

Chapter - 6

Thermodynamic

- **System** : Specific part of universe in which observations are made.
- **Surroundings** : Everything which surrounds the system.
- **Types of the System** :
 - (i) **Open System** : Exchange both matter and energy with the surroundings. For example : Reactant in an open test tube.
 - (ii) **Closed System** : Exchange energy but no matter with the surroundings. For example : Reactants in a closed vessel.
 - (iii) **Isolated System** : Neither exchange energy nor matter with the surroundings. For example : Reactants in a thermos flask.
- Please note no system is perfectly isolated.
- **Thermodynamic Processes** :
 - (i) Isothermal process : $\Delta T = 0$
 - (ii) Adiabatic process : $\Delta q = 0$
 - (iii) Isobaric process : $\Delta P = 0$
 - (iv) Isochoric process : $\Delta V = 0$
 - (v) Cyclic process : $\Delta U = 0$
 - (vi) Reversible process : Process which proceeds infinitely slowly by a series of equilibrium steps.
 - (vii) Irreversible process : Process which proceeds rapidly and the system does not have chance to achieve equilibrium.
- **Extensive Properties** : Properties which depend upon the quantity or size of matter present in the system. For example : mass, volume, internal energy, enthalpy, heat capacity, work etc.

- **Intensive Properties :** Properties which do not depend upon the quantity or size of matter present in the system. For example : temperature, density, pressure, surface tension, viscosity, refractive index, boiling point, melting point etc.
- **State Functions :** The variables of functions whose value depend only on the state of a system or they are path independent. For example : pressure (P), volume (V), temperature (T), enthalpy (H), free energy (G), internal energy (U), entropy (S), amount (n) etc.
- **Internal Energy :** It is the sum of all kind of energies possessed by the system.
- **First Law of Thermodynamics :** “The energy of an isolated system is constant.”

$$\text{Mathematical Form : } \Delta U = q + w$$

- **Sign Conventions for Heat (q) and Work (w) :**

- (i) $W = +ve$, if work is done on system
- (ii) $W = -ve$, if work is done by system
- (iii) $q = +ve$, if heat is absorbed by the system
- (iv) $q = -ve$, if heat is evolved by the system

- Work of Expansion/compression : $w = -P_{ext}(V_f - V_i)$

- **Work done in Isothermal Reversible Expansion of an Ideal Gas :**

$$w_{rev} = -2.303 nRT \log \frac{V_f}{V_i}$$

$$\text{Or, } w_{rev} = -2.303 nRT \log \frac{P_i}{P_f}$$

- Significance of ΔH and ΔU : $\Delta H = q_p$ and $\Delta U = q_v$
- **Relation** between ΔH and ΔU : $\Delta H = \Delta U + (n_p - n_r)RT$ for gaseous reaction.
 - (i) $\Delta H = \Delta U$ if $(n_p - n_r)$ is zero; e.g., $H_2(g) + I_2(g) \rightarrow 2HI(g)$
 - (ii) $\Delta H > \Delta U$ if $(n_p - n_r)$ is positive; e.g., $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$
 - (iii) $\Delta H < \Delta U$ if $(n_p - n_r)$ is negative; e.g., $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
- **Heat capacity (C) :** Amount of heat required to raise the temperature of a substance by $1^\circ C$ to 1 K.

$$q = C\Delta T$$

- **Specific heat capacity (C_s) :** Amount of heat required to raise the

temperature of 1g of a substance by 1°C or 1K.

$$q = C_s \times m \times \Delta T$$

- **Molar Heat Capacity (C_m)** : Amount of heat required to raise the temperature of 1 mole of a substance by 1°C or 1K.

$$q = C_m \times n \times \Delta T$$

- **Standard State of a Substance** : The standard state of a substance at a specified temperature is its, pure form at 1 bar.
- **Standard Enthalpy of Formation ($\Delta_f H^\circ$)** : Enthalpy change accompanying the formation of one mole of a substance from its constituent elements under standard condition of temperature (normally 298 K) and pressure (1 bar).
 - $\Delta_f H^\circ$ of an element in standard state is taken as zero.
 - Compounds with – ve value of $\Delta_f H^\circ$ are more stable than their constituents.
 - $\Delta_r H^\circ = \sum_i a_i \Delta_f H^\circ (\text{products}) - \sum_i b_i \Delta_f H^\circ (\text{reactants})$: Where ‘a’ and ‘b’ are coefficients of products and reactants in balanced equation.
- **Standard Enthalpy of Combustion ($\Delta_c H^\circ$)** : Enthalpy change accompanying the complete combustion of one mole of a substance under standard conditions (298 K, 1 bar)
- **Hess’s Law of Constant Heat Summation** : The total enthalpy change of a reaction remains same whether it takes place in one step or in several steps.
- **Bond Dissociation Enthalpy** : Enthalpy change when one mole of a gaseous covalent bond is broken to form products in gas phase. For example: $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g})$; $\Delta_{\text{Cl-Cl}} H^\circ = 242 \text{ kJ/mol}^{-1}$.
- For diatomic gaseous molecules; Bond enthalpy = Bond dissociation Enthalpy = Atomization Enthalpy
- For Polyatomic gaseous molecules; Bond Enthalpy = Average of the bond dissociation enthalpies of the bonds of the same type.
- $\Delta_r H^\circ = \sum \Delta_{\text{bond}} H^\circ (\text{Reactants}) - \sum \Delta_{\text{bond}} H^\circ (\text{Products})$
- **Spontaneous Reaction** : A reaction which can take place either of its own or under some initiation.

- **Entropy (S)** : It is measure of degree of randomness or disorder of a system.
- $\Delta S_{sys} = \frac{(q_{rev})_{sys}}{\Delta T} = \frac{(\Delta H)_{sys}}{\Delta T}$
- Unit of Entropy = $\text{JK}^{-1} \text{mol}^{-1}$
- **Second Law of Thermodynamics** : For all the spontaneous processes totally entropy change must positive.

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0$$
- **Gibbs Helmholtz Equation for determination of Spontaneity** :

$$\Delta G = \Delta H - T\Delta S$$
 - (i) If $\Delta G = -ve$, the process is spontaneous
 - (ii) If $\Delta G = +ve$, the process is nonspontaneous
 - (iii) If $\Delta G = 0$, the process is in equilibrium
- **Relation between Gibbs Energy Change and Equilibrium Constant** :

$$\Delta G^0 = -2.303 RT \log K_c$$
- **Third law of thermodynamic** : The entropy of a perfectly crystalline solid at absolute zero (0 K) is taken to be zero.

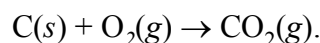
1-Mark Questions

Thermodynamic Concepts and First Law of Thermodynamics

1. Day temp. Name the thermodynamic system to which following belong:
 (i) Human body (ii) Milk in Thermos flask (iii) Tea in steel kettle
2. Identity State functions out of the following : Enthalpy, Entropy, Heat, Temperature, Work, Free energy.
3. Give two examples of state functions.
4. Write the mathematical statement of first law of thermodynamics.

Work, Enthalpy, Internal Energy and Heat Capacity

5. Predict the internal energy change for an isolated system ? [Ans. Zero]
6. Why ΔH is more significant than ΔU ?
7. Write one example each of extensive and intensive properties.
8. Write a chemical equation in which ΔH and ΔU are equal.
9. Write the relationship between ΔH and ΔU for the reaction :



Different types of Enthalpy Changes and Hess's Law

10. Define standard enthalpy of formation.
11. Why is the standard enthalpy of formation of diamond not zero although it is an element ?
12. The enthalpy of atomization of CH_4 is 1665 kJ mol^{-1} . What is the bond enthalpy of C-H bond ? [Ans. 416.25 kJ]
13. Identify the species for which $\Delta_f H^\circ = 0$, at 298 K : $-\text{Br}_2$, Cl_2 , CH_4 .
[Hint : Cl_2 (Br_2 is liquid at 298K)]

Spontaneity, Entropy, Second and Third Law of Thermodynamics

14. For the reaction $2\text{Cl(g)} \rightarrow \text{Cl}_2\text{(g)}$; what are the sign of ΔH and ΔS ?
15. For an isolated system $\Delta U = 0$, what will be ΔS ?
16. Why entropy of steam is more than that of water at its boiling point ?
17. Out of Diamond and Graphite which has higher entropy ?
18. Write an example of endothermic spontaneous reaction.
19. State second law of thermodynamics.
20. State third law of thermodynamics.
21. Which has more entropy ? 1 mol $\text{H}_2\text{O(l)}$ at 25°C or 1 mol $\text{H}_2\text{O(l)}$ at 35°C .
22. At what temperature the entropy of a perfectly crystalline solid is zero?

Gibbs Energy and Spontaneity, Effect of Temperature on Spontaneity

23. For a certain reaction $\Delta G^\circ = 0$, what is the value of K_c ?
24. How can a non spontaneous reaction be made spontaneous ?
25. For a reaction both ΔH and ΔS are negative. Under what conditions does the reaction occur.

2 Marks Question

Thermodynamic Concepts and First Law of Thermodynamics

1. In a process 701 J of heat is absorbed by a system and 394 J work is done by the system. What is the change in internal energy for the process ?
[Ans. 307 J]

2. Neither q nor w is state functions but $q + w$ is a state function. Explain.

Work, Enthalpy, Internal Energy and Heat Capacity

3. Classify the following as extensive or intensive properties :
Heat capacity, Density, Temperature, Molar heat capacity.
4. Derive the relationship between ΔH and ΔU .
5. Derive the relationship $C_p - C_v = R$.
6. A 1.25g sample of octane ($C_{18}H_{18}$) is burnt in excess of oxygen in a bomb calorimeter. The temperature of the calorimeter rises from 294.05 to 300.78K. If heat capacity of the calorimeter is 8.93 kJ K^{-1} . Find the heat transferred to calorimeter. [Ans. 0.075 kJ]
7. Show that for an ideal gas, the molar heat capacity under constant volume conditions is equal to $3/2 R$.
8. Expansion of a gas in vacuum is called free expansion. Calculate the work done and change in internal energy when 1 mol of an ideal gas expands isothermally from 1 L to 5 L into vacuum.

Different types of Enthalpy Changes and Hess's Law

9. State and explain Hess's Law of Constant Heat Summation with a suitable example.
10. Derive the relationship between ΔH and ΔU . Given, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$; $\Delta_f H^\circ = -92.4 \text{ kJ mol}^{-1}$; What is the standard enthalpy of formation of NH_3 gas ? [Ans. $-46.2 \text{ kJ mol}^{-1}$]
11. Calculate the enthalpy change for the reaction : $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$. Given the bond enthalpies H_2 , Br_2 and HBr are 435 kJ mol^{-1} , 192 kJ mol^{-1} and 368 kJ mol^{-1} respectively. [Ans. -109 kJ mol^{-1}]
12. Is the bond dissociation enthalpy of all the four C-H bonds in CH_4 same? Give reason in support of your.

Spontaneity, Entropy, Second and Third Law of Thermodynamics

13. Define the term entropy. Write its unit. How does entropy of a system change on increasing temperature?
14. Dissolution of ammonium chloride in water is endothermic but still it dissolves in water readily. Why ?
15. Calculate the entropy change in the surroundings when 1.00 mol of $HI(OI)$ is formed under standard conditions; $\Delta_f H^\circ = -286 \text{ kJ mol}^{-1}$.

[Ans. 959.7 J K⁻¹ mol⁻¹]

16. The enthalpy of vaporization of a liquid is 30 kJ mol⁻¹ and entropy of vaporization is 75 J K⁻¹ mol⁻¹. Calculate the boiling point of liquid at 1 atm. [Ans. 400 K]

Gibbs Energy and Spontaneity, Effect of Temperature on Spontaneity

17. The equilibrium constant for a reaction is 10. What will be the value of ΔG° ? $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 300 \text{ K}$. [Ans. - 5.527 kJ mol⁻¹]
18. Derive the relationship, $\Delta G = -T\Delta S_{\text{total}}$ for a system.
19. The ΔH and ΔS for $2\text{Ag}_2\text{O}(s) \rightarrow 4\text{Ag}(s) + \text{O}(g)$ are given + 61.17 kJ mol⁻¹ and + 132 K⁻¹ mol⁻¹ respectively. Above what temperature will the reaction be spontaneous? [Ans. > 463.4 K]

3 Mark Questions

Thermodynamic Concepts and First Law of Thermodynamics

1. Differentiate between the following (with examples) :
- (i) Open and Closed System.
 - (ii) Adiabatic and Isothermal process
 - (iii) State function and path function

Work, Enthalpy, Internal Energy and Heat Capacity

2. Calculate the maximum work obtained when 0.75 mole of an ideal gas expands isothermally and reversibly at 27°C from a volume of 15 L to 25 L. [Ans. - 955.7 J]
3. Calculate the number of kJ necessary to raise the temperature of 60 g of aluminium from 35 to 55°C. Molar heat capacity of Al is 24 J mol⁻¹ K⁻¹. [Ans. 1.067 kJ]
4. The reaction of cyanamide, $\text{NH}_2\text{CN}(s)$, with Dioxygen was carried out in a bomb calorimeter, and ΔU was found to be - 742.7 kJ mol⁻¹ at 298K. Calculate Enthalpy change for the reaction at 298K, $\text{NH}_2\text{CN}(s) + \frac{3}{2} \text{O}_2(g) \rightarrow \text{N}_2(g) + \text{CO}_2(g) + \text{H}_2\text{O}(l)$ [Ans. - 741.5 kJ mol⁻¹]

Different types of Enthalpy Changes and Hess's Law

5. The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are - 890.3 kJ mol⁻¹, - 393.5 kJ mol⁻¹ and - 285.8 kJ mol⁻¹ respectively.

Calculate enthalpy of formation of methane gas. [**Ans.** $-74.8 \text{ kJ mol}^{-1}$]

6. Explain the Born Haber Cycle to determine the lattice enthalpy of NaCl.
7. Enthalpies of formation of CO(g) , $\text{CO}_2\text{(g)}$, $\text{N}_2\text{O(g)}$ and $\text{N}_2\text{O}_4\text{(g)}$ are -110 , -393 , 81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H^\circ$ for the reaction; $\text{N}_2\text{O}_4\text{(g)} + 3\text{CO(g)} \rightarrow \text{N}_2\text{O(g)} + 3\text{CO}_2\text{(g)}$

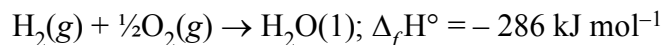
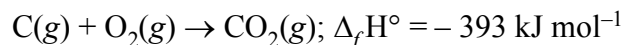
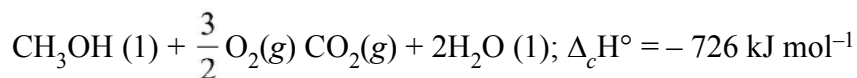
[**Ans.** $-777.7 \text{ kJ mol}^{-1}$]

8. The combustion of 1 mol of benzene takes place at 298K . After combustion CO_2 and H_2O are formed and 3267 kJ mol^{-1} of heat is liberated. Calculate $\Delta_f H^\circ(\text{C}_6\text{H}_6)$.

Given : $\Delta_f H^\circ(\text{CO}_2) = -286 \text{ kJ mol}^{-1}$, $\Delta_f H^\circ(\text{H}_2\text{O}) = -393 \text{ kJ mol}^{-1}$

[**Ans.** $48.51 \text{ kJ mol}^{-1}$]

9. Calculate the standard enthalpy of formation of $\text{CH}_3\text{OH (l)}$ from the following data :



[**Ans.** -239 kJ mol^{-1}]

Spontaneity, Entropy, Second and Third Law of Thermodynamics

10. For oxidation of iron, $4\text{Fe(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Fe}_2\text{O}_3$ entropy change is $-549.4 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K . In spite of negative entropy change of this reaction, why is the reaction spontaneous ? ($\Delta_r H^\circ$ for this reaction is $-1648 \text{ kJ mol}^{-1}$)

[**Ans.** $\Delta S_{\text{total}} = +4980.6 \text{ J K}^{-1} \text{ mol}^{-1}$]

11. Give reasons :

- (i) Evaporation of water is an endothermic process but it is spontaneous,
- (ii) A real crystal has more entropy than an ideal crystal,
- (iii) Entropy of universe is increasing.

Gibbs Energy and Spontaneity, Effect of Temperature on Spontaneity

12. For the reaction at 298 K , $2\text{A} + \text{B} \rightarrow \text{C}$; $\Delta H = 400 \text{ kJ mol}^{-1}$, $\Delta S = 0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}$. At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range.

[**Ans.** $T > 2000 \text{ K}$]

13. Reaction $X \rightarrow Y$; $\Delta H = +ve$ is spontaneous at temperature “T”. Determine
- Sign of ΔS for this reaction,
 - Sign of ΔG for $Y \rightarrow X$
 - Sign of ΔG at a temperature $< T$.

5-Mark Questions

Thermodynamic Concepts and First Law of Thermodynamics

- What is reversible process in Thermodynamics?
 - Name the thermodynamic processes for which : (i) $q = 0$ (ii) $\Delta U = 0$ (iii) $\Delta V = 0$ (iv) $\Delta P = 0$.
 - Water decomposes by absorbing 286.2 kJ of electrical energy per mole. When H_2 and O_2 combine to form one mole of H_2O , 286.2 kJ of heat is produced. Which thermodynamic law is proved? Write its statement.

Work, Enthalpy, Internal Energy and Heat Capacity .

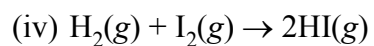
- Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions ? Explain. [Hint : $q_v = \Delta U$ and $q_p = \Delta H$]
 - It has been found that 221.4 J is needed to heat 30g of ethanol from $15^\circ C$ to $18^\circ C$. Calculate (a) specific heat capacity, and (b) molar heat capacity of ethanol. [Ans. (a) $2.46 \text{ Jg}^{-1}^\circ C^{-1}$, (b) $113.2 \text{ J mol}^{-1}^\circ C^{-1}$]

Different types of Enthalpy Changes and Hess's Law

- Differentiate the terms Bond dissociation enthalpy and Bond Enthalpy.
 - Calculate enthalpy change for the process $CCl_4(g) \rightarrow C(g) + 4Cl(g)$ and calculate Bond enthalpy of C-Cl bond in CCl_4 . Given : $\Delta_{vap} H^\circ(CCl_4) = 30.5 \text{ kJ mol}^{-1}$; $\Delta_f H^\circ(CCl_4) = -135.5 \text{ kJ mol}^{-1}$; $\Delta_a H^\circ(C) = 715 \text{ kJ mol}^{-1}$ and $\Delta_a H^\circ(Cl_2) = 242 \text{ kJ mol}^{-1}$. [Ans. 1304 kJ mol^{-1} , 326 kJ mol^{-1}]

Spontaneity, Entropy, Second and Third Law

- Predict the sign of ΔS for the following changes :
 - Freezing of water,
 - $C(\text{graphite}) \rightarrow C(\text{diamond})$
 - $H_2(g)$ at 298 k and 1 bar $\rightarrow H_2(g)$ at 298 k and 10 bar



Gibbs Energy and Spontaneity, Effect of Temperature of Spontaneity

5. (i) Define Gibbs energy. Give its mathematical expression. What is Gibbs's energy criteria of spontaneity.
- (ii) For the reaction : $2\text{A}(\text{g}) + \text{B}(\text{g}) \rightarrow 2\text{D}(\text{g})$, $\Delta U^\circ = -10.5 \text{ kJ}$ and $\Delta S^\circ = -44.1 \text{ J K}^{-1}$. Calculate $\Delta_r G^\circ$ for the reaction, and predict whether it will occur spontaneously. [Ans. $\Delta_r G^\circ = +0.16 \text{ kJ}$, Non spontaneous]