

Chapter 6 Thermodynamics

Thermodynamics Laws in Pdf Notes Zeroth Law Second Law 3rd Law

Thermodynamics :

Science which deals with study of different forms of energy and quantitative relationship.

System & Surroundings :

The part of universe for study is called system and remaining portion is surroundings.

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.

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.

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.

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).

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 U is state function.

Enthalpy (H):

At constant volume $\Delta V = 0$, $q_v = \Delta H$ So $H = U + p \cdot V$, $\Delta H = \Delta U + p \cdot \Delta V$.

Relationship between q_p , q_v i.e. ΔH & ΔU It is $\Delta H = \Delta U + \Delta n_g RT$ or $q_p = q_v + \Delta n_g RT$

Exothermic and Endothermic reactions :

$\Delta H = -Ve$ for exothermic and $\Delta H = +Ve$ for endothermic reaction i.e. evolution and absorption of heat.
 $\text{Eg } C + O_2 \rightarrow CO_2 + 393.5 \text{ KJ}$, $H = -393.5 \text{ KJ}$ (exothermic) $N_2 + O_2 \rightarrow 2NO - 180.7 \text{ KJ}$, $H = 180.7 \text{ KJ}$ (Endothermic)

Enthalpy of reaction ($\Delta_r H$) :

The amount of heat evolved or absorbed when the reaction is completed.

Standard Enthalpy of reaction ($\Delta_r H^\circ$) at 1 bar pressure and specific temp. (290K) i.e. standard state.

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 ($\Delta_{sub} H$) |

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

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 $\Delta_r H = \sum B.E. (\text{Reactants}) - \sum B.E. (\text{Products})$

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.

Driving forces for spontaneous process :

- (i) Tendency for minimum energy state.
- (ii) Tendency for maximum randomness.

Entropy (S) :

It is measure of randomness or disorder of system.i.e. Gas>Liquid>Solid.

Spontaneity in term of (ΔS) $\Delta S_{(total)} = \Delta S_{(universe)} = \Delta S_{(system)} + \Delta S_{(surrounding)}$ If $\Delta S_{(total)}$ is +ve, the process is spontaneous If $\Delta S_{(total)}$ is -ve, the process is non spontaneous.

Second Law of thermodynamics :

In any spontaneous process, the entropy of the universe always increases. A spontaneous process cannot be reversed.

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 .e. $-\Delta G = W_{(useful)} = W_{(max)}$. If G is ve, process is spontaneous.

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.

Calculation of ($\Delta_r G^\circ$)

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

Relationship between ($\Delta_r G^\circ$) & equilibrium constant (K)

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

Calculation of entropy change:

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

SUMMARY

6. Thermodynamics

Some Important Points and Terms of the Chapter

1. **System and the Surroundings:** A system in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings. The surroundings include everything other than the system. System and the surroundings together constitute the universe. The wall that separates the system from the surroundings is called **boundary**
2. **Types of the System:**
 - **Open System:** In an open system, there is exchange of energy and matter between system and surroundings.
 - **Closed System** In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings.
 - **Isolated system** :In an isolated system, there is no exchange of energy or matter between the system and the surroundings
3. **State of a System:** The state of a system means the condition of the system which is described in terms of certain observable properties such as temp(T), pressure(p), volume (v), etc. of the systems. These properties of a system are called state variables.
4. **State Functions:** A physical quantity is said to be state functions of its value depends only upon the state of the system and does not depend upon the path by which this state has been attained.
5. **Internal Energy:** a quantity which represents the total energy of the system. It may be chemical, electrical and mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the internal energy, U of the system.

6. **Isothermal Process:** When a process is carried out in such a manner that the temp remains constant throughout this process, it is called an isothermal process.
7. **Adiabatic Process:** Process is carried out in such a manner that no heat can flow from the system to the surrounding or vice versa.
8. **Isochoric Process:** Process during which the volume of the system is kept constant.
9. **Isobaric Process:** Process during which the pressure of the system is kept constant. .
10. The positive sign expresses that Work (w_{ad}) is positive when work is done **on** the system. Similarly, if the work is done **by** the system, w_{ad} will be negative.
11. The q is positive, when heat is transferred from the surroundings to the system and q is negative when heat is transferred from system to the surroundings.
12. **First law of Thermodynamics:** Statement: Energy can neither be created nor destroyed, however it may be converted from one form to another.

or

The total energy of the universe remains constant although it may undergo transformation from one to another.

Mathematical expression = $\Delta U = q + w$

13. A process or change is said to be **reversible**, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. A **reversible process** proceeds infinitely slowly by a series of equilibrium states such that system and the surroundings are always in near equilibrium with each other. Processes other than reversible processes are known as **irreversible processes**.

14. Difference between Reversible Process & Irreversible Process

Reversible Process	Irreversible Process
<ol style="list-style-type: none"> 1. The process is carried out infinitesimally slowly 2. At any stage, the equilibrium is not disturbed 3. It takes infinite time for completion. 4. Work obtained in this process is maximum. 	<ol style="list-style-type: none"> 1. It is carried out rapidly 2. Equilibrium may exist only after the completion of the process. 3. It takes a finite time for completion. 4. Work obtained in this process is not maximum

15. **Enthalpy, H :** The enthalpy H [Greek word *enthalpien*, heat content] is defined as : $H = U + pV$ For finite changes at constant pressure, we can write above equation as $\Delta H = \Delta U + \Delta pV$ Since p is constant, we can write

$$\boxed{\Delta H = \Delta U + p\Delta V} \text{ since } p\Delta V = \Delta n_g RT, \text{ therefore } \boxed{\Delta H = \Delta U + \Delta n_g RT}$$

16. **Extensive property:** An extensive property is a property whose value depends on the quantity or size of matter present in the system. For example, mass, volume, internal energy, enthalpy, heat capacity, etc. are extensive properties.

17. **Intensive property:** Those properties which do not depend on the quantity or size of matter present are known as intensive properties. For example temperature, density, pressure etc. are intensive properties.

18. **Specific heat capacity** is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one kelvin). For finding out the heat, q , required to raise the temperatures of a sample, we multiply the specific heat of the substance, c , by the mass m , and temperatures change, ΔT as $q = c \times m \times \Delta T = C\Delta T$.

19. **Relationship between C_p and C_v for an ideal gas:** $\boxed{C_p - C_v = R}$

20. **Bomb calorimeter:** For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter . Here, a steel vessel (the bomb)

is immersed in a water bath. The whole device is called calorimeter. The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb calorimeter is sealed, its volume does not change i.e., the energy changes associated with reactions are measured at constant volume. Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as $\Delta V = 0$. Temperature change of the calorimeter produced by the completed reaction is then converted to q_V , by using the known heat capacity of the calorimeter with the help of equation (18).

21. **Enthalpy Change of a reaction:** The enthalpy change accompanying a reaction is called the reaction enthalpy. The enthalpy change of a chemical reaction is given by the symbol $\Delta_r H$.

$\Delta_r H = (\text{sum of enthalpies of products}) - (\text{sum of enthalpies of reactants}).$

$$\Delta_r H = \sum a_i H_{\text{Products}} - \sum b_i H_{\text{Reactants}}$$

22. The **standard enthalpy of reaction** is the enthalpy change for a reaction when all the participating substances are in their standard states. The standard state of a substance at a specified temperature is its pure form at 1 bar. Standard conditions are denoted by adding the superscript $^\circ$ to the symbol ΔH , e.g., ΔH°

23. The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called **standard enthalpy of fusion or molar enthalpy of fusion**, $\Delta_{\text{fus}} H^\circ$. e.g. $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l}); \Delta_{\text{fus}} H^\circ = 6.00 \text{ kJ mol}^{-1}$.

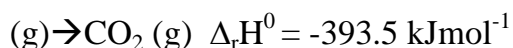
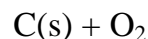
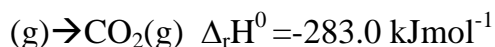
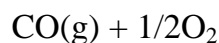
24. Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1 bar) is called its **standard enthalpy of vaporization or molar enthalpy of vaporization**, $\Delta_{\text{vap}} H^\circ$. e.g. $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g}); \Delta_{\text{vap}} H^\circ = 40.79 \text{ kJ mol}^{-1}$

25. **Standard enthalpy of sublimation**, $\Delta_{sub}H^0$ is the change in enthalpy when one mole of a solid substance sublimates at a constant temperature and under standard pressure (1bar). Sublimation is direct conversion of a solid into its vapour. Solid CO_2 (dry ice) sublimates at 195K with $\Delta_{sub}H^0=25.2 \text{ kJ mol}^{-1}$; naphthalene sublimates slowly and for this $\Delta_{sub}H^0=73.0 \text{ kJ mol}^{-1}$
26. 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. Its symbol is $\Delta_f H^0$.
27. **Standard enthalpy of combustion** is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the **reactants and products** being in their standard states at the specified temperature.
28. **Enthalpy of atomization (symbol: $\Delta_a H^0$)**: It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase. In case of diatomic molecules, like dihydrogen the enthalpy of atomization is also the bond dissociation enthalpy. In some cases, the enthalpy of atomization is same as the enthalpy of sublimation.
29. **Bond Enthalpy (symbol: $\Delta_{bond} H^0$)**:
- $$\Delta_r H = \sum \text{bond enthalpies}_{\text{reactants}} - \sum \text{bond enthalpies}_{\text{products}}$$
30. **Enthalpy of Solution (symbol : $\Delta_{sol} H^0$)**: Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.
31. **Lattice Enthalpy** The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

32. **Hess's Law:** Enthalpy change for a reaction is the same whether it occurs in one step or in a series of steps. This may be stated as follows in the form of:
If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature. $\Delta_r H^0$

$$\Delta_r H^0 = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$$

For example: $C(s) +$



33. **Spontaneous Process:** A process which occurs by its own i.e. Without the intervention of an outside agency.

34. **Non Spontaneous Process:** A process which can neither take place by itself nor by initiation is called a non spontaneous process.

35. **Driving Force:** The force which is responsible for spontaneity of a process is called the driving force.

36. **Entropy(S):** Entropy is a measure of randomness or disorder of the system.

37. **Entropy change (ΔS):** It is defined as the amount of heat (q) observed isothermally and reversibly divided by the absolute temp(T) at which the heat is absorbed.

$$\Delta S = \frac{q}{T}$$

38. **Entropy of fusion :** $\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_m}$

Where, ΔH_{fusion} = Entropy of fusion per mole

T_m = Melting point

$$\Delta S_{\text{VAP}} = \frac{\Delta H_{\text{VAP}}}{T_b}$$

ΔH_{VAP} = Entropy of vaporization per mole

T_b = Boiling point

39. Second Law Of Thermodynamics

The entropy of universe is continuously increasing due to spontaneous process taking place in it.

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$$

$$\text{i.e. } \Delta S_{\text{total}} > 0$$

40. **Gibbs Free Energy (G)** : It is defined as max^m amount of energy available to a system during the process that can be converted into useful work. It is a measure of capacity to do useful work.

$$G = H - TS$$

this equation is also known as Gibb's Helmholtz equation

G is a state function. ΔG is change in free energy.

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

41. **If ΔG is negative, process is spontaneous** when $\Delta G=0$, the process is in equilibrium if ΔG is positive, the process does not take place.
42. **Standard Free Energy Change (ΔG^0)** : It is defined as free energy change measured at 298 K and 1 atm Pressure.
43. **Standard Free energy of formation: ($\Delta_f G^0$)** It is free energy change when 1 mole of compound is formed from its constituting elements in their standard state.

$$\Delta_r G^0 = \sum \nu_p \Delta_f G^0(\text{products}) - \sum \nu_R \Delta_f G^0(\text{reactants})$$

44. Gibbs Energy Change and Work

In case of galvanic cell, Gibbs energy change $\Delta_r G$, is related to the electrical work done by the cell.

$$\text{Thus } \Delta_r G = -nFE_{\text{cell}}$$

If reactants and products are in their standard states

$$\Delta_r G^0 = -nFE^0_{\text{cell}}, \text{ Here } E^0_{\text{cell}} \text{ is the standard cell potential.}$$

45. Gibbs Energy Change and Equilibrium Constant

$$\Delta_r G^0 = -RT \ln K$$

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

Some Important Formulas(Thermodynamics)

- $\Delta U = q + w$

- $\Delta H = \Delta U + p\Delta V$

- $\Delta H = \Delta U + \Delta ngRT$

- $C_p - C_v = R$

- $\Delta_r H = \sum a_i H_{\text{Products}} - \sum b_i H_{\text{Reactants}}$

- $\Delta_r H = \sum \text{bond enthalpies}_{\text{reactants}} - \sum \text{bond enthalpies}_{\text{products}}$

- $\Delta_r H^0 = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$

- $\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_m}$

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

- $\Delta_r G^0 = \sum \nu_p \Delta_f G^0(\text{products}) - \sum \nu_R \Delta_f G^0(\text{reactants})$

- $\Delta_r G = -nFE_{\text{cell}}$

- $\Delta_r G = -2.303RT \log K$