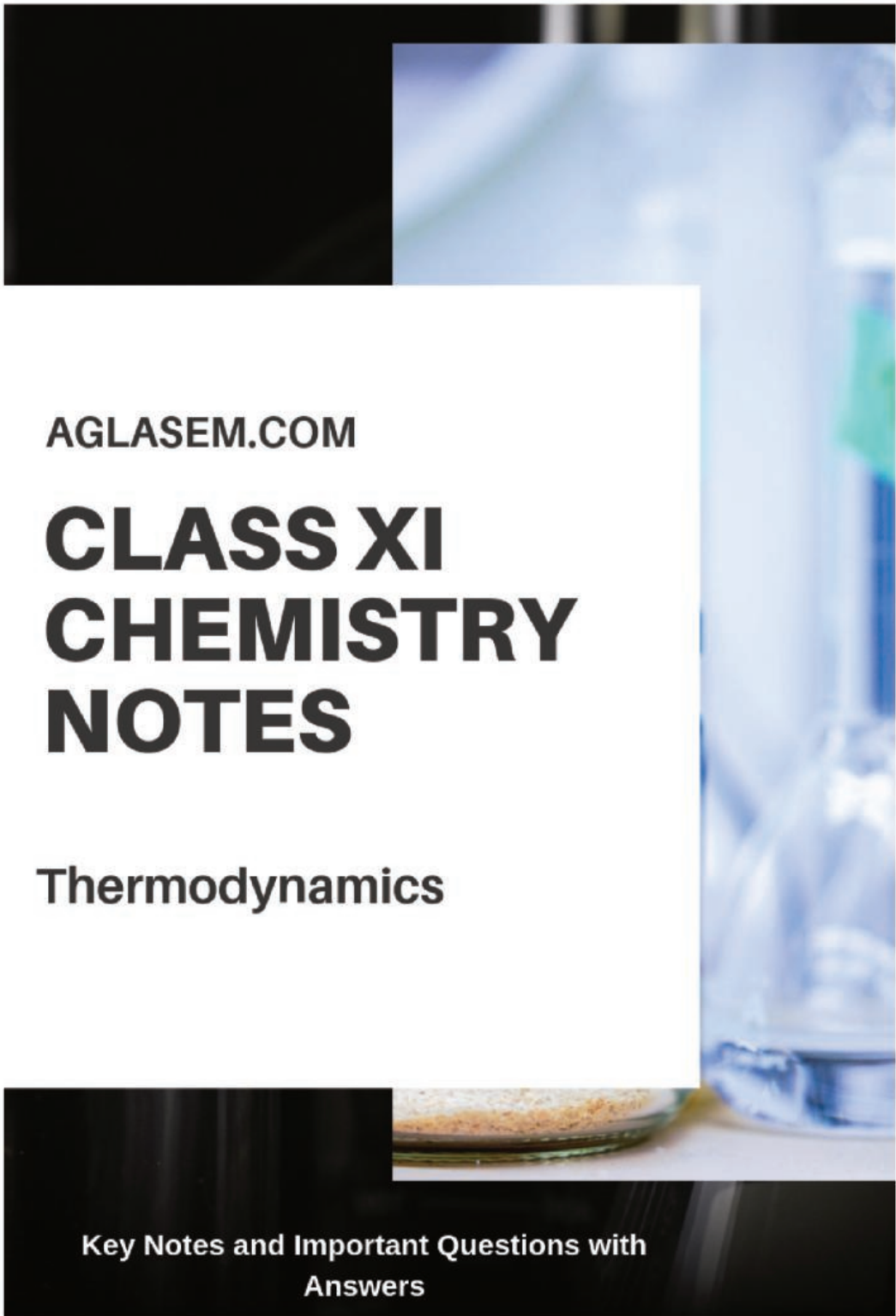


The background of the cover features a photograph of laboratory glassware, including a large Erlenmeyer flask and a beaker, both containing liquids. The image is partially obscured by a white rectangular area containing the text.

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CLASS XI CHEMISTRY NOTES

Thermodynamics

**Key Notes and Important Questions with
Answers**



Chapter - 6

Chemical Thermodynamic

- **System** : Specific part of universe in which thermodynamic 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 : Reactants 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. 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), etc.
- **Internal Energy (U) :** 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°C or 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 ($\Delta_f H^\theta$)** : 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).

- $\Delta_f H^\theta$ of an element in standard state is taken as zero.
- Compounds with – ve value of $\Delta_f H^\theta$ are more stable than their constituents.
- $\Delta_r H^\theta = \sum_i a_i \Delta_f H^\theta (\text{products}) - \sum_i b_i \Delta_f H^\theta (\text{reactants})$: Where ‘a’ and ‘b’ are coefficients of products and reactants in balanced equation.

- **Standard Enthalpy of Combustion ($\Delta_c H^\theta$)** : 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 : $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g})$; $\Delta_{\text{Cl-Cl}} H^\theta = 242 \text{ kJ mol}^{-1}$.

- (i) For diatomic gaseous molecules; Bond enthalpy = Bond dissociation Enthalpy = Atomization Enthalpy.

- (ii) For Polyatomic gaseous molecules; Bond Enthalpy = Average of the bond dissociation enthalpies of the bonds of the same type.

- $\Delta_r H^\theta = \sum \Delta_{\text{bond}} H^\theta (\text{Reactants}) - \sum \Delta_{\text{bond}} H^\theta (\text{Products})$.

- **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 be positive.

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

- **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 non-spontaneous
- (iii) If $\Delta G = 0$, the process is in equilibrium
- **Relation between Gibbs Energy Change and Equilibrium Constant :**
 $\Delta G^\theta = -2.303 RT \log K_c$.
- **Third law of thermodynamic :** The entropy of a perfectly crystalline solid at absolute zero (0 K) is taken to be zero.

1 - Mark Questions

1. 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.
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 :
 $\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$.

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 : – Br_2 , Cl_2 , CH_4 .
[Hint : Cl_2 (Br_2 is liquid at 298K)]
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?
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

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]

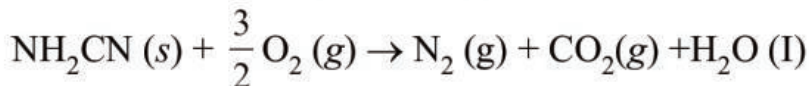
2. Neither q nor w is state functions but $q + w$ is a state function. Explain.
3. Classify the following as extensive or intensive properties :
Heat capacity, Density, Temperature, Molar heat capacity.
4. Derive the relationship between ΔH and ΔU .
5. Derive the relationship $C_p - C_v = R$.
6. A 1.25g sample of octane (C_8H_{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.
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.
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 $\text{H}_2\text{O}(\text{l})$ is formed under standard conditions; $\Delta_f H^\theta = -286 \text{ kJ mol}^{-1}$.
[Ans. $959.7 \text{ J K}^{-1} \text{ mol}^{-1}$]
16. The enthalpy of vaporization of a liquid is 30 kJ mol^{-1} and entropy of vaporization is $75 \text{ J K}^{-1} \text{ mol}^{-1}$. Calculate the boiling point of liquid at 1 atm.
[Ans. 400 K]
17. The equilibrium constant for a reaction is 10. What will be the value of ΔG^θ ? $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 300 \text{ K}$.
[Ans. $-5.527 \text{ kJ mol}^{-1}$]
18. Derive the relationship, $\Delta G = -T\Delta S_{\text{total}}$ for a system.
19. The ΔH and ΔS for $2\text{Ag}_2\text{O}(\text{s}) \rightarrow 4\text{Ag}(\text{s}) + \text{O}_2(\text{g})$ are given $61.17 \text{ kJ mol}^{-1}$ and $132 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively. Above what temperature will the reaction be spontaneous ?
[Ans. $> 463.4 \text{ K}$]

3 - Mark Questions

1. Differentiate between the following (with examples) :
- (i) Open and Closed System.
 - (ii) Adiabatic and Isothermal process
 - (iii) State function and path function
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 $24 \text{ J mol}^{-1} \text{ K}^{-1}$.
[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 $-742.7 \text{ kJ mol}^{-1}$ at 298K. Calculate Enthalpy change for the reaction at 298K,



[Ans. $-741.5 \text{ kJ mol}^{-1}$]

5. The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are $-890.3 \text{ kJ mol}^{-1}$, $-393.5 \text{ kJ mol}^{-1}$ and $-285.8 \text{ kJ mol}^{-1}$ 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 $\text{CO}(g)$, $\text{CO}_2(g)$, $\text{N}_2\text{O}(g)$ and $\text{N}_2\text{O}_4(g)$ are -110 , -393 , 81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H^\circ$ for the reaction; $\text{N}_2\text{O}_4(g) + 3\text{CO}(g) \rightarrow \text{N}_2\text{O}(g) + 3\text{CO}_2(g)$.

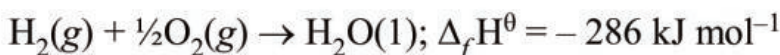
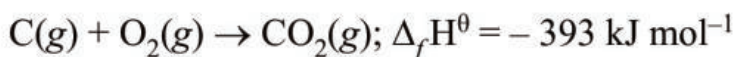
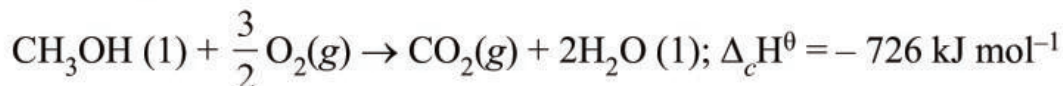
[Ans. $-777.7 \text{ kJ mol}^{-1}$]

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}]

10. For oxidation of iron, $4 \text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$ 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.

12. For the reaction at 298 K, $2A + B \rightarrow C$; $\Delta H = 400 \text{ kJ mol}^{-1}$, $\Delta S = 0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}$. 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

- (i) Sign of ΔS for this reaction.
- (ii) Sign of ΔG for $Y \rightarrow X$
- (iii) Sign of ΔG at a temperature $< T$.

5 - Mark Questions

1. (a) What is reversible process in Thermodynamics?

(b) Name the thermodynamic processes for which : (i) $q = 0$ (ii) $\Delta U = 0$
(iii) $\Delta V = 0$ (iv) $\Delta P = 0$.

(c) 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.

2. (a) 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 $q_p = \Delta H$]

(b) It has been found that 221.4 J is needed to heat 30g of ethanol from 15°C to 18°C . Calculate (a) specific heat capacity, and (b) molar heat capacity of ethanol. [Ans. (a) $2.46 \text{ Jg}^{-1}\text{C}^{-1}$, (b) $113.2 \text{ J mol}^{-1}\text{C}^{-1}$]

3. (a) Differentiate the terms Bond dissociation enthalpy and Bond Enthalpy.

(b) Calculate enthalpy change for the process $\text{CCl}_4(\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{Cl}(\text{g})$ and calculate Bond enthalpy of C-Cl bond in CCl_4 . Given : $\Delta_{\text{vap}} H^\theta(\text{CCl}_4) = 30.5 \text{ kJ mol}^{-1}$; $\Delta_f H^\theta(\text{CCl}_4) = -135.5 \text{ kJ mol}^{-1}$; $\Delta_a H^\theta(\text{C}) = 715 \text{ kJ mol}^{-1}$ and $\Delta_a H^\theta(\text{Cl}_2) = 242 \text{ kJ mol}^{-1}$. [Ans. 1304 kJ mol⁻¹, 326 kJ mol⁻¹]

4. Predict the sign of ΔS for the following changes :

(i) Freezing of water,

(ii) $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{diamond})$

(iii) $\text{H}_2(\text{g})$ at 298 K and 1 bar $\rightarrow \text{H}_2(\text{g})$ at 298 K and 10 bar

(iv) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$

(v) $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$

5. (i) Define Gibbs free energy. Give its mathematical expression. What is Gibb's energy criteria of spontaneity.

(ii) For the reaction : $2\text{A}(\text{g}) + \text{B}(\text{g}) \rightarrow 2\text{D}(\text{g})$, $\Delta U^\theta = -10.5 \text{ kJ}$ and $\Delta S^\theta = -44.1 \text{ J K}^{-1}$. Calculate $\Delta_r G^\theta$ for the reaction, and predict whether will occur spontaneously. [Ans. $\Delta_r G^\theta = +0.16 \text{ kJ}$, Non spontaneous]

