

CHAPTER 6 **THERMODYNAMICS**

Brief Summary of the chapter:

1. Thermodynamics: Science which deals with study of different forms of energy and quantitative relationship.
2. System & Surroundings: The part of universe for study is called system and remaining portion is surroundings.
3. State of system & state function: State of system is described in terms of T, P, V etc. The property which depends only on state of system not upon path is called state function eg. P, V, T, E, H, S etc.
4. Extensive & Intensive Properties: Properties which depends on quantity of matter called extensive prop. eg. mass, volume, heat capacity, enthalpy, entropy etc. The properties which do not depends on matter present depends upon nature of substance called Intensive properties. eg. T, P, density, refractive index, viscosity, bp, pH, mole fraction etc.
5. Internal energy: The total energy with a system.
i.e. $U = E_e + E_n + E_c + E_p + E_k + \dots$
 $\Delta U = U_2 - U_1$ or $U_P - U_R$ & U is state function and extensive properly. If $U_1 > U_2$ energy is released.
6. Heat (q): It is a form of energy which is exchanged between system and surrounding due to difference of temperature. Unit is Joule (J) or Calorie (1 Calorie = 4.18 J).
7. First Law of Thermodynamics: It is law of conservation energy. Energy can neither be created nor destroyed, it may be converted from one form into another.

Mathematically $\Delta U = q + w$, $w = -p \cdot \Delta V$ (work of expansion)

$\Delta U = q - p \cdot \Delta V$ or $q = \Delta U + p \cdot \Delta V$, q, w are not state function.

But ΔU is state function.

8. Enthalpy (H): At constant volume $\Delta V = 0$, $\rightarrow q_v = \Delta U$

So $H = U + p \cdot \Delta V$, $q_p = H_2 - H_1 = \Delta H$

$$\Rightarrow \Delta H = \Delta U + P \cdot \Delta V.$$

9. Relationship between q_p , q_v i.e. ΔH & ΔU

It is $\Delta H = \Delta U + \Delta n_g \cdot RT$ or $q_p = q_v + \Delta n_g \cdot RT$

10. Exothermic and Endothermic reactions: $\Delta H = -Ve$ for exothermic and $\Delta H = +Ve$ for endothermic reaction i.e. evolution and absorption of heat.

Eg $C + O_2 \rightarrow CO_2 + 393.5 \text{ KJ}$, $\Delta H = -393.5 \text{ KJ}$ (exothermic)

$N_2 + O_2 \rightarrow 2NO - 180.7 \text{ KJ}$, $\Delta H = 180.7 \text{ KJ}$ (Endothermic)

11. Enthalpy of reaction ($\Delta_r H$): The amount of heat evolved or absorbed when the reaction is completed.
12. Standard Enthalpy of reaction ($\Delta_r H^0$) at 1 bar pressure and specific temp. (290K) i.e. standard state.
13. Different types of Enthalpies of reactions:

- | | |
|--|--|
| (i) Enthalpy of combustion ($\Delta_c H$), | (ii) Enthalpy of formation ($\Delta_f H$) |
| (iii) Enthalpy of neutralization | (iv) Enthalpy of solution |
| (v) Enthalpy of atomization ($\Delta_a H$), | (vi) Enthalpy of Ionisation ($\Delta_i H$) |
| (vii) Enthalpy of Hydration ($\Delta_{hyd} H$) | (viii) Enthalpy of fusion ($\Delta_{fus} H$) |
| (ix) Enthalpy of vaporization ($\Delta_{vap} H$) | (x) Enthalpy of sublimation ($\Delta_{sub} H$) |

$$(\Delta_{sub} H) = \Delta_{fus} H - \Delta_{vap} H$$

14. Hess's Law of constant heat summation: The total amount of heat change is same whether the reaction takes place in one step or in several steps.

i.e. $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \dots$

15. Bond enthalpy: It is amount of energy released when gaseous atoms combines to form one mole of bonds between them or heat absorbed when one mole of bonds between them are broken to give free gaseous atoms.
Further $\Delta_r H = \Sigma B.E. (\text{Reactants}) - \Sigma B.E. (\text{Products})$
16. Spontaneous & Non Spontaneous Processes: A process which can take place by itself is called spontaneous process. A process which can neither take place by itself or by initiation is called non Spontaneous.
17. Driving forces for spontaneous process: (i) Tendency for minimum energy state. (ii) Tendency for maximum randomness.
18. Entropy (S): It is measure of randomness or disorder of system.

i.e. Gas > Liquid > Solid.

$$\text{Entropy change } (\Delta S) = \frac{q_{(\text{rev.})}}{T} \text{ J.K}^{-1}.\text{mol}^{-1}$$

19. Spontaneity in term of (ΔS)

$$\Delta S_{(\text{total})} = \Delta S_{(\text{universe})} = \Delta S_{(\text{system})} + \Delta S_{(\text{surrounding})}$$

If $\Delta S_{(\text{total})}$ is +ve, the process is spontaneous.

If $\Delta S_{(\text{total})}$ is -ve, the process is non spontaneous.

20. Second Law of thermodynamics: In any spontaneous process, the entropy of the universe always increases. A spontaneous process cannot be reversed.
21. Gibb's free energy (G): defined as $G = H - T.S$ & $\Delta G = \Delta H - T. \Delta S$ (Gibb's Helmholtz equation) it is equal useful work i.e. $-\Delta G = W_{(\text{useful})} = W_{(\text{max.})}$

If $\Delta G = \text{ve}$, process is spontaneous.
22. Effects of T on spontaneity of a process: $\Delta G = \Delta H - T. \Delta S$.

(i) For endothermic process may be non spontaneous at low temp.

(ii) For exothermic process may be non spontaneous at high temp. and spontaneous at low temp.

23. Calculation of ($\Delta_r G^0$)

$$\Delta_r G^0 = \sum \Delta_f G^0 (p) - \sum \Delta_f G^0 (r)$$

24. Relationship between ($\Delta_r G^0$) & equilibrium constant (k)

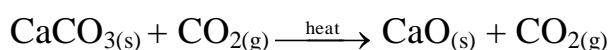
$$\Delta G = \Delta G^0 + RT \ln Q \text{ \& } \Delta G^0 = -2.303RT \log k.$$

25. Calculation of entropy change:

$$\Delta_r S^0 = \sum \Delta S^0 (p) - \sum S^0 (r)$$

ONE MARK QUESTIONS:

1. State First Law of thermodynamics.
2. What is a thermodynamic state function?
3. Give enthalpy (H) of all elements in their standard state.
4. From thermodynamic point to which system the animals and plants belong?
5. Predict the sign of ΔS for the following reactions.



6. For the reaction $2\text{Cl}_{(g)} \rightarrow \text{Cl}_{2(g)}$, What will be the sign of ΔH and ΔS ?
7. State Hess's Law for constant heat summation?
8. What is Gibbs's Helmholtz equation?
9. Define extensive properties.
10. Give relationship between ΔH , ΔU for a reaction in gaseous state.

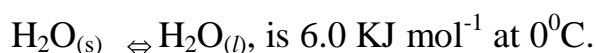
ANSWERS FOR ONE MARK QUESTIONS

1. Energy can neither be created nor destroyed. The energy of an isolated system is constant. $\Delta U = q + w$.
2. A function whose value is independent of path. eg. P, V, E, H
3. In standard state enthalpies of all elements is zero.
4. Open system.
5. ΔS is positive (entropy increases)
6. ΔH : (–ve) b/c energy is released in bond formation and
 ΔS : (–ve) b/c atoms combines to form molecules.
7. The change of enthalpy of reaction remains same, whether the reaction is carried out in one step or several steps.
8. $\Delta G = \Delta H - T. \Delta S$
9. Properties which depends upon amount of substance called extensive properties. Volume, enthalpy, entropy.
10. $\Delta H = \Delta U + ng. RT$.

TWO MARKS QUESTIONS:-

- Q.1 In a process, 701J heat is absorbed and 394J work is done by system. What is change in Internal energy for process?
- Q.2 Given: $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$, $\Delta_r H^0 = -92.4 \text{ KJ.mol}^{-1}$. What is the standard enthalpy of formation of $NH_{3(g)}$.
- Q.3 Calculate entropy change in surroundings when 1.0 mol of $H_2O(l)$ is formed under standard conditions? Given $\Delta H^0 = -286 \text{ KJ.mol}^{-1}$.
- Q.4 Give relationship between entropy change and heat absorbed/evolved in a reversible reaction at temperature T.
- Q.5 What is spontaneous change? Give one example.

- Q.6 A real crystal has more entropy than an Ideal Crystal. Why?
- Q.7 Under what condition, the heat evolved/absorbed in a reaction is equal to its free energy change?
- Q.8 Predict the entropy change in-
- A liquid crystallizes into solid
 - Temperature of a crystallize solid raised from OK to 115K
- Q.9 What is bond energy? Why is it called enthalpy of atomization?
- Q.10 Calculate entropy change for the following process.



ANSWER FOR TWO MARKS QUESTIONS:

- $q = 701\text{J}$, $w = 394\text{J}$, so $\Delta U = q + w = 701 - 394 = 307\text{J}$.
- $\Delta_f H^\ominus \text{NH}_{3(g)} = -\frac{92.4}{2} = 46.2 \text{ KJ} \cdot \text{mol}^{-1}$
- $q_{(\text{rev.})} = -\Delta H^0 = -286 \text{ KJmol}^{-1} = 286000 \text{ Jmol}^{-1}$

$$\Delta S = \frac{q_{(\text{rev.})}}{T} = \frac{286000 \text{ J} \cdot \text{mol}^{-1}}{298 \text{ K}} = 959 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$
- $$\Delta S = \frac{q_{(\text{rev})}}{T}$$
- A process which can take place of its own or initiate under some condition.
eg. Common salt dissolve in water of its own.
- A real crystal has some disorder due to presence of defects in their structural arrangement, and Ideal crystal does not have any disorder.
- In $\Delta G = \Delta H - T \cdot \Delta S$, when reaction is carried out at OK or $\Delta S = 0$, then $\Delta G = \Delta H$.

8. (i) Entropy decreases b/c molecules attain an ordered state.
(ii) entropy increase b/c from 0K to 115K particles begin to move.
9. It is the amount of energy required to dissociate one mole of bonds present b/w atoms in gas phase. As molecules dissociates into atoms in gas phase so bond energy of diatomic molecules is called enthalpy of atomization.
10. $\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{H}_2\text{O}_{(l)}$ at 0°C , $\Delta_{\text{fus}}H = 6\text{KJ mol}^{-1}$
 $= 6000\text{J mol}^{-1}$

$$\Delta T_f = 0^\circ\text{C} = 0 + 273 = 273\text{K}$$

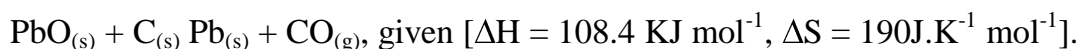
$$\text{Do } \Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T} = \frac{6000\text{J.mol}^{-1}}{273\text{K}} = 21.98\text{J.K}^{-1}\text{mol}^{-1}$$

THREE MARKS QUESTIONS:

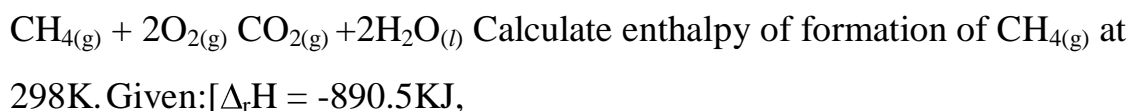
- Q.1 For oxidation of iron, $4\text{Fe}_{(s)} + 3\text{O}_{2(g)} \rightarrow 2\text{Fe}_2\text{O}_{3(s)}$
 ΔS is $-549.4\text{J.K}^{-1}\text{mol}^{-1}$, at 298K . In spite of $-ve$ entropy change of this reaction, Why the reaction is spontaneous? ($\Delta_r H^0 = -1648 \times 10^3\text{J.mol}^{-1}$)
- Q.2 Using the bond energy of $H_r = 435\text{KJ mol}^{-1}$, $Br_2 = 192\text{KJ mol}^{-1}$, $HBr = 368\text{KJ mol}^{-1}$. Calculate enthalpy change for the reaction $\text{H}_{2(g)} + \text{Br}_{2(g)} \rightarrow 2\text{HBr}_{(g)}$
- Q.3 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 9.7KJ mol^{-1} respectively. Find value $\Delta_r H$ for the reaction $\text{N}_2\text{O}_{4(g)} + 3\text{CO}_{(g)}$
- Q.4 For the reaction at 298K , $2A+B \rightarrow C$, $\Delta H = 400\text{KJ mol}^{-1}$, $\Delta S = 0.2\text{KJ mol}^{-1}\text{K}^{-1}$. At what temperature will the reaction become spontaneous, considering ΔH , ΔS be constant at the temp.
- Q.5 The equilibrium constant for a reaction is 10. What will be the value of ΔG^0 ? $R = 8.314\text{J.K}^{-1}\text{mol}^{-1}$ $T = 300\text{K}$.
- Q.6 What do you understand by state function? Neither q nor w is a state function but $q + w$ is a state function? Explain.
- Q.7 Justify the following statements:

- (i) An endothermic reaction is always thermodynamically spontaneous.
- (ii) The entropy always increases on going from liquid to vapour state at any temperature T.

Q.8 Calculate the temperature above which the reduction reaction becomes spontaneous:



Q.9 From the data given below at 298K for the reaction:



$[\Delta_f H_{(\text{CO}_2)} = -393.5 \text{ KJ.mol}^{-1}, \Delta_f H_{(\text{H}_2\text{O})} = -286.0 \text{ KJ.mol}^{-1}]$

Q.10 For the reaction $\text{NH}_4\text{Cl}_{(s)} \rightarrow \text{NH}_{3(g)} + \text{HCl}_{(g)}$ at 25°C enthalpy change $\Delta H = 177 \text{ KJ.mol}^{-1}$ and $\Delta S = 285 \text{ J.K}^{-1} \text{ mol}^{-1}$. Calculate free energy change ΔG at 25°C and predict whether the reaction is spontaneous or not.

ANSWER TO THREE MARKS QUESTIONS:

Ans.1 $\Delta_{(\text{surr.})} = -\frac{\Delta_r H^0}{T} = -\frac{C - 1648 \times 10^3 \text{ J.mol}^{-1}}{298 \text{ K}} = 5530 \text{ JK}^{-1} \text{ mol}^{-1}$.

& $\Delta S_{(\text{system})} = -549.4 \text{ JK}^{-1} \text{ mol}^{-1}$.

$\Delta_r S_{(\text{total})} = 5530 - 5494 = 4980.6 \text{ J.K}^{-1} \text{ mol}^{-1}$

Since $\Delta_r S_{(\text{total})}$ is +ve, so the reaction is spontaneous.

Ans.2 $\Delta_r H^0 = \Sigma \text{bond enthalpies}_{(\text{rect.})} - \Sigma \text{bond enthalpies}_{(\text{prod.})}$

$= [4 \text{H-H} + 3 \text{H-Br}] - [4 \text{H-H} + 2 \text{H-Br}]$

$= [435 - 192] - [2 \times 368] \text{ KJ mol}^{-1}$

$= 627 - 736 = -109 \text{ KJ. Mol}^{-1}$ Ans.

Ans.3 $\Delta_r H = \Delta_f H^0_{(\text{prod.})} - \Delta_f H^0_{(\text{rect.})}$

$= [\Delta_f H^0_{(\text{N}_2\text{O})} + 3\Delta_f H^0_{(\text{CO}_2)}] - [\Delta_f H^0_{\text{N}_2\text{O}_4} + 3\Delta_f H^0_{(\text{CO})}]$

$= [81 + 3(-393)] - [9.7 + (-110)]$

$$= [81 + 1179] - [9.7 - 330] = -777.7 \text{ KJ}$$

Ans.4 $\Delta H = 400 \text{ KJ mol}^{-1}$, $\Delta S = 0.2 \text{ KJK}^{-1} \text{ mol}^{-1}$.

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

$$0 = 400 - 0.2 \times T \quad (\Delta G = 0 \text{ at equilibrium})$$

$$T = \frac{400}{0.2} = 2000 \text{ K}, \text{ so reaction will be spontaneous above } 2000 \text{ K}.$$

Ans.5 $\Delta_r G^0 = -2.303 RT \log K$

$$= -2.303 \times 8.314 \times 300 \times \log 10$$

$$= -19.147 \times 300 \times 1 = -5744.1 \text{ J}$$

$$\Delta_r G^0 = -5.7441 \text{ KJ.mol}^{-1}$$

Ans.6 The property whose value depends upon state of system and is independent of path. $q + w = \Delta U$, which is a state function as value of ΔU does not depend upon path.

Ans.7 (a) It is false, exothermic reaction is not always spontaneous. If $\Delta S = +ve$ and $T. \Delta S > \Delta H$. The process will be non spontaneous even it. It is endothermic.

(b) The entropy of vapour is more than that of liquid, so entropy increases during vaporization.

Ans.8 $\Delta G = \Delta H - T. \Delta S$, at equilibrium $\Delta G = 0$, $\Rightarrow \Delta H = T. \Delta S$

$$\Rightarrow T = \frac{\Delta H}{\Delta S} = \frac{108.4 \times 10^3 \text{ J.mol}^{-1}}{190 \text{ J.K}^{-1} \text{ mol}^{-1}} = 570.526 \text{ K}$$

So the reaction will be spontaneous above 570.52 K, as above this temperature ΔG will be -ve.

Ans.9 $\Delta_r H = \Delta_f H_{(\text{CO}_2)} + 2\Delta_f H_{\text{CH}_4(\text{g})} - \Delta_f H_{(\text{O}_2)}$

$$-890.5 \text{ KJ} = -393.5 \text{ KJ} + 2v - 286 - \Delta H_f(\text{CH}_4) - 0$$

$$= \Delta H_f(\text{CH}_4) = -75.0 \text{ KJ.mol}^{-1}.$$

$$= \Delta H_{f(\text{CH}_4)} = -75.0 \text{ KJ.mol}^{-1}.$$

Ans.10 $\Delta H = 177 \text{ KJ mol}^{-1}$, $\Delta S = 285 \text{ JK}^{-1} \text{ mol}^{-1}$

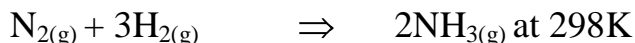
$$\Delta G = \Delta H - T. \Delta S = 177 \text{ KJ} - \frac{298 \times 285}{1000} \text{ KJ}$$

$$= 177 \text{ KJ} - 84.93 \text{ KJ} = 92.07 \text{ KJ.mol}^{-1}.$$

Since ΔG is +ve, so the reaction is non spontaneous.

FIVE MARKS QUESTIONS:-

Q.1 What is entropy? Why is the entropy of a substance taken as zero at 0K? Calculate the $\Delta_r G$ for the reaction?



The value of equilibrium constant (K) is 6.6×10^5 , $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$.

Ans: It is measure of randomness or disorder of system.

Because at 0 K there is complete order in the system.

$$\Delta G^0 = -2.303 RT \log K = -2.303 \times 8.314 \times 298 \times \log 6.6 \times 10^5$$

$$= -5705.8 [\log 6.6 + \log 10^5]$$

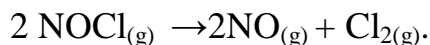
$$= -5705.8 [0.8195 + 5.0] = -5705.8 + 5.8195J$$

$$= -33204.903J$$

$$\Delta G^0 = -33.205 \text{ KJ mol}^{-1}.$$

Q.2 (i) What are extensive property and intensive properties?

(ii) Calculate the value of equilibrium constant (K) at 400K for



$$\Delta H^0 = 77.2 \text{ KJ.mol}^{-1}, \Delta S^0 = 122 \text{ J.K}^{-1} \text{ mol}^{-1} \text{ at } 400\text{K}, R = 8.314 \text{ J.K}^{-1} \text{ mol}^{-1}.$$

Ans. (i) An **extensive property** is a property whose value depends on the quantity or size of matter present in the system Those properties which do not depend on the quantity or size of matter present are known as **intensive properties**

$$(ii) \Delta H^0 = \Delta H^0 - T. \Delta S^0 = 77.2 \text{ KJ} - \frac{400 \times 122}{1000} \text{ KJ.mol}^{-1}$$

$$= 77.2 - 48.8 = 28.4 \text{ KJ mol}^{-1}$$

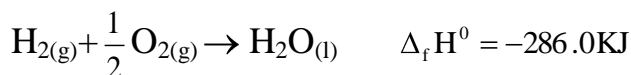
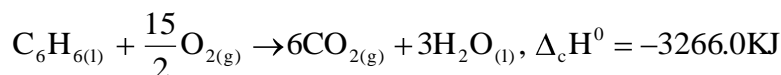
$$\text{and } \Delta G^0 = -2.303 RT \log K.$$

$$28400 = -2.303 \times 8.314 \times 400 \log K.$$

$$\log K = \frac{7.1}{2.303 \times 8.314} = -3.7081 = \bar{4}.2919K$$

$$K - \text{antilog } (\bar{4}.2919) = 1.95 \times 10^{-4} \text{ Ans.}$$

Q.3 Define standard enthalpy of formation. Calculate the enthalpy of formation of benzene from data



Ans. The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation.

$$\Delta_c H^0 = 6\Delta_f H^0_{(\text{CO}_2)} + 3\Delta_f H^0_{(\text{H}_2\text{O})} - \Delta_f H^0_{(\text{C}_6\text{H}_6)} - \frac{15}{2}\Delta H^0_{f(\text{O}_2)}$$

$$= -3266\text{KJ} = 6 \times -393.1 + 3 \times -286 - \Delta_f H^0_{(\text{C}_6\text{H}_6)} - 0$$

$$= -3218 \text{ kJ/mol}$$

HOTS QUESTIONS

1. Why standard entropy of an elementary substance is not zero whereas standard enthalpy of formation is taken as zero?

Ans. A substance has a perfectly ordered arrangement only at absolute zero. Hence, entropy is zero only at absolute zero. Enthalpy of formation is the heat change involved in the formation of one mole of the substance from its elements. An element formed from it means no heat change.

2. The equilibrium constant for a reaction is one or more if ΔG° for it is less than zero. Explain

Ans. $-\Delta G^\circ = RT \ln K$, thus if ΔG° is less than zero, i.e., it is negative, then $\ln K$ will be positive and hence K will be greater than one.

3. Many thermodynamically feasible reactions do not occur under ordinary conditions. Why?

Ans. Under ordinary conditions, the average energy of the reactants may be less than threshold energy. They require some activation energy to initiate the reaction.