature. Explain. 2

(ii) Derive the expression for the hydrolysis constant, degree of hydrolysis and pH for hydrolysis of a weak acid and strong base.

1+1+2=4

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(8)

- (iii) Explain the pH titration curve for a strong acid-strong base with reference to (1) pH value against volume of base added and (2) differential curve for the same.

2+2=4

- (b) (i) Calculate the pH obtained by mixing equal volume of 0.015 N NH_4OH and 0.15 N NH_4NO_3 solutions. ($K_b = 1.8 \times 10^{-5}$) 3
- (ii) Mention two limitations of pH scale. 2
- (iii) Derive the Henderson's equation for basic buffer. 3
- (iv) Discuss the factors affecting degree of ionization. 2

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