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?

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 $C_6H_{12}O_6$ (s) is $-2816\ kJ\ mol^{-1}$ at 25 °C. Calculate ΔH_f° ($C_6H_{12}O_6$). The ΔH_f° values for CO_2 (g) and H_2O (l) are $-393{\cdot}5\ kJ\ mol^{-1}$ and $-285{\cdot}9\ kJ\ mol^{-1}$ respectively. 2

(ii) Deduce Kirchhoff's equation. 3

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

(Continued)

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

- Heat of formation of CH_4 = –75 kJ
- Heat of sublimation of carbon = 720 kJ
- Bond enthalpy of H_2 gas = 435 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

(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.

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 : 1½×2=3

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

(2) $CaCl_2 \cdot 6H_2O$, 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

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 $\Delta G_{mix} = RT \Sigma n_i \ln x_i$, 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

(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

(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. ($K_b = 1{\cdot}8 \times 10^{-5}$) 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

★ ★ ★