

## THERMODYNAMICS

### Topic: 5

Gibbs free energy, concept, applications to spontaneous and non-spontaneous processes

### VERY SHORT ANSWER QUESTIONS

#### 1. What is Gibbs energy?

**Gibbs energy (G):** The amount of energy available from a system which can be put to useful work at constant temperature and pressure is called Gibb's energy.

For explaining the criteria for spontaneity of a reaction, Gibb's introduced thermodynamic function which involved both enthalpy (H) and entropy (S) functions. This is known as free energy function (G)

This is given by the equation,  $G = H - TS$

Where 'G' is known as Gibbs energy (or) Gibbs function.

#### 2. What is Gibbs equation?

**Ans. Gibbs equation:** For explaining the criteria for spontaneity of a reaction, Gibbs introduced thermodynamic function which involved both enthalpy (H) and entropy (S) functions. This is known as free energy function (G).

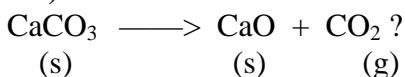
This is given by the equation,  $G = H - TS$

Where 'G' is known as Gibbs energy (or) Gibbs function.

$$\Delta G = \Delta H - T\Delta S$$

### SHORT ANSWER QUESTIONS

#### 1. How are $\Delta H$ and $\Delta E$ related for a gaseous equilibrium reaction? What is ( $\Delta H - \Delta E$ ) for



Relation between  $\Delta H$  and  $\Delta E$  for gaseous reactions is

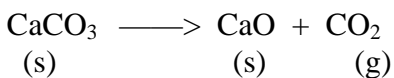
$$\Delta H = \Delta E + \Delta n RT$$

$\Delta n = [\text{total no. of molecules of gaseous products}] - [\text{total no. of molecules of gaseous reactants}]$

R = gas constant

T = temperature in kelvin scale ( $t^{\circ}\text{C} + 273$ )

**Solutions:**



$$\Delta n = [(1 + 0) - 0] = 1 \quad (\because \text{only gaseous molecules are taken into consideration})$$

$$\therefore \Delta H = \Delta E + \Delta n RT$$

$$\Rightarrow \Delta H - \Delta E = \Delta n RT$$

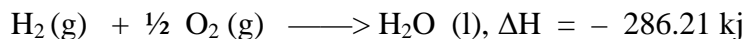
$$\text{But } \Delta n = 1$$

$$\therefore (\Delta H - \Delta E) = 1 \times RT = RT$$

$$\therefore \Delta H - \Delta E = RT$$

**2. Define and explain “heat of formation” of a compound.**

**Ans: Heat of formation ( $\Delta H_f$ ):** The amount of heat evolved (or) absorbed during the formation of one mole of the compound at constant temperature from the constituent elements in the standard state is heat of formation.



Compounds which liberate heat in their formation reaction from constituent elements are called exothermic compounds.

For this reactions,  $\Delta H_f = \text{negative}$

Compounds which absorb heat in the formation reaction from the constituent elements are called endothermic compounds.

For this reactions,  $\Delta H_f = \text{positive}$ .

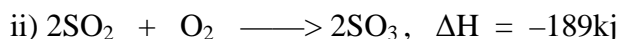
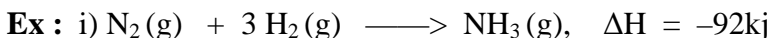
### 3. Define and explain “heat of reaction”.

**Ans. Heat of reaction:** The heat of reaction is the quantity of heat evolved or absorbed at constant temperature when the reactants of a reaction undergo complete transformation into the products as per the stoichiometric equation.

Heat of reaction = Heat content of products – Heat content of reactants

(or) Heat of reaction = enthalpy of products – enthalpy of reactants

$$(or) \Delta H = H_p - H_r$$



## LONG ANSWER QUESTIONS

### 10. Explain Gibbs energy, enthalpy, entropy

**Ans: Enthalpy (H):** Enthalpy is the amount of heat exchanged by a system with its surroundings at constant pressure and temperature.

The energy change taking place at constant pressure and at a constant temperature is called enthalpy change ( $\Delta H$ ).

Mathematically  $\Delta H = \Delta E + P \cdot \Delta V$ . When  $\Delta E$  = Internal energy change.

Enthalpy is state function. Thus, the magnitude of enthalpy change depends only upon the enthalpies in the initial and the final states.

$$\Delta H = [H_{\text{products}} - H_{\text{reactants}}]$$

For gaseous reactions,  $\Delta H = \Delta E + \Delta nRT$

**Entropy(S):** Entropy is taken as a measure of disorder of molecules (or) randomness of the system. It depends on the temperature, pressure of the state.

$$\text{Entropy change, } \Delta S = \frac{q_{\text{rev}}}{T} \quad [q_{\text{rev}} = \text{heat absorbed by the system isothermally and reversibly at } T]$$

For a spontaneous process in an isolated system the entropy change is positive.

$$(\Delta S = \text{positive})$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

**Gibbs energy ( $\Delta G$ ):** The amount of energy available from a system which can be put to useful work at constant temperature and pressure is called Gibb's energy. For explaining the criteria for spontaneity of a reaction, Gibb's introduced thermodynamic function which involved both enthalpy (H) and entropy (S) functions. This is known as free energy function (G). This is given by the equation,  $G = H - TS$ .

Where 'G' is known as Gibbs energy (or) Gibbs function.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G_{\text{sys}} = \text{negative for spontaneous reactions } (\Delta G < 0)$$

$$\Delta G_{\text{sys}} = \text{positive for non - spontaneous reactions } (\Delta G > 0)$$

$$\Delta G_{\text{sys}} = \text{Zero for equilibrium reactions } (\Delta G = 0)$$

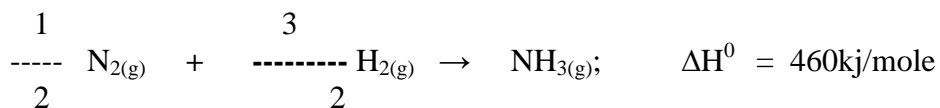
### SELECTED NUMERICALS WITH PROBLEMS

**1. The bond enthalpy of  $\text{H}_{2(g)}$  is 436kJ/mole. The bond enthalpy of  $\text{N}_{2(g)}$  is 941.3 kJ/mole.**

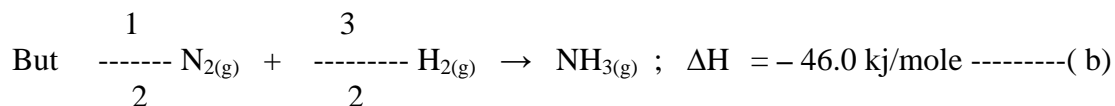
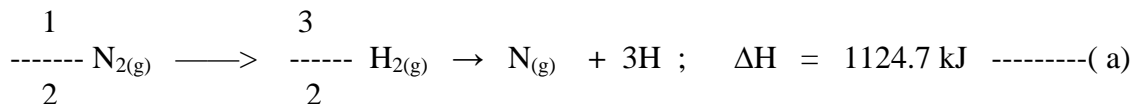
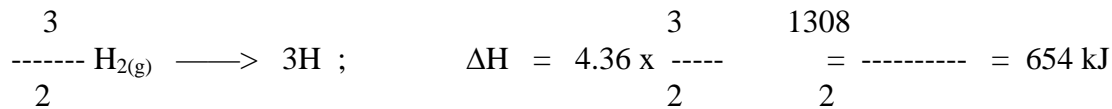
**What is the bond enthalpy of N-H in  $\text{NH}_{3(g)}$ ?  $\text{NH}_3$  formation energy - 46.0 kJ/mole**

**Sol:**  $\text{N}_{2(g)} \longrightarrow 2 \text{N}_{(g)} ; \Delta H^0 = 941.3 \text{ kJ/mole}$

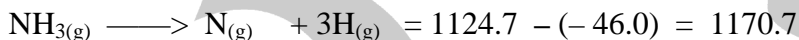
$\text{H}_{2(g)} \longrightarrow 2\text{H}_{(g)} ; \Delta H^0 = 436 \text{ kJ/mole}$



$$\therefore \frac{1}{2} \text{N}_{2(g)} \longrightarrow 1\text{N}_{(g)} ; \quad \Delta H = \frac{941.3}{2} = 470.7 \text{ kJ}$$



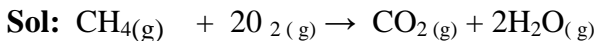
Subtracting ( b) from (a)



Dividing by 3, we have bond dissociation energy of N – H bond

$$= \frac{1170.7}{3} = 390.2 \text{ kJ/mole}$$

**2. In combustion reaction of methane to give  $\text{CO}_2$  and  $\text{H}_2\text{O}$ : the relation between  $\Delta H$  and  $\Delta E$  is**



$$\Delta H = \Delta E \quad \because \Delta n = 3 - 3 = 0$$

**3. Calculate the ionization enthalpy of  $\text{NH}_4\text{OH}$  from  $\Delta H$  of neutralization of  $(\text{HCl} + \text{NaOH}) (-57.4 \text{ kJ})$ ,  $(\text{HCl} + \text{NH}_4\text{OH}) (-51.46 \text{ kJ})$**

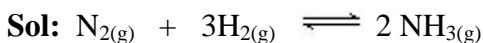
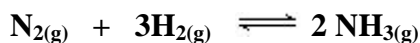


$$= \Delta H \text{ of ionization } \text{NH}_4\text{OH}$$

$$\Delta H = \{ (-51.46) - (-57.40) \} \text{ kJ}$$

$$\Delta H = \{ 57.40 - 51.46 \} = 5.94 \text{ kJ}$$

4. Calculate the difference between  $\Delta H$  and  $\Delta E$  for the reaction at  $527^{\circ}\text{C}$  in k. Cal.



$$\Delta n = \{ 2 - (1+3) \} = -2$$

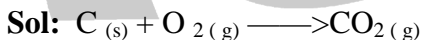
$$\Delta H = \Delta E + \Delta n (RT); T = 527 + 273 = 800\text{K}$$

$$(\Delta H - \Delta E) = \Delta n (RT) = (-2) \times (2 \times 10^{-3}) \times 800 \text{ k.cals}$$

$$= -2 \times 2 \times 10^{-3} \times 10^2 \times 8$$

$$= -32 \times 10^{-1} = -3.2 \text{ k.cals}$$

5. What is  $\Delta E$  for the reaction in kJ.  $\text{C}_{(\text{s})} + \text{O}_{2(\text{g})} \longrightarrow \text{CO}_{2(\text{g})}$  at  $327^{\circ}\text{C}$  if  $\Delta H$  is  $-393.5 \text{ kJ}$



$$\Delta n = (1 - 1) = 0 \quad [ \because \text{C} = \text{solid} ]$$

$$T = 327^{\circ}\text{C} + 273 = 600 \text{ K}$$

$$R = 8.3 \times 10^{-3} \text{ kJ}$$

$$\Delta H = \Delta E + \Delta n RT$$

$$= \Delta E + 0 \times R \times T = \Delta E$$

$$\therefore \Delta E = -393.5 \text{ kJ}$$

6.  $\Delta H$  for the reaction.  $\text{H}_{2(\text{g})} + \text{Cl}_{2(\text{g})} \longrightarrow 2\text{HCl}_{(\text{g})}$  is  $-184.6 \text{ kJ}$ . What is heat of formation of HCl

**Sol:** Heat of formation is  $\Delta H$  for 1 mole

$$\therefore \Delta H = -\frac{184.6}{2} = -92.3 \text{ kJ}$$

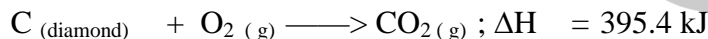
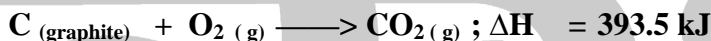
7. The heat evolved when 10 grms of CH<sub>4</sub> is burnt in excess O<sub>2</sub> is 558.6 kJ. Calculate heat of combustion of CH<sub>4</sub>.

**Sol:** Heat of combustion of CH<sub>4</sub> is heat evolved when 16g of CH<sub>4</sub> is burnt in an excess oxygen.

For 10gms  $\longrightarrow$  - 558.6 kJ of heat is evolved.

$$16 \text{ grms} \longrightarrow -\frac{558.6}{10} \times 16 = -893.76 \text{ kJ heat is evolved.}$$

8. Calculate  $\Delta H$  For C<sub>(graphite)</sub>  $\rightarrow$  C<sub>(diamond)</sub> from the equations.



On subtraction C<sub>(graphite)</sub> - C<sub>(diamond)</sub> = - 393.5 - (- 395.4)

$$\Delta H = + 1.9 \text{ kJ}$$

9. Heat of reaction for HCl<sub>(aq)</sub> + NaOH  $\longrightarrow$  NaCl<sub>(aq)</sub> + H<sub>2</sub>O<sub>(l)</sub>

$\Delta H = -57.3 \text{ kJ}$ . Heat of reaction for HCl<sub>(aq)</sub> + NH<sub>4</sub>OH<sub>(aq)</sub>  $\longrightarrow$  NH<sub>4</sub>Cl<sub>(aq)</sub> + H<sub>2</sub>O<sub>(l)</sub>;

$\Delta H = -51.46 \text{ kJ}$ . Calculate heat of ionization of NH<sub>4</sub>OH<sub>(aq)</sub>.

**Sol:** Heat ionization of NH<sub>4</sub>OH

[Heat of neutralization of (NH<sub>4</sub>OH + HCl) - Heat of neutralization of (NaOH + HCl)]

$$= 51.46 \text{ kJ} - (-57.3)$$

$$= 57.3 - 51.46 = + 5.84 \text{ kJ}$$

### **IMPORTANT QUESTIONS**

#### **I. Long answer questions.**

1. Give the criteria for spontaneity of a reaction.
2. What is the heat of neutralization? How does its value change with the chemical nature of the acid and base? Give reasons.
3. State Hess's law of constant heat formation and explain it with an example.
4. What is  $C_p$  and  $C_v$  ?

#### **II. Short answer questions.**

1. State first law of thermodynamics
2. State second law of thermodynamics
3. Define Gibbs energy.
4. What is absolute entropy?
5. Explain the terms 'entropy', 'Gibb's Free energy' with examples.
6. State and explain enthalpy and internal energy in terms of a substance.
7. Define and explain heat of formation of a compound.

#### **III. Very short answer questions.**

1. Define and explain heat of a reaction.
2. Name three intensive properties.
3. Name three extensive properties.
4. What is heat capacity? Explain.
5. What is Gibb's equation?