

1. Answer the following questions.

- (a) State and explain different types of systems with examples.
- (b) What is a boundary ? Write different types of boundaries with definitions.
- (c) What are state variables and state functions ?
- (d) Explain intensive and extensive variables with examples.
- (e) Explain the Euler's theorem of exactness.
- (f) State and explain zeroth law of thermodynamics.
- (g) What are path functions ? Give examples.

- (h) State the first law of thermodynamics. Give the mathematical formulation of this law.
- (i) Write the sign convention of q , dU and dH .
- (j) What are the limitations of first law of thermodynamics ?
- (k) What is enthalpy ? Give its mathematical expression.
- (l) What are heat capacities at constant pressure and constant volume ?
- (m) What is cyclic rule ? What is its utility ?
- (n) What is Thermochemistry ? Give the sign conventions of the heat of reaction.
- (o) Explain standard states with reference to thermochemistry.
- (p) Define and explain enthalpy of formation of molecules.
- (q) What is enthalpy of formation of ions ?
- (r) Define and explain the enthalpy of combustion.
- (s) State and explain bond energy, bond dissociation energy and resonance energy.
2. State and derive first law of thermodynamics.
3. Calculate the work done by the system.
- (i) When the change is carried out at constant volume.
- (ii) When the change is carried out reversibly and isothermally.
- (iii) When the change is carried out with zero and constant opposing pressure.
4. Compare between the reversible work done in isothermal and adiabatic expansion of an ideal gas from pressure P_1 to P_2 .
5. Show from thermodynamic consideration that for one mole of ideal gas, $\bar{C}_P - \bar{C}_V = R$.
6. (a) Show that the enthalpy change is equal to the heat absorbed when the reaction is carried out at constant pressure.
- (b) What are meant by isothermal and adiabatic changes ? Derive the equation for work of expansion in reversible adiabatic process.
7. Derive the value of w , ΔU , q and ΔH for isothermal expansion of a van der Waals gas. Show that the volume is a state function for a gas obeying the equation. $\left(P + \frac{a}{V^2}\right)V = RT$
8. Show that for adiabatic processes,
- (a) $TV^{\gamma-1} = \text{constant}$
- (b) $PV^\gamma = \text{constant}$,
- (c) $TP^{R/C_P} = \text{a constant}$
9. (a) Find the work done when 2 moles of H_2 expand isothermally from 25 to 50 dm^3 against a constant pressure of 1 atm. at 298 K.

- (b) 2 moles of an ideal gas expand reversibly and isothermally from 15 dm³ to 50 dm³ at 298K. Calculate the values of w, q ΔU and ΔH.

10. Derive the following relations.

$$(a) \quad C_p - C_v = \left[P + \left(\frac{\partial U}{\partial V} \right)_P \right] \left(\frac{\partial U}{\partial T} \right)_P$$

$$(b) \quad C_p - C_v = \left[V - \left(\frac{\partial H}{\partial P} \right)_T \right] \left(\frac{\partial P}{\partial T} \right)_P$$

$$(c) \quad \left(\frac{\partial U}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_V = - \left(\frac{\partial U}{\partial P} \right)_V \left(\frac{\partial V}{\partial T} \right)_P$$

11. (a) Give the relationship between C_p and C_v for an ideal gas.

(b) Compare between w_{rev} and w_{irr} for isothermal expansion of an ideal gas.

12. (a) Calculate the work done for isothermal expansion of a van der Waals gas.

(b) Give a comparison between the work of expansion of an ideal gas and a van der Waals gas.

13. Establish a relation between heat of reaction at constant volume and heat of reaction at constant pressure.

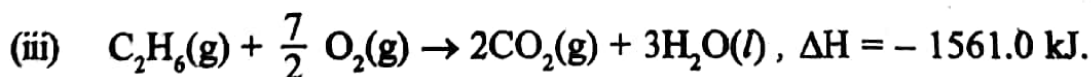
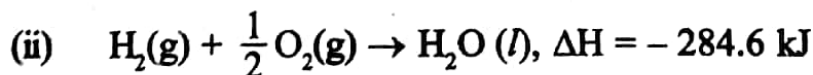
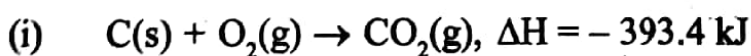
14. Derive the expressions showing the effect of temperature and pressure on enthalpy of reactions.

15. (a) One mole of an ideal monoatomic gas occupying volume V₁ at T₁ and P₁ compressed

adiabatically to a pressure at 2P₁. Prove that $\Delta V = \frac{3RT}{10P_1}$ and $\Delta T = \frac{2}{5} T_1$.

(b) Calculate ΔU when 65.4g of Zn dissolves in dil. HCl at 298 K. One mole of H₂ is liberated and 151.4 kJ of heat evolved.

16. Define enthalpy of formation. Calculate the enthalpy of formation of ethane from the following data.



17. Define heat of combustion. Calculate the heat of formation of ethyl alcohol from the data given below.

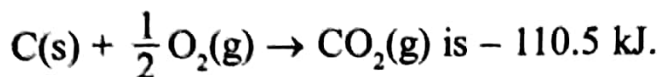
$$\Delta_c H^\circ (\text{ethyl alcohol}) = -1368.5 \text{ kJ}$$

$$\Delta_f H^\circ (CO_2(g)) = -393.4 \text{ kJ}$$

$$\Delta_f H^\circ (H_2O(l)) = -286.3 \text{ kJ}$$

18. (a) The heat of combustion of ethane at 300 K and at constant volume is 1339.6 kJ. Find the heat of combustion at constant pressure.

(b) The heat of reaction at 298 K and at constant pressure for the reaction,



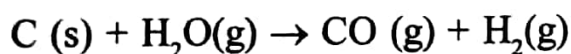
Find the heat of reaction at constant volume.

19. (a) State and derive Kirchhoff's equation.

(b) What is bond energy? How is it calculated?

20. (a) $\Delta_f H^\circ (\text{CO (g)}) = -110.4 \text{ kJ}$, and $\Delta_f H^\circ (\text{steam}) = -243 \text{ kJ}$.

Calculate the heat of reaction for



(b) The heat of dissociation of gaseous water at 291K is 241.5 kJ. Calculate its value at 341 K. \bar{C}_P Values for H_2O , H_2 and O_2 are respectively, 33.6, 28.8 and 29.1 $\text{JK}^{-1} \text{mol}^{-1}$.

1. Write the answers for the following :

- (a) Give the combined form of the first and second laws of thermodynamics.**
- (b) Write the essence of the second law of thermodynamics.**
- (c) Write the Gibbs-Helmholtz equation and define each term involved therein.**
- (d) What is third law of thermodynamics ?**
- (e) Explain residual entropy.**
- (f) What is Joule-Thomson co-efficient ? What is inversion temperature ?**

- (g) Will entropy increase or decrease in the following changes ?
- Sugar dissolves in water.
 - Normal egg to hard boiled egg.
- (h) Which of the following does not have zero entropy at absolute zero ?
CO, CO₂, NaCl and NO.
- What does the term TΔS represent ?
 - Which has larger absolute entropy per mole ?
 - H₂O(l) at 298K or H₂O(l) at 350K.
 - N₂ or NO both at 298K.
 - Why does entropy of a solid increase on fusion ?
 - Predict the sign of ΔG for the reaction at a very low temperature for which both ΔH and ΔS are +ve.
 - What is the need for introducing the concept of free energy ? What are uses of free energy ?
 - What are the units of entropy ?

- Derive Gibbs-Helmholtz equation and derive the expressions for the dependence of free energy.
- Derive the following relations starting with the fundamental equations in each case.

$$(i) \quad \Delta G = -SdT + VdP \qquad (ii) \quad dA = -SdT - RdV$$

$$(iii) \quad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad (iv) \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

4. Show that

$$(a) \quad \left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial(V/T)}{\partial(1/T)}\right)_P$$

$$(b) \quad \text{For an ideal gas, } \left(\frac{\partial H}{\partial P}\right)_T \equiv 0$$

- Starting with the relation, $A = U - TS$, derive $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$.
 - Calculate the entropy change when 2 moles of an ideal gas expand isothermally and reversibly from a volume of 1 dm³ to 10 dm³ at 300K.

- Discuss and explain the third law of thermodynamics. Give its application.
- State the second law of thermodynamics in different ways.
- Calculate the net entropy change during a reversible process. What is the physical significance of entropy ?
- A Carnot cycle working between 373K and 273K, takes up 80J from the high temperature reservoir. Calculate the work done, heat rejected and efficiency.
- Write notes on :
 - Maxwell's relations
 - Thermodynamic equation of state.

1. Answer the following questions.

- (a) What is partial molar quantity ? Give examples.
- (b) Define chemical potential. Give its notation.
- (c) Why the term, fugacity is used ?
- (d) What is the difference between molar property and partial molar property ? Explain with examples.
- (e) Write the expressions of van't Hoff isotherm and van't Hoff isochore.
- (f) Write the expressions for ideal gas mixtures.
- (g) Give the relative magnitudes of ΔG° and $\ln Q_p$.
- (h) What are the thermodynamic criteria of equilibrium ? Give expressions.
- (i) What are the Gibbs-Duhem relations ?

2. (a) Derive $\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j}$
- (b) Show that $\mu_i = \left(\frac{\partial H}{\partial n_i} \right)_{S,P,n_j}$ where the symbols have their usual meanings.
3. Derive the expression for the free energy of mixing and arrive at the Gibbs-Duhem equation.
4. (a) What is meant by chemical potential ?
What is its significance ?
- (b) Derive the relation $\Delta G^\circ = -RT \ln K_p$.
5. Deduce thermodynamically van't Hoff reaction isotherm, i.e., $-\Delta G = RT \ln K_p - \sum n_i \ln P_i$
6. Deduce the relationship between K_p , K_c and K_x .
7. (a) Calculate the equilibrium constant of the reaction at 300K if ΔG at this temperature is 29.4 kJ mol⁻¹.
- (b) At 300K, ΔG° for the reaction,
 $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 5743J. Calculate K_p for the reaction.
8. Derive the equilibrium constant from thermodynamic considerations.
9. Deduce the expressions for equilibrium constants and their quantitative dependence on temperature and pressure.
10. Write notes on :
- (a) Concept of fugacity.
- (b) Integration of van't Hoff equation.
11. Discuss the free energy of mixing and spontaneity of reactions.
12. Discuss the methods of determination of partial molar property of a component in a binary mixture.
13. Discuss the quantitative treatment of Le Chatelier's principle.
14. Write notes on :
- (a) Degree of advancement of a reaction.
- (b) Reaction quotient.
- (c) Volume of mixing of ideal gases.
15. Discuss the relation between fugacity and pressure of a gas.
16. The equilibrium constant of the reaction,
 $2SO_2 + O_2 \rightleftharpoons 2SO_3$ at 528°C is 98.0 and at 680°C is 10.5. Find the heat of reaction.
17. At 102°C and total pressure of 1 atm, sulphuryl chloride is dissociated as $SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$ to the extent of 91.2%. Find K_p and net work by this reaction of this temperature.

1. Answer the following questions:
- (a) What is an ideal solution ? Write its thermodynamic expression.
 - (b) State the Raoult's laws for dilute solutions.
 - (c) What is Henry's law ? Define Henry's law constant.
 - (d) Define osmotic and osmotic pressure of a solution.
 - (e) What are colligative properties ?
 - (f) Define K_f and give its units.
 - (g) What is K_b ? Write its units.
 - (h) What happens when a solute undergoes dissociation and association in solution with respect to its colligative properties ?

- (i) What are lowering of vapour pressure and relative lowering of vapour pressure of a solution.
- (j) Write the relation between osmotic pressure and relative lowering of vapour pressure.
- (k) Define van't Hoff 'i' factor.
- (l) State the laws of Osmotic pressure.
- (m) Why the osmotic pressures of 0.1M glucose solution and 0.1M sodium chloride solution are not equal ?
- Define molal depression freezing point constant. Derive an expression relating the freezing point depression of a solution with the molality of the dissolved solute. Discuss the utility of the derived expression.
 - Derive thermodynamically the van't Hoff equation, $\pi V = n_2 RT$.
 - Deduce the value of K_b in terms of latent heat of vaporisation thermodynamically.
 - State Raoult's law relating elevation of boiling point and molecular weight.
 - Derive the relative lowering of vapour pressure thermodynamically.
 - Deduce the value of K_f in terms of latent heat of fusion thermodynamically.
 - Derive the relation between molecular weight and depression of freezing point of a solution containing a non-volatile solute.
 - A solution containing 2.5g of a non-volatile solute in 100g of benzene boiled at a temperature of 0.42°C higher than did the pure solvent. What is the mol. wt of the solute if molal elevation constant of benzene is 2.67 ?
 - Derive an expression relating the b.pt. elevation and the mole fraction of the dissolved solute. Discuss the validity of the expression in determining the molar mass of a non-volatile solute.
 - In terms of molecular weights of solutes, define van't Hoff factor.
 - The molecular weight of acetic acid in benzene as determined by freezing point depression is 118. Give comments about this.
 - State and explain van't Hoff theory of dilute solutions. Calculate osmotic pressure of 10% anhydrous MgCl_2 solution at 20°C assuming that the salt is completely ionized.
 - Calculate the van't Hoff factor for the solution of 0.001 kg of NaCl in 0.1 kg of water. The solution freezes at 272.4 K (K_f (water) = 1.86 K molal⁻¹).
 - Write notes on :
 - Ebullioscopic constant, (b) Van't Hoff factor, (c) Cryoscopic constant, (d) Abnormal behaviour of solution.
 - A solution of 0.001 kg of NaCl in 1 kg of water freezes at -0.604°C , K_f (water) = 1.86 K molal⁻¹. Calculate the degree of dissociation of NaCl.
 - When 2.8 g of an organic compound dissolved in 24.2 gm of chloroform raised the b.pt. of the solvent by 0.29K. Calculate the mol.wt of the substance (K_b for 1000 g of chloroform = 8.322)
 - Show that the relative lowering in the freezing point, $\Delta T_f/T_f^\circ$, when a non-volatile solute is dissolved in a volatile solvent is given by $RT^\circ X_2 / \Delta \bar{H}_{\text{fus}}$, where X_2 is the mole fraction of the solute in the solution. Does the freezing point remain constant as more and more of the solvent crystallise out ?