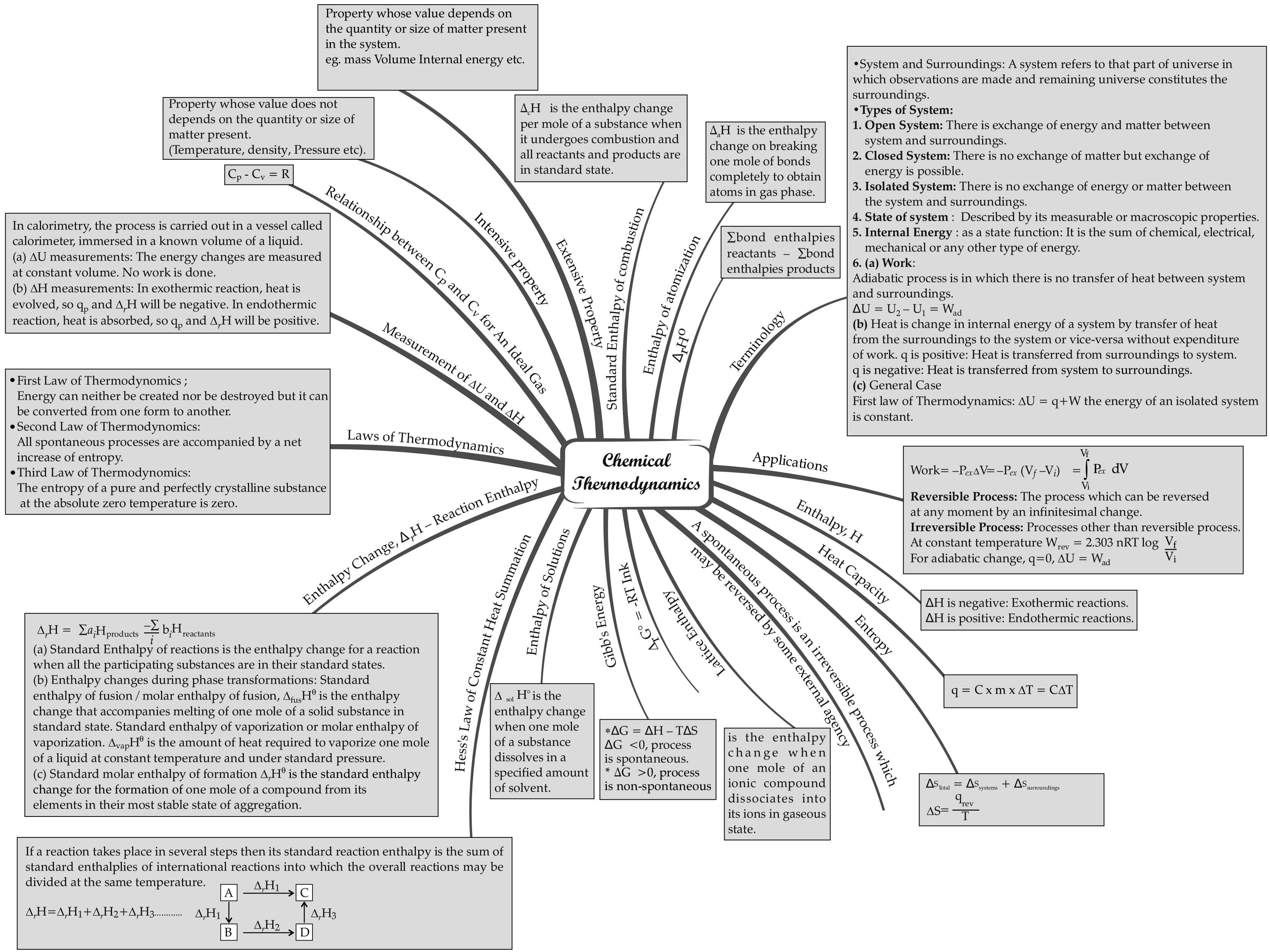


## Chemical Thermodynamics

**Terminology**

- System and Surroundings: A system refers to that part of universe in which observations are made and remaining universe constitutes the surroundings.
- **Types of System:**

**1. Open System:** There is exchange of energy and matter between system and surroundings.

**2. Closed System:** There is no exchange of matter but exchange of energy is possible.

**3. Isolated System:** There is no exchange of energy or matter between the system and surroundings.

**4. State of system** : Described by its measurable or macroscopic properties.

**5. Internal Energy** : as a state function: It is the sum of chemical, electrical, mechanical or any other type of energy.

**6. (a) Work**:
Adiabatic process is in which there is no transfer of heat between system and surroundings.
$\Delta U = U_2 - U_1 = W_{ad}$

**(b)** Heat is change in internal energy of a system by transfer of heat from the surroundings to the system or vice-versa without expenditure of work. q is positive: Heat is transferred from surroundings to system.
q is negative: Heat is transferred from system to surroundings.

**(c)** General Case
First law of Thermodynamics: $\Delta U = q+W$ the energy of an isolated system is constant.

**Applications**

$$\text{Work} = -P_{ex}\Delta V = -P_{ex}(V_f - V_i) = \int_{V_i}^{V_f} P_{ex}\, dV$$

**Reversible Process:** The process which can be reversed at any moment by an infinitesimal change.

**Irreversible Process:** Processes other than reversible process.

At constant temperature $W_{rev} = 2.303\ nRT \log \frac{V_f}{V_i}$

For adiabatic change, q=0, $\Delta U = W_{ad}$

**Enthalpy, H**

$\Delta H$ is negative: Exothermic reactions.
$\Delta H$ is positive: Endothermic reactions.

**Heat Capacity**

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

**Entropy**

$\Delta S_{Total} = \Delta S_{systems} + \Delta S_{surroundings}$

$\Delta S = \frac{q_{rev}}{T}$

**A spontaneous process is an irreversible process which may be reversed by some external agency**

**Lattice Enthalpy**

is the enthalpy change when one mole of an ionic compound dissociates into its ions in gaseous state.

**$\Delta_r G^\circ = -RT\ lnk$**

**Gibb's Energy**

$*\Delta G = \Delta H - T\Delta S$
$\Delta G < 0$, process is spontaneous.
$* \Delta G > 0$, process is non-spontaneous

**Enthalpy of Solutions**

$\Delta_{sol}H^\circ$ is the enthalpy change when one mole of a substance dissolves in a specified amount of solvent.

**Hess's Law of Constant Heat Summation**

If a reaction takes place in several steps then its standard reaction enthalpy is the sum of standard enthalpies of international reactions into which the overall reactions may be divided at the same temperature.

$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$............

$$\begin{tikzcd} A \arrow[r, "\Delta_r H_1"] \arrow[d, "\Delta_r H_1"'] & C \\ B \arrow[r, "\Delta_r H_2"] & D \arrow[u, "\Delta_r H_3"'] \end{tikzcd}$$

**Enthalpy Change, $\Delta_r H$ – Reaction Enthalpy**

$\Delta_r H = \sum a_i H_{products} - \sum_i b_i H_{reactants}$

(a) Standard Enthalpy of reactions is the enthalpy change for a reaction when all the participating substances are in their standard states.

(b) Enthalpy changes during phase transformations: Standard enthalpy of fusion / molar enthalpy of fusion, $\Delta_{fus}H^\theta$ is the enthalpy change that accompanies melting of one mole of a solid substance in standard state. Standard enthalpy of vaporization or molar enthalpy of vaporization. $\Delta_{vap}H^\theta$ is the amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure.

(c) Standard molar enthalpy of formation $\Delta_f H^\theta$ is the standard enthalpy change for the formation of one mole of a compound from its elements in their most stable state of aggregation.

**Laws of Thermodynamics**

- First Law of Thermodynomics ;
  Energy can neither be created nor be destroyed but it can be converted from one form to another.
- Second Law of Thermodynomics:
  All spontaneous processes are accompanied by a net increase of entropy.
- Third Law of Thermodynomics:
  The entropy of a pure and perfectly crystalline substance at the absolute zero temperature is zero.

**Measurement of $\Delta U$ and $\Delta H$**

In calorimetry, the process is carried out in a vessel called calorimeter, immersed in a known volume of a liquid.
(a) $\Delta U$ measurements: The energy changes are measured at constant volume. No work is done.
(b) $\Delta H$ measurements: In exothermic reaction, heat is evolved, so $q_p$ and $\Delta_r H$ will be negative. In endothermic reaction, heat is absorbed, so $q_p$ and $\Delta_r H$ will be positive.

**Relationship between $C_p$ and $C_v$ for An Ideal Gas**

$C_p - C_v = R$

**Intensive property**

Property whose value does not depends on the quantity or size of matter present.
(Temperature, density, Pressure etc).

**Extensive Property**

Property whose value depends on the quantity or size of matter present in the system.
eg. mass Volume Internal energy etc.

**Standard Enthalpy of combustion**

$\Delta_c H$ is the enthalpy change per mole of a substance when it undergoes combustion and all reactants and products are in standard state.

**Enthalpy of atomization**

$\Delta_a H$ is the enthalpy change on breaking one mole of bonds completely to obtain atoms in gas phase.

**$\Delta_r H^o$**

$\sum$bond enthalpies reactants – $\sum$bond enthalpies products

CHAPTER

# 6 CHEMICAL THERMODYNAMICS

## Chapter Objectives

- *Fundamentals of thermodynamics : System and surroundings, Extensive and intensive properties, and thermodynamic State functions.*
- *First law of thermodynamics : Concept of work, heat, internal energy and enthalpy, Heat capacity, Molar heat capacity, Hess's law of constant heat summation, Enthalpies of bond dissociation, combustion, formation, neutralization, solution, hydration, fusion, vaporisation and sublimation, Carnot engine.*
- *Second law of thermodynamics : Entropy, Spontaneity of processes, $\Delta S$ for universe, $\Delta G$ of the system as criteria for spontaneity, Gibb's Helmholtz equation, $\Delta G$ (standard Gibb's energy change) and equilibrium constant.*
- *Third law of thermodynamics : Brief introduction.*

## STUDY MATERIAL

### I. Concept Clarified :

- **Thermodynamics**

The branch of science that deals with the study of quantitative relationship between heat energy (Thermos) and other forms of energy, i.e., work (dynamics) during a physical or chemical transformation is called thermodynamics.

The study of thermodynamics is based on three generalisations which is derived from experiments. These are first, second and third laws of thermodynamics that help us to determine the following :

**(i)** Derivation of quantitative relation ship between heat and other forms of energy.
**(ii)** An idea to predict whether a chemical reaction takes place under the given set of conditions.
**(iii)** Predict the extent of reaction before the equilibrium is attained.
**(iv)** To deduce various laws such as law of mass action, distribution law etc.
**(v)** Predict the spontaneity of a process.
**(vi)** Determine the efficiency of various types of engines.

**Limitations of Thermodynamics**

**(i)** It is applicable only to macroscopic systems (i.e., bulk) and not to microscopic systems, i.e., to individual atoms or molecules.
**(ii)** It does not give any indication of how fast the reaction will proceed.
**(iii)** Thermodynamic methods provide only a limiting value for the work obtainable from a chemical or physical transformation.
**(iv)** It deals only with initial and final state of a system but remains silent about the mechanism of the process.

- **Thermodynamical Equilibrium**

A system is said to have obtained a state of thermodynamical equilibrium when it shows no further tendency to change its property with time.

- **Thermal equilibrium :** When the temperature is same throughout the process.
- **Mechanical equilibrium :** It involves no flow of matter with the system or its boundaries.
- **Chemical equilibrium :** If the chemical composition remains constant with changing time.

- **Fundamentals of Thermodynamics :**

Some important terms are used in thermodynamics which are as follows.

- **System :** It is any region of space that is under observation.
- **Surroundings :** The remaining part of the universe outside the system.

- **Boundary :**

The actual or imaginary wall of layer that separates the system from the surroundings.

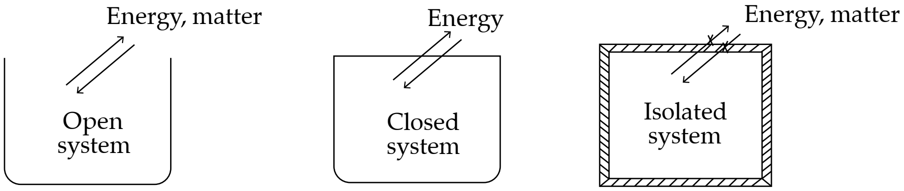
There are various types of boundaries :

**(a)** **A rigid boundary :** Its boundary and shape are fixed.
**(b)** **An impermeable boundary :** Such boundary does not permit the passage of matter.
**(c)** **Permeable boundary :** Its permits the passage of matter and energy.
**(d)** **An adiabatic boundary :** It does not permit the passage of matter or energy.
**Example :** A thermos bottle.
**(e)** **A diathermal or diathermic boundary :** A boundary that allows heat to flow through it is called diathermal whereas a boundary which does not allow heat to flow through it is called adiabatic. It means that a diathermal wall is impermeable but not adiabatic.

**Universe :** System + Surroundings = Universe.

- **Types of Systems :**

**(i)** **Open system :** It can exchange matter as well as energy with surroundings.
**(ii)** **Closed system :** Only energy is exchanged with the surroundings but not matter.
**(iii)** **Isolated system :** Neither matter nor energy is exchanged with surroundings.



- **Homogeneous system :** Uniform throughout one phase.
- **Heterogeneous systems :** Non-uniform, two or more phases.

- **Thermodynamic Properties :**

**(i)** **Intensive properties :** Properties that are independent of the quantity of matter present in the system, or size of the system.

**Examples :** Pressure, temperature, density, concentration terms, pH, specific heat, molar heat capacity, molar entropy, molar enthalpy , molar internal energy , boiling point, melting point, etc.

**(ii)** **Extensive properties :** Properties whose magnitude depends upon the quantity of matter present in the system or the size of the system. Extensive properties are additive.

**Examples :** Mass, volume, number of moles, internal energy, entropy, Gibb's free energy and heat capacity.

**Two important aspects regarding intensive and extensive properties :**

**(i)** The ratio of two extensive properties to always an intensive property.

**Example :** Density $= \frac{\text{Mass}}{\text{Volume}}$

Mass and volume are extensive properties of a system but density is intensive property .

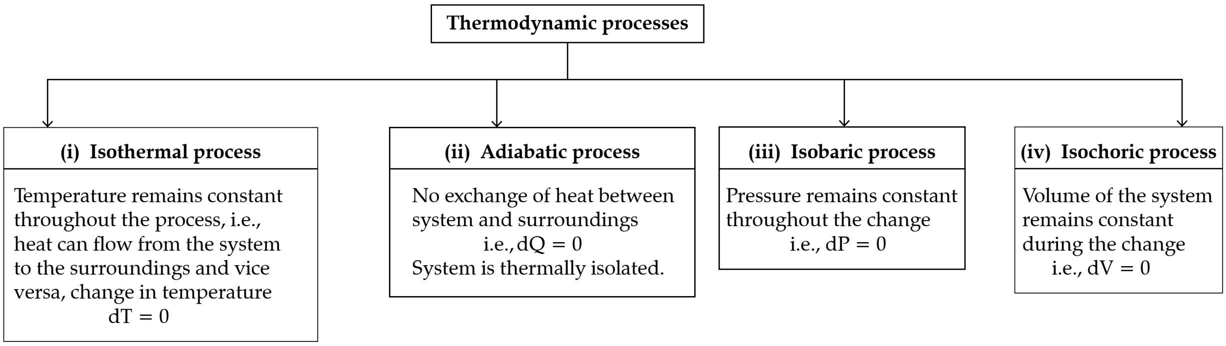
**(ii)** Extensive property can be converted to intensive property by specifying a system with the quantity of matter.

**Examples : (a)** Molar entropy or entropy per mole

**(b)** Molar internal energy or internal energy per mole or internal energy per gram.

- **Thermodynamic Processes :**

When the system changes from one state into another final state.

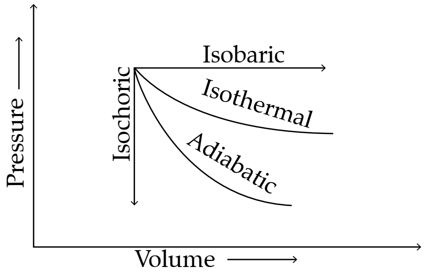


**(i) Isothermal process**
Temperature remains constant throughout the process, i.e., heat can flow from the system to the surroundings and vice versa, change in temperature
dT = 0

**(ii) Adiabatic process**
No exchange of heat between system and surroundings
i.e., dQ = 0
System is thermally isolated.

**(iii) Isobaric process**
Pressure remains constant throughout the change
i.e., dP = 0

**(iv) Isochoric process**
Volume of the system remains constant during the change
i.e., dV = 0



Graphical representation of four thermodynamic processes

**(v) Reversible process :** A process which is carried out infinitesimally slowly in such a way so that it can be reversed by applying the reversible condition and at any time the system and surroundings are in equilibrium.

$$P_{system} = P_{surr} \pm dP$$

**(vi) Irreversible process :** A process which is carried out rapidly in such a way that the successive steps of the direct process cannot be retraced without the help of external agency and no equilibrium exists between system and surrounding.

$$P_{system} = P_{surr} \pm \Delta P$$

## ➢ State Functions or State Variables

The thermodynamic properties whose value is dependent upon the initial and final states of the system and are independent of the path or route.

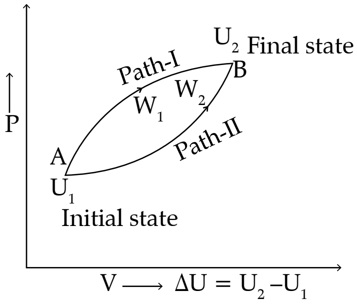
**Examples :** Internal energy (U), enthalpy (H), pressure (P), temperature (T), Gibb's free energy (G), entropy (S), volume (V), number of moles (*n*).

**Path functions :** The thermodynamic properties whose value depends upon the path or process of transformation.

**Examples :** Work and heat.

**Internal energy (U) :** The total of all possible kinds of energies stored under a given set of conditions is called internal energy. When a system is in thermodynamic equilibrium, the internal energy of that system remains same. Internal energy depends on pressure (P), volume (V) and temperature (T) of the system.

Therefore internal energy $U = f(P, T) = f'(P, T) = f''(V, T), f, f'', f''$ are called functions.



When a system moves from initial state A to final state B, internal energy of that system will be changed. If in A, internal energy is $U_1$ and in B the internal energy is $U_2$, follow through Path – I and Path – II respectively, we can measure the change in internal energy as follows :

By the path – I; $U_2 = U_1 + W_1$ [$W_1$ = amount of work done in Path – I]

∴ $U_2 - U_1 = W_1$ **...(i)**

By the Path – II, $U_2 - U_1 = W_2$ **...(ii)**

[$W_2$ = amount of work done in Path – II]

Comparing the two equations, we get $W_1 = W_2$, i.e., it is not a path function, it is a state function.

It is the sum of all microscopic forms of energy;

$$U = U_{electronic} + U_{nuclear} + U_{chemical} + U_{potential} + U_{vibrational} + U_{rotational} + \ldots\ldots$$

**Characteristics of Internal Energy :**

**(i)** It is an extensive property.

**(ii)** It is a state function.

**(iii)** The exact value of internal energy can not be determined but the change of internal energy can be measured accurately.

## Work, Energy and Heat

**Work :** Work is generally expressed as the force multiplied by the distance. If F is the force and is the displacement, work done will be

$$W = F \times dl$$

**Mechanical Work :**

Mechanical work, $W = F \times dl$

Where F= force, $dl$ = displacement

Again, Pressure (P) = $\dfrac{\text{Force (F)}}{\text{Area (A)}}$

$\therefore \quad F = PA$

Small work done by the gas

$\delta W = P \times A \times dl \quad [dl = \text{difference of distance}]$

$= PdV \quad A \times dl = dV$ (difference in volume)

Integrating on both sides

$$W = P\int_{V_1}^{V_2} dV = P(V_2 - V_1) = P\Delta V$$

**Unit of work done :** J (S.I), ergs (C.G.S)

The general expression for the work done is written as

$$W = -P_{ext}\,\Delta V$$
$$= -P_{ext}(V_2 - V_1)$$
$$= -P_{ext}(V_f - V_t)$$

[According to SI conversion, if work is done on the system, *W* is +ve and if work is done by system , *W* is –ve]

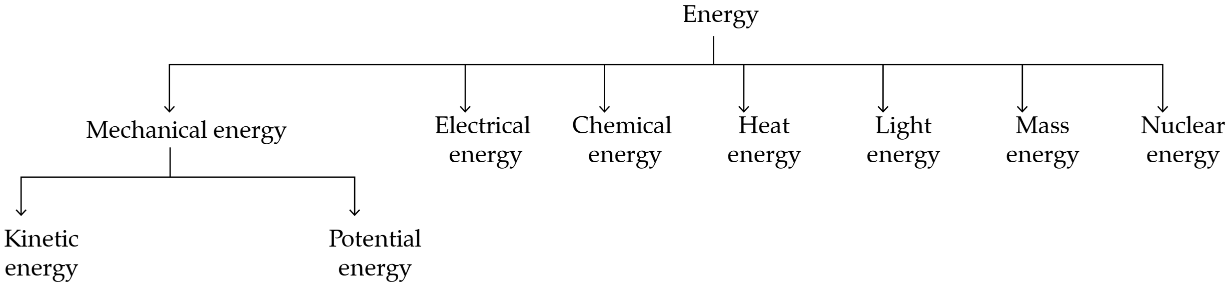
Electrical work = Potential difference × Charge flown

$= V \times Q = E \times F$

Gravitational work = Gravitational force × Height

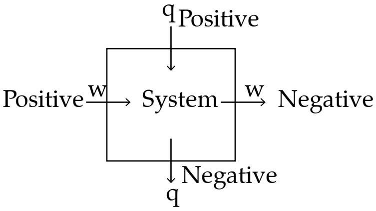
$= mg \times h$

**Energy :** Energy is the capacity for doing work.



**Heat (Q) :** This type of energy is related with the molecular velocity proportionally, which can transform from one body to another through conduction, convection or radiation.

Sign convention according to IUPAC :



## Enthalpy (H)

**Enthalpy (H) :** The pressure and volume of a system are thermodynamic variables and product of PV is the energy. The total heat content, i.e., enthalpy of the system is the sum of internal energy plus PV work done.

$\therefore \quad H = U + PV$ (At constant volume PV = 0, actually in chemical laboratories, most processes occur at constant pressure.)

**Characteristics of enthalpy :**

**(i)** It is a state function.

**(ii)** It is an extensive property.

**(iii)** Its exact value can not be determined but enthalpy change can be determined accurately.

**Consider a system ;**

| | **Initial conditions** | **Final conditions** |
|---|---|---|
| Enthalpy | $H_1$ | $H_2$ |
| Pressure | P | P |
| Volume | $V_1$ | $V_2$ |
| Internal energy | $U_1$ | $U_2$ |

$\therefore \quad H_1 = U_1 + PV_1 \quad \text{... (i)}$

$H_2 = U_2 + PV_2 \quad \text{... (ii)}$

Subtracting (i) from (ii) we get

$$H_2 - H_1 = U_2 - U_1 + P(V_2 - V_1)$$

$\Rightarrow \quad \Delta H = \Delta U + P\Delta V \quad \text{... (iii)}$

For n moles, ideal gas equation is,

$PV_1 = n_1RT \quad \text{... (iv)}$

$PV_2 = n_2RT \quad \text{... (v)}$

$P(V_1 - V_2) = (n_1 - n_2)\,RT$

$\Rightarrow \quad P\Delta V = \Delta n_gRT \quad \text{... (vi)}$

$\boxed{\Delta n_g = \text{change in number of moles for gases}}$

From equations (iii) & (vi) we get

$$\boxed{\Delta H = \Delta U + \Delta n_gRT}$$

## ➢ First Law of Thermodynamics :

The first law of thermodynamics is the law of conservation of energy. Some of the selected statements are as follows :

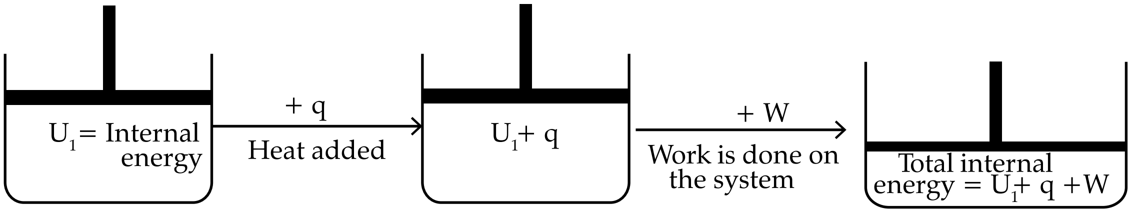
**(i)** Energy can neither be created nor be destroyed but it can be converted from one form to another.

**(ii)** The total energy of the universe remains constant.

**(iii)** If some amount of energy is disappeared from a system, equal amount of energy come to the system by means of else where.

**(iv)** It is very impossible to construct a perpetual motion that could produce work without applying energy or applying small amount of energy to get greater work.

**Mathematical formulation of the first law of thermodynamics :** The internal energy of a system can be increased (i) by supplying heat to the system. (ii) by applying work on the system.



Suppose a gas is enclosed fitted with a weightless, frictionless piston having internal energy $U_1$. Now q amount of heat is supplied to the system and the energy is raised to become $U_1 + q$.

If further work 'w' is done on the system, the internal energy again increases and finally becomes $U_1 + q + W$ which is equal to $U_2$, then

$$U_2 = U_1 + q + W$$

$$\Rightarrow \quad U_2 - U_1 = q + W$$

$$\Rightarrow \quad \Delta U = q + W$$

For a small change ;

$$\boxed{dU = \delta q + \delta W}$$

$$\Rightarrow \quad \boxed{dU = \delta q + PdV}$$

If work is done on surroundings , the above equation becomes

$$\boxed{\delta q = dU + \delta W}$$

$$\Rightarrow \quad \boxed{\delta q = dU + PdV}$$

## ➢ Work done in isothermal reversible expansion of an Ideal gas :

The small amount of work done δw, when the gas expands through a small volume dV, against the external pressure, $P_{ext}$ is given by

$$\delta W = -P_{ext}\, dV \qquad \text{... (i)}$$

As it is a reversible expansion

$$\therefore \quad P_{ext} = P_{int} - dP \qquad \text{... (ii)}$$

$$\therefore \quad \delta W = -(P_{int} - dP)\, dV$$

$$\Rightarrow \quad \delta W = -P_{int}\, dV + dP \times dV$$

$$\Rightarrow \quad \delta W = -P_{int}\, dV \quad \text{(As } dP \times dV \text{ is negligible)} \qquad \text{... (iii)}$$

From ideal gas equation, PV = nRT

$$\therefore \quad P = \frac{nRT}{V}$$

Total work done can be obtained when the volume expands from $V_1$ to $V_2$.

Hence, we get from equation (i)

$$W = -\int_{v_1}^{v_2} \frac{nRT}{V} dV$$

$$\Rightarrow \quad W = -nRT \int_{v_1}^{v_2} \frac{1}{V} dV$$

$$\Rightarrow \quad W = -nRT \ln \frac{V_2}{V_1}$$

$$\Rightarrow \quad \boxed{W = -2.303\ nRT\log \frac{V_2}{V_1}} \qquad \text{... (iv)}$$

$$\Rightarrow \quad \boxed{W = -2.303\ PV \log \frac{P_1}{P_2}} \qquad \text{... (v)}$$

[At constant temperature $P_1V_1 = P_2V_2$ ]

## ➢ Heat Capacity

The amount of heat required to increase the temperature of 1 g of substance by 1 K is called specific heat . The heat input required to increase by 1K, the temperature of one mole of substance is called its molar heat capacity or simply heat capacity. If δq amount of heat is required to increase temperature for one mole of substance, then

$$C = \frac{\delta q}{dT}$$

But $\delta q$ is path function and its value depends on the actual process followed.

To get precise values of heat capacity we can introduce certain restriction, for example, the restriction is heat capacity at constant pressure and heat capacity at constant volume.

**Molar heat capacity at constant volume**

From first law of thermodynamics,

$$\delta q = dU + \delta W$$

$$\Rightarrow \quad \delta q = dU + PdV$$

$$\Rightarrow \quad \frac{\delta q}{dT} = \frac{dU}{dT} + \frac{PdV}{dT}$$

$$\Rightarrow \quad \left(\frac{\delta q}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V + P.0$$

$$\Rightarrow \quad C_v = \left(\frac{dU}{dT}\right)_V \qquad \text{... (i)}$$

**Molar heat capacity at constant pressure,**

$$H = U + PV$$

$$\Rightarrow \quad dH = dU + PdV + VdP$$

$$\Rightarrow \quad dH = \delta q + VdP$$

$$\Rightarrow \quad \left(\frac{dH}{dT}\right) = \frac{\delta q}{dT} + V\left(\frac{dP}{dT}\right)$$

$$\Rightarrow \quad \left(\frac{dH}{dT}\right)_P = \left(\frac{\delta q}{dT}\right)_P + V.0$$

$$\Rightarrow \quad C_P = \left(\frac{dH}{dT}\right)_P \qquad \text{... (ii)}$$

**Relation between $C_p$ & $C_v$**

As $\quad U = f(V,T)$

$$\therefore \quad \Delta U = \left(\frac{\partial U}{\partial T}\right)_v \times \Delta T + \left(\frac{\partial U}{\partial T}\right)_v \times \Delta V$$

Hence $\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \times \left(\frac{\partial V}{\partial T}\right)_P$

$$C_P - C_v = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$= \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial v}{\partial T}\right)_P - \left(\frac{\partial U}{\partial V}\right)_V$$

$$= \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$= \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

For a *n*-mole of ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$$C_P - C_v = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$\Rightarrow \quad C_P - C_v = P\left(\frac{\partial V}{\partial T}\right)_P$$

$$\Rightarrow \quad C_P - C_v = P \times \frac{R}{P} = R$$

$$\therefore \quad \boxed{C_P - C_v = R}$$

## ➢ Relation between T, P and V during Adiabatic Reversible Change

**(i) Relation between pressure and volume :**

According to 1st law of thermodynamics,

$$\delta q = dU + \delta W \qquad \text{... (i)}$$

For Adiabatic change $\delta q = 0$ ... (ii)

$$dU = C_v\, dT \qquad \text{... (iii)}$$

$$\delta W = PdV \qquad \text{... (iv)}$$

From equation (i), (ii), (iii) and (iv) we get

$$C_v dT + PdV = 0 \qquad \text{... (v)}$$

According to ideal gas equation,

$$PV = RT$$

Differentiating both sides we get,

$$PdV + VdP = RdT$$

$$\Rightarrow \quad dT = \frac{PdV + VdP}{R} \qquad \text{... (vi)}$$

From equation (v) and (vi) we get,

$$C_V = \frac{(PdV + VdP)}{R} + PdV = 0$$

$$\Rightarrow \quad C_vPdV + C_vVdP + PRdV = 0$$

$$\Rightarrow \quad PdV(C_v + R) + C_vVdP = 0$$

$$\Rightarrow \quad C_pPdV + C_vVdP = 0$$

$$\Rightarrow \quad \frac{C_PPdV}{C_vVP} + \frac{C_vVdP}{C_vVP} = 0$$

[Dividing by $C_v$ VP]

$$\Rightarrow \quad \gamma\, \frac{1}{V}dV + \frac{1}{P}\,dP = 0 \qquad \text{... (vii)}$$

Integrating both sides,

$$\gamma \int \frac{1}{V}dV + \int \frac{1}{P}dP = \text{constant}$$

$$\Rightarrow \quad \text{In } v^{\gamma} + \ln P = \text{constant}$$

$$\Rightarrow \quad \text{In } PV^{\gamma} = \text{constant}$$

$$\Rightarrow \quad PV^{\gamma} = \text{constant} \qquad \text{... (viii)}$$

This is the equation for adiabatic change.

**(ii) Relation between temperature and volume.**

$$PV^{\gamma} = K \qquad \text{... (i)}$$

For 1 mole of ideal gas,

$$PV = RT$$

$$\Rightarrow \quad P = \frac{RT}{V} \qquad \text{... (ii)}$$

From equation (i) and (ii) we get

$$\frac{RT}{V}\, V^{\gamma} = K$$

$$\Rightarrow \quad TV^{\gamma - 1} = \text{constant}$$

## ➢ Calculation of Work Done in Adiabatic Expansion of Ideal Gas :

From 1st law of thermodynamics,

$$\delta q = dU + \delta W \qquad \text{... (i)}$$

For adiabatic change $\delta q = 0$ ... (ii)

$$dU = C_v\, dT \qquad \text{... (iii)}$$

From equation (i), (ii), (iii) we get

$$\delta W = -C_v dT \qquad \text{... (iv)}$$

Integrating the above equations between the temperature $T_1$ to $T_2$, we get

$$W = -C_v\int_{T_1}^{T_2} dT$$

$$\Rightarrow \quad W = -C_v(T_2 - T_1) \quad \text{... (v)}$$

$$\Rightarrow W = \frac{C_v(\gamma - 1)(T_1 - T_2)}{(\gamma - 1)} \quad [\text{Multiplying and dividing}]$$

$$\Rightarrow W = \frac{C_v\left(\frac{C_P}{C_v} - 1\right)(T_1 - T_2)}{(\gamma - 1)}$$

$$\Rightarrow W = \frac{C_v\left(\frac{C_P - C_v}{C_v}\right)(T_1 - T_2)}{(\gamma - 1)}$$

$$\Rightarrow W = \frac{R(T_1 - T_2)}{(\gamma - 1)}$$

For *n* number of moles

$$\therefore \quad W = \frac{nR(T_1 - T_2)}{(\gamma - 1)} \quad \text{... (vi)}$$

**(i) Isochoric process**

From 1st law of thermodynamics,

$\Rightarrow \Delta U = q_v + W[W = PdV$ sin isochoric $dV = 0]$

$\Rightarrow \Delta U = q_v$

**(ii) Isobaric process**

$$W = -P_{ext}(V_2 - V_1)$$

$$\Rightarrow \quad \Delta H = q_P$$

**(iii) Cyclic process :**

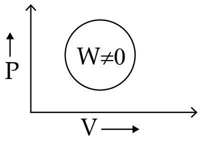
Work done = Area enclosed in PV diagram

**Case 1 :** For clockwise

$W = -ve$

**Case 2 :** For anti-clockwise

$W = +ve$



In irreversible work done

$$W = P_2(V_2 - V_1) \quad \text{... (i)}$$

For isothermal process, $P_1V_1 = RT \quad P_2V_2 = RT$

$$\therefore \quad V_1 = \frac{RT}{P_1} \quad \text{... (ii)}$$

$$\therefore \quad V_2 = \frac{RT}{P_2} \quad \text{... (iii)}$$

$$\therefore \quad W_{irr} = P_2\left(\frac{RT}{P_1} - \frac{RT}{P_2}\right)$$

$$= RT\left(1 - \frac{P_2}{P_1}\right) \quad \text{... (iv)}$$

Now $\quad W_r - W_{irr}$

$$= RT \ln\frac{P_1}{P_2} - RT\left(1 - \frac{P_2}{P_1}\right) \quad \text{... (v)}$$

Reversible process occurs through infinitesimally slowly :

$$\ln\frac{P_1}{P_2} = \frac{P_1 - P_2}{P_2} \quad \text{... (vi)}$$

From (v) and (vi) we get

$$W_r - W_{irr} = RT\left(\frac{P_1 - P_2}{P_2}\right) - RT\left(\frac{P_1 - P_2}{P_1}\right)$$

$$= RT(P_1 - P_2)\left(\frac{1}{P_2} - \frac{1}{P_1}\right)$$

$$= RT(P_1 - P_2)\left(\frac{P_1 - P_2}{P_1P_2}\right)$$

$$= \frac{RT}{P_1P_2}(P_1 - P_2)^2$$

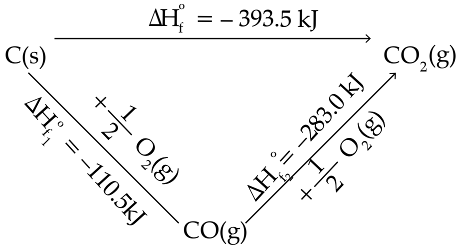
As $\frac{RT}{P_1P_2}(P_1 - P_2)^2$ positive quantity, so

$W_r - W_{irr} = +ve,$

$\therefore \quad W_r > W_{irr}$

## ➢ Hess's Law of Constant Heat Summation :

Provided the other condition remaining the same, the heat of reaction will be the same no matter whether the reaction takes place directly or alternatively in a number of steps.



$$\therefore \quad \Delta H_f^\circ = \Delta H_{f_1}^\circ + \Delta H_{f_2}^\circ$$

**Applications of Hess's law :**

**(i)** Heat of formation of intermediate compounds which are not stable, non-isolable and can't be determined experimentally are determined by applying Hess's law.

Example: Benzene cannot be synthesised directly from its element.

$$6C + 3H_2 \rightarrow C_6H_6, \Delta H_f$$

By considering following reactions $\Delta H_f$ can be calculated :

**(a)** $C(s) + O_2(s) \rightarrow CO_2(s)$ $\Delta H = -393.1$ kJ

**(b)** $H_2 + \frac{1}{2}O_2 \rightarrow H_2O(l)$ $\Delta H = -286.0$ kJ

**(c)** $C_6H_6(l) + \frac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O$ $\Delta H -3266.0$kJ

$\Delta H_f(C_6H_6)$

= Equation (i) × 6 + Equation (ii) × 3 - Equation (iii)

= [–393. × 6 + (–286.0 ×3) + 3266] kJ

= + 49.6 kJ

**(ii)** **To determine heat of reaction :** The reactions which are either very fast or occur simultaneously with other reactions and cannot be studied experimentally, by applying Hess's law, heat of reaction of such reactions can be be evaluated.

**(iii)** Heat of transitions can be determined.

**(iv)** Lattice energy of ionic compounds can be calculated.

## ➢ Enthalpy of Bond Dissociation :

The amount of energy required to dissociate one mole of bonds between the atoms in a molecule in the gaseous state is called enthalpy of bond dissociation.

$$H_2(g) \rightarrow 2H_2 \qquad \Delta H = 435.4 \text{ kJ mol}^{-1}$$

The amount of energy released when a bond is formed between two atoms to form one mole of a compound is called bond enthalpy.

$$2H \rightarrow H_2 \qquad \Delta H = -435.4 \text{ kJ mol}^{-1}$$

So, from the above two reactions it is evident that bond enthalpy is same as enthalpy of bond dissociation for a diatomic molecule.

In case of polyatomic molecules the average value of enthalpy of bond dissociation is referred to as bond enthalpy.

Examples:

$CH_3 - H(g) \rightarrow CH_3(g) + H(g)$ $\Delta H = 425 \text{ kJ mol}^{-1}$

$H_2C - H(g) \rightarrow CH_2(g) + H(g)$ $\Delta H = 470 \text{ kJ mol}^{-1}$

$HC - H(g) \rightarrow CH(g) + H(g)$ $\Delta H = 416 \text{ kJ mol}^{-1}$

$C - H(g) \rightarrow C(g) + H(g)$ $\Delta H = 335 \text{ kJ mol}^{-1}$

The variation in breaking of individual C – H bonds is high, that is why we consider the average of those four dissociation enthalpies;

Bond dissociation enthalpy of C – H bond

$$= \frac{425 + 470 + 416 + 335}{4}$$

$$= 411.5 \text{ kJ}$$

Thus, bond enthalpy is defined as the average amount of energy needed to dissociate bond of a given type present in one mole of the gaseous molecules.

➢ **Kirchoff's reaction (Variation of enthalpy of a reaction with temperature ) :** When a system changes from a given state to another state both the internal energy and the heat energy would change.

$$\therefore \quad U_2 - U_1 = \Delta U \qquad \text{... (i)}$$

$$H_2 - H_1 = \Delta H \qquad \text{... (ii)}$$

The suffixes 2 and 1 denote final and initial states.

Equation (i) differentiating with respect to temperature at constant volume and equation (ii) differentiating with respect to temperature at constant pressure we get,

$$\left(\frac{\partial \Delta U}{\partial T}\right)_V = \left(\frac{\partial U_2}{\partial T}\right)_V - \left(\frac{\partial U_1}{\partial T}\right)_V = C_{V_2} - C_{V_1} = \Delta C_V \qquad \text{... (iii)}$$

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \left(\frac{\partial H_2}{\partial T}\right)_P - \left(\frac{\partial H_1}{\partial T}\right)_P = C_{P_2} - C_{P_1} = \Delta C_P \qquad \text{... (iv)}$$

Or, $$\int \partial \Delta U = \int \Delta C_v dT$$

and $$\int \partial \Delta H = \int \Delta C_P dT$$

Integrating between the limit TK an 0K we get;

$$\Delta U_T = \Delta U_o + \int_0^T \Delta C_v dT \qquad \text{... (v)}$$

$$\Delta H_T = \Delta H_o + \int_0^T \Delta C p dT \qquad \text{... (vi)}$$

Equations (v) and (vi) are called Kirchoff's equations.

**Lavoisier Laplace law :** When a same reaction is reversed, heat of formation is equal to the heat of absorption in the reaction.

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H = -285.8 \text{ kJ mol}^{-1}$$

$$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g) \qquad \Delta H = +285.8 \text{ kJ mol}^{-1}$$

## ➢ Different Types of Enthalpies of Reactions :

**(1) Enthalpy of combustion :** The change in enthalpy when one mole of substance is completely burnt or oxidized in oxygen. It is denoted by $\Delta Hc$. $\Delta Hc$ is always negative as it is exothermic reaction.

**(2) Enthalpy of formation :** The change of enthalpy when one mole of the substance is formed from its element under given conditions. It is denoted by $\Delta H_f$. It is negative for exothermic reaction and positive for endothermic reaction.

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_f = -393.5 \text{ kJ}$$

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow 2NO \qquad \Delta H_J = 90.15 \text{ kJ}$$

**Standard enthalpy of formation :** The change in enthalpy when one mole of a substance is formed from its constituent standard states (at 298 K and 1 atm pressure). It is denoted as $\Delta H_f^o$.

During determination of standard enthalpies, the following points are to be followed :

**(i)** If an element has two or more allotropes, during calculation of enthalpy of formation that allotrope is to be considered which is very stable at 298 K and 1 atm pressure.

**(ii)** Under standard conditions, the enthalpy of any element (stable allotrope) is taken as zero. [$\Delta H_f^o$ (graphite) = 0 but $\Delta H_f^o$ (diamond $\neq 0$)]

**(3) Enthalpy of neutralization :** The enthalpy of neutralization of an acid by a base is the change of enthalpy when one gram equivalent of acid is neutralized by one gram equivalent base in a dilute solution.

- The enthalpy of neutralization is maximum when a strong base is neutralized by a strong acid.

$$HCl\,(aq) + NaOH\,(aq) \rightarrow NaCl\,(aq) + H_2O\,(l) \qquad \Delta H = -57.1 \text{ kJ}$$

- If the acid is strong, base is weak or acid is weak, base is strong. The evolved enthalpy is less than 57.1 kJ.

$$HCl\,(aq) + NH_4OH\,(aq) \rightarrow NH_4Cl(aq) + H_2O\,(l)$$

$$\Delta H = -(57.1 - 5.6) \text{ kJ}$$

$$= -51.5 \text{ kJ}$$

$$CH_3COOH\,(aq) + NaOH\,(aq) \rightarrow CH_3COONa\,(aq) + H_2O(l)$$

$$\Delta H = -(57.1 - 1.9) \text{ kJ}$$

$$= -55.2 \text{ kJ}$$

A part of heat produced in the above two cases during the combination of $H^+$ ions and $OH^-$ ions, $OH^-$ ions are used up for complete dissociation of weak base ($NH_4OH$) or weak acid ($CH_3COOH$), i.e., enthalpy of ionisation.

**(4) Enthalpy of solution :** It is the change in enthalpy when mole of a substance is dissolved in large amount of water so that further dilution does not produce any more heat change.

$$KCl\,(s) + aq \longrightarrow KCl(aq) \quad \Delta H = +18.6 \text{ kJ}$$

**(5) Enthalpy of hydration :** It is the change in enthalpy when one mole of the anhydrous salt combines with the specific number of moles of water so as to get a hydrated salt.

$$CuSO_4\,(s) + 5H_2O\,(l) \rightarrow CuSO_4 . 5\,H_2O(s) \qquad \Delta H = -78.2 \text{ kJ}$$

**(6) Enthalpy of fusion :** It is the change in enthalpy of the melting point when one mole of a solid is completely converted into liquid state.

$$H_2O\,(g) \rightarrow H_2O\,(l) \qquad \Delta H = +6 \text{ kJ/mol}$$

**(7) Enthalpy of vaporisation :** It is the change in enthalpy at its boiling point when one mole of a liquid is completely converted into its vapour.

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H = +40.6 \text{ kJ/mol}$$

**(8) Enthalpy of sublimation :** It is the change in enthalpy when one mole of a solid is completely converted into its vapour at its sublimation temperature.

$$I_2(s) \rightarrow I_2(g) \qquad \Delta H = +62.4 \text{ kJ/mol}$$

**(9) Enthalpy of phase transition** : It is the change of enthalpy when one mole of one allotropic form changes into another allotropic form.

$$C(Graphite) \rightarrow C(Diamond) \qquad \Delta H_{trans} = 1.9 \text{ kJ mol}^{-1}$$

## ➢ Limitations of First Law of Thermodynamics

**(i)** The first law cannot explain the feasibility of the process in the direction of change.

**(ii)** The first law is unable to give any information about the extent to which the charge takes place. All other forms of energy can be converted into another form but heat energy cannot be completely converted into mechanical energy.

**Spontaneous process :** The process which can take place by itself or after proper initiation.

**(i)** Process which occurs itself

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

**(ii)** Salt dissolves in water.

**(iii)** Process which occurs after initiation.

Coal on ignition keeps on burning.

$$C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$$

**Non-spontaneous process :** The process which neither takes place itself nor by proper initiation.

Examples: **(i)** Flow of water upstream.

**(ii)** Flow of heat from cold to hot body.

**Driving force for a spontaneous process :** Overall tendency for a process to be spontaneous when it has

**(i)** tendency for minimum energy (E).

**(ii)** tendency for maximum randomness.

The resultant of the two tendencies which gives over all tendency for a process to take place is known as driving force.

Some examples of spontaneous process are :

**(i) Evaporation of water :** $H_2O(l) \rightarrow H_2O(g)$ $\qquad \Delta H = +44 \text{ kJ mol}^{-1}$

Energy opposes but randomness favours.

**(ii) Dissolution of $NH_4Cl$ in water :**

$$NH_4Cl(s)\, aq \longrightarrow NH_4^+(aq) + Cl^-(aq) \qquad \Delta H = +15.1 \text{ kJ mol}^{-1}$$

(Here R > E)

**(iii) Formation of $H_2O$**

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) \qquad \Delta H = -286.2 \text{ kJ mol}^{-1}$$

(Here E > R)

**(iv) Formation of $CO_2$**

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -393.5 \text{ kJ mol}^{-1}$$

(E, R both favours)

## ➢ Carnot Engine

When one mole of an ideal gas is filled with a weightless frictionless piston, it is called Carnot engine.

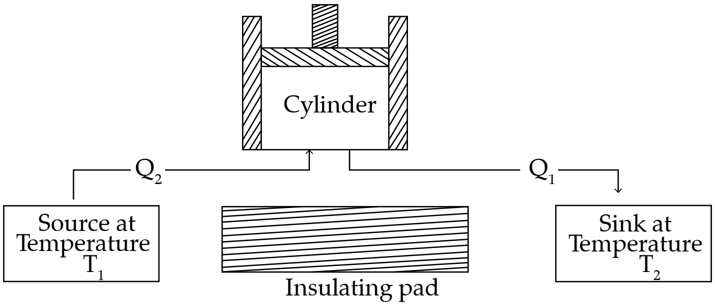


**Fig :** Carnot Engine

**Source :** It is a big temperature bath and acts at a fixed temperature $T_2$. Heat engine draws heat for the work of expansion but temperature suffers no change.

**Sink :** It is a lower temperature bath. The heat is rejected by the engine to it, it also suffers no change in temperature. It is kept at $T_1$K.

There are four steps in a Carnot engine and all steps are reversible. In them two are isothermal and two are adiabatic. The four steps are :

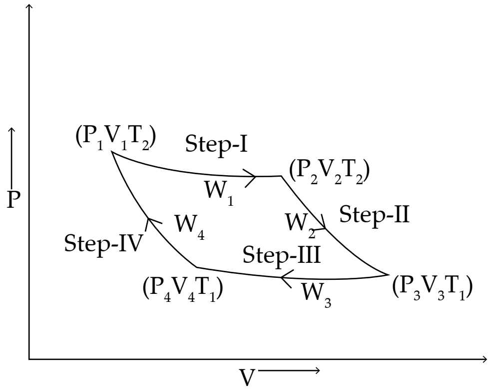
**(1)** Isothermal reversible expansion.

**(2)** Adiabatic reversible expansion.

**(3)** Isothermal reversible compression.

**(4)** Adiabatic reversible compression.

The Carnot engine can be understood by considering the given P-V diagram.



**Step – 1**

$$W_1 = -RT_2 \times 2.303 \log \frac{V_2}{V_1} = Q_2 = \text{heat absorbed} \quad \text{... (i)}$$

**Step – 2**

$$W_2 = -C_v(T_1 - T_2) \quad \text{... (ii)}$$

**Step – 3**

$$W_3 = -RT_1 \times 2.303 \log \frac{V_4}{V_3}$$

$$= Q_1 = \text{heat released} \quad \text{... (iii)}$$

**Step – 4**

$$W_4 = -C_v(T_2 - T_1)$$

$$= -W_2 \quad \text{... (iv)}$$

$\therefore$ Total work done (W)

$$= W_1 + \cancel{W_2} + W_3 + \cancel{W_4}$$

$$= -2.303\ RT_2 \log \frac{V_2}{V_1} - 2.303RT_1 \log \frac{V_4}{V_3} \quad \text{... (v)}$$

Step – 2 and Step – 4 are adiabatic

$\therefore \quad T_2V_2^{\gamma-1} = T_1V_3^{\gamma-1}$

$$\Rightarrow \quad \frac{T_2}{T_1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} \quad \text{... (vi)}$$

Again

$$T_1V_4^{\gamma-1} = T_2V_1^{\gamma-1}$$

$$\Rightarrow \quad \left(\frac{V_4}{V_1}\right)^{\gamma-1} = \frac{T_2}{T_1} \quad \text{... (vii)}$$

Comparing (vi) & (vii) equation we get

$$\frac{V_3}{V_2} = \frac{V_4}{V_1}$$

$$\Rightarrow \quad \frac{V_2}{V_1} = \frac{V_3}{V_4} \quad \text{... (viii)}$$

from equation (v) and (viii) we get

$$W = -2.303\ RT_2 \log \frac{V_2}{V_1} + 2.303\ RT_1 \log \frac{V_2}{V_1}$$

$$= -2.303\ (T_2 - T_1)RT \log \frac{V_2}{V_1} \quad \text{... (ix)}$$

**Efficiency of engine :**

$$\text{Efficiency of engine} \quad (\eta) = \frac{\text{Work done}}{\text{Heat absorbed}}$$

$$\Rightarrow \quad \eta = \frac{-2.303(T_2 - T_1)R \log \frac{V_2}{V_1}}{-2.303\ RT_2 \log \frac{V_2}{V_1}}$$

$$\Rightarrow \quad \eta = \frac{T_2 - T_1}{T_2}$$

$$\Rightarrow \quad \eta = 1 - \frac{T_1}{T_2}$$

**Case – 1** $T_2$ is always greater than $T_1$. Therefore η is always less than 1.

**Case – 2** If $T_1$ = 0 K

η = 1

However, 0 K cannot be achieved. So efficiency of an engine is always less than one.

## ➢ Second Law of Thermodynamics :

Second Law of Thermodynamics can be defined in a number of ways as follows :

**(i)** "All spontaneous processes (or naturally occurring processes) are thermodynamically irreversible."

**(ii)** "Without the help of an external agency, a spontaneous process cannot be reversed". For example, heat cannot by itself flow from a colder to hotter region.

**(iii)** "The complete conversion of heat into work is impossible without leaving some effect elsewhere".

**(iv)** "All spontaneous processes are accompanied by a net increase of entropy".

**(v)** "The entropy of the universe is continuously increasing".

➢ **Entropy :** Entropy is a thermodynamic state quantity which measures the disorderness or randomness of a system (E*n* – Energy, trope – change). It is denoted by 'S'.

**Entropy change :** It is defined as integral of all terms involving heat exchanged (Eq) reversibly divided by absolute temperature (T).

$$\therefore \qquad dS = \frac{Sq_{rev}}{T}$$

**Calculating of change in entropy :**

From Carnot theorem, we get,

$$\text{Efficiency} \qquad (\eta) = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2}$$

$$\Rightarrow \qquad \frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2}$$

$$\Rightarrow \qquad \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

$$\Rightarrow \qquad \frac{Q_2}{T_2} = \frac{Q_1}{T_1} = 0$$

$$\Rightarrow \quad \frac{\text{Heat absorbed at } T_2}{T_2} - \frac{\text{Heat released at } T_2}{T_2} = 0$$

In reversible process heat released = – heat absorbed

$$\therefore \quad \frac{\text{Heat absorbed at } T_2}{T_2} + \frac{\text{Heat released at } T_2}{T_2} = 0$$

Therefore, in any reversible process heat absorbed in different steps divided by state temperature, the summation of these quantities will be zero. If T is small and absorbed heat is δq amount the ratio of these two quantities will be $\frac{\delta q}{T}$ which is expressed mathematically $\oint \frac{\delta q}{T} = 0$. This ratio $\frac{\delta q}{V}$ in reversible process is called entropy.

$$\therefore \quad \text{Entropy } dS = \frac{\delta q_{rev}}{T}$$

$$\Rightarrow dS = \frac{du + (-\delta q)}{T} \quad \left[\text{From 1}^{st} \text{ law of Thermodynamics}\right]$$

$$\Rightarrow \qquad dS = \frac{nC_v\, dT + P dV}{T}$$

$$\Rightarrow \qquad dS = \frac{nC_v\, dT}{T} + \frac{nRT}{VT} dV \qquad \left[\because P = \frac{nRT}{V}\right]$$

$$\Rightarrow \qquad dS = \frac{nC_v\, dT}{T} + \frac{nR}{V} dV$$

Integrating the above equation with appropriate limits, we get

$$\boxed{\Delta S_{sys} = nC_v \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}}$$

$$\Rightarrow \left[\Delta S_{sys} = nC_v \ln\frac{T_2}{T_1} + nR\ln\frac{P_1 T_2}{P_2 T_1}\right. \qquad \left[\because \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}\right]$$

$$\Rightarrow \quad \Delta S_{sys} = nC_v \ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2} + nR\ln\frac{T_2}{T_1}$$

$$\Rightarrow \quad \Delta S_{sys} = (C_v + R)n\ln\frac{T_2}{T_1} + nR\ln\frac{P_2}{P_1}$$

$$\Rightarrow \quad \boxed{\Delta S_{sys} = nC_p \ln\frac{T_2}{T_1} + nR\ln\frac{P_2}{P_1}}$$

Entropy change for an isothermal process :

$$\Delta U = 0$$

$$\therefore \qquad \boxed{\Delta S_{sys} = nR\ln\frac{V_2}{V_1}}$$

The entropy of mixing of ideal gases is given as;

$\Delta S_m = -n_1 R \ln N_1 + n_2 R \ln N_2 + \text{------}$

$N_1$, $N_2$ are mole fractions of gases and $n_1$, $n_2$ are the number of moles of two gases.

**Unit of Entropy :** $JK^{-1}$(SI)

**Characteristics of Entropy :**

**(i)** Entropy is a state function.
**(ii)** Entropy is an extensive property.
**(iii)** The exact value of entropy can be determined from third law of thermodynamics.

**ΔS and Spontaneity :**

**(i)** For a spontaneous process :

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

Here $\Delta S_{total}$ is also called $\Delta S_{universe}$

**(ii)** At equilibrium $\Delta S = 0$ ( for an isolated system.)
**(iii)** $\Delta S < 0$; direct process non-spontaneous and reverse process spontaneous.

## ➢ Gibb's Free Energy

Heat energy cannot be converted completely into other energy or cannot be converted completely into work. By fraction of it which cannot be converted into useful work is termed as unavailable energy. This unavailable energy affects the internal energy of the system. In every system internal energy as well as PV work is always present. The summation of these two energies is enthalpy (H), i.e., H = U + PV. Some of its part of total energy is released as free energy which is denoted as G and other part remains as unavailable energy. Unavailable energy is the product of temperature and entropy of the system, i.e., unavailable energy = TS

∴ Total energy of system = Free energy + Unavailable energy

$$\therefore \quad H = G + TS$$

$$\Rightarrow \quad G = H - TS \qquad \text{... (i)}$$

Suppose a system passes from the initial to the final state at constant temperature then,
For initial state of the system equation (i) becomes

$$G_1 = H_1 - TS_1 \qquad \text{... (ii)}$$

and for final state

$$G_2 = H_2 - TS_2 \qquad \text{... (iii)}$$

∴ Change in free energy,

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

$$\Rightarrow \quad \Delta G = \Delta H - T\Delta S \qquad \text{... (iv)}$$

Equation (iv) is known as Gibb's equation.

**Gibb's free energy change and spontaneity :**

| **ΔH** | **TΔS** | **Conditions** | **ΔG** |
|---|---|---|---|
| –ve<br>(favourable) | +ve<br>(favourable) | (any) | –ve<br>spontaneous |
| –ve<br>(favourable) | –ve<br>(unfavourable) | $\|\Delta H\| > \|T\Delta S\|$ | –ve<br>spontaneous |
| –ve<br>(unfavourable) | +ve<br>(unfavourable) | $\|T\Delta S\| > \|\Delta H\|$ | –ve<br>spontaneous |

**Criteria for spontaneity for a process :**

| **ΔH (Enthalpy)** | **ΔS (Entropy)** | **ΔG (Gibb's energy)** | **Remarks** |
|---|---|---|---|
| $\Delta H < 0$ | $\Delta S > 0$ | $\Delta G < 0$ | Spontaneous |
| $\Delta H > 0$ | $\Delta S < 0$ | $\Delta G > 0$ | Non-spontaneous |
| $\Delta H > 0$ | $\Delta S > 0$ | $\Delta G < 0$ at high temperature<br>$\Delta G > 0$ at low temperature | Spontaneous at high temperature<br>Non-spontaneous at low temperature |
| $\Delta H < 0$ | $\Delta S < 0$ | $\Delta G < 0$ at low temperature<br>$\Delta G > 0$ at high temperature | Spontaneous at low temperature<br>Non-spontaneous at high temperature |

### Gibb's Helmholtz equation :

Gibb’s free energy function G is defined by the equation.

$$G = H - TS \qquad \text{... (i)}$$

Differentiating equation(i) we get

$$dG = dH - TdS - SdT \qquad \text{... (ii)}$$

$\Rightarrow$ $dG = (dH + PdV) + VdP - TdS - SdT$ [As $H = U + PV$]

$\Rightarrow$ $dG = \delta q + VdP - \delta q - SdT$

$\Rightarrow$ $dG = +VdP - SdT$

$$\Rightarrow \quad \left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \text{... (iii)}$$

At two different temperatures, if the free energy are $G_1$, $G_2$ and entropy are $S_1$, $S_2$ then

$$\left(\frac{\partial G_1}{\partial T}\right)_P = -S_1 \qquad \text{... (iv)}$$

$$\text{and} \quad \left(\frac{\partial G_2}{\partial T}\right)_P = -S_2 \qquad \text{... (v)}$$

From (iv) and (v) we get

$$\therefore \quad S_2 - S_1 = -\left[\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P\right]$$

$$\Rightarrow \quad \Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P \qquad \text{... (vi)}$$

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

$$\therefore \quad \text{But } \Delta G = \Delta H - T\left(\frac{\partial \Delta G}{\partial T}\right)_P \qquad \text{... (vii)}$$

This equation (vii) is known as Gibb's Helmholtz equation.

### Relation between standard free energy change ($\Delta G°$) and equilibrium constant :

Consider a general reaction,

$$A + B \rightleftharpoons C + D$$

The free energy change and standard free energy change related with each other by the following equation :

$$\Delta G = \Delta G° + RT \ln Q \qquad \text{... (i)}$$

Where, $\Delta G$ = Gibb's energy change

$\Delta G°$ = difference in standard Gibb's energies of formation of the products and reactants which are in standard states.

$$Q = \text{Reaction quotient} = \frac{[C][D]}{[A][B]} \qquad \text{... (ii)}$$

R = Universal gas constant

= 8.314 $JK^{-1}$ $mol^{-1}$

At equilibrium $\Delta G = 0$ and $Q = K_{eq}$

$$0 = \Delta G^o + RT \ln K_{eq}$$

$$\Rightarrow \quad \Delta G^o = -2.303\, RT \log K_{eq} \qquad \text{... (iii)}$$

This equation (iii) is known as van’t Hoff reaction isotherm. If $\Delta G^o$ of the reaction is known, $K_{eq}$ can be calculated by the above equation. The above equation (iii) can be written as

$$K_{eq} = e^{\frac{-\Delta G^o}{RT}} \qquad \text{... (iv)}$$

$$\Rightarrow \quad K_{eq} = 10^{-\Delta G^o/2.303RT} \qquad \text{... (v)}$$

### Relation between free energy charge and electrical work done in a cell :

Electrical work done by a cell is the decrease of free energy of the cell.

$\therefore$ Electrical work done = Decrease in free energy

$\therefore$ $\Delta G$ = Electrical work done. ... (i)

Electrical work done = Electrical energy produced

$$= \text{Quantity of electricity flowing} \times \text{EMF}$$

$$= nFE_{cell} \quad \text{... (ii)}$$

[As n number of moles of electrons get transferred, the quantity of electricity flowing = nF]

From equation (i) and (ii) we get,

$$-\Delta G = nFE_{cell} \quad \text{... (iii)}$$

∴ Standard cell potential $E^o_{cell}$ is given as;

$$\Delta G^o = -nF\,E^o_{cell} \quad \text{... (iv)}$$

Thus, knowing $E^o_{cell}$, $\Delta G^o$ can be calculated by using above equation.

- **Effect of Temperature : van't Hoff equation :**

From van't Hoff equation we get;

$$\Delta G^\circ = -RT\ln K \quad \text{... (i)}$$

$$\Rightarrow \quad \ln K = -\frac{\Delta G^\circ}{RT}$$

Differentiating w.r.t to T, we get

$$\frac{\partial \ln K}{\partial T} = -\frac{1}{R}\left(\frac{\left(\Delta G^\circ/_T\right)}{\partial T}\right)$$

$$\Rightarrow \quad \frac{\partial \ln K}{\partial T} = -\frac{1}{R}\times\left(\frac{(\Delta H^\circ)}{\partial T^2}\right) \quad \text{[by Gibb's Helmholtz equation]}$$

$$\Rightarrow \quad \frac{\partial \ln K}{\partial T} = -\frac{\Delta H}{RT^2} \quad \text{... (ii) [}\because \Delta H \text{ does not vary with pressure; } \Delta H^\circ = \Delta H\text{]}$$

This equation (ii) is known as van't Hoff equation.

Integrating equation (ii) we get

$$\ln K = -\frac{\Delta H}{RT} + \text{constant}$$

$$\Rightarrow \quad \ln K = -\frac{\Delta H}{2.303\ RT} + \text{constant} \quad \text{... (iii)}$$

when $T = T_1$ ; $K = K_1$

and when $T = T_2$ ; $K = K_2$

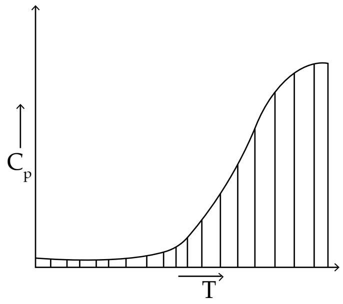
Therefore, from equation (iii) we get;

$$\log\frac{K_2}{K_1} = -\frac{\Delta H}{2.303\ R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

- **Third Law of Thermodynamics :**

This is also known as Nernst heat theorem.

"The entropy of a pure and perfectly crystalline substance at the absolute zero temperature is zero".



For a solid of entropy at 0 K is $S_0$ and at T K is S then,

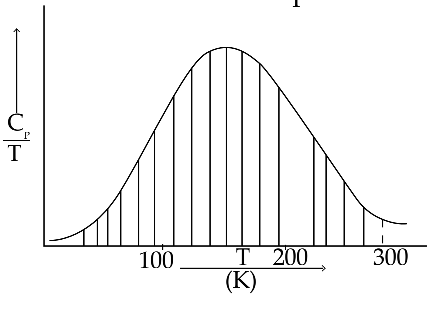
$$S - S_0 = \int_0^t \frac{Cp\,dT}{T}$$

According to third law $S_0 = 0$ at 0K

$$\therefore \quad S = \int_o^T \frac{C_P\,dT}{T}$$

$$= \int_o^T C_P\,d\ln T = C_P\ \ln T$$

$$= 2.303\ C_p \log T$$



Entropy 'S' can be calculated from the shaded area. Crystals of CO, $N_2O$, NO and $H_2O$ do not have zero entropy even at absolute temperature.

## II. Important points :

**(1)** Mathematical statement of first law of thermodynamics is $dU = \delta q + \delta W$

**(2)** Sign conversion used in chemical thermodynamics;

- **(a)** Work done by the system (expansion) – ve
- **(b)** Work done on the system (compression) +ve
- **(c)** Heat gain by the system +ve
- **(d)** Heat loss by the system – ve

$$\boxed{\text{Work done } W = -P_{ext}dV}$$

**(3)** Work done under different thermodynamic conditions;

**(a)** For irreversible process

$$W_{irr} = -P_{ext}[V_f - V_i]$$

**(b)** For isothermal reversible system for $n$ mole of gas;

$$W_r = -2.303\, nRT \log \frac{V_2}{V_1}$$

$$= -2.303\, nRT \log \frac{P_1}{P_2}$$

$$= -2.303\, PV \log \frac{V_2}{V_1}$$

**(c)** Work done in irreversible adiabatic processes for $n$ mole of gas;

$$\Delta U = W = nC_v\Delta T$$

$$W = \frac{nr}{(\gamma - 1)}(T_2 - T_1)$$

**(4)** • Heat capacity =

$$\begin{tikzcd}[row sep=small] & C_v = \left(\frac{dU}{dT}\right)_v \\ \frac{\delta V}{dT} \arrow[ur] \arrow[dr] & \\ & C_p = \left(\frac{dH}{dT}\right)_p \end{tikzcd}$$

- $C_P - C_V = R$ (gas constant)
- Relation between P, V, T for adiabatic process

**(i)** $PV^{\gamma - 1}$ = Constant

**(ii)** $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

Value of $\gamma = \frac{C_P}{C_V}$ for

- **(a)** Monoatomic = 1.66
- **(b)** Diatomic = 1.4
- **(c)** Polyatomic = 1.3

**(5)** $C_v$ for the mixture $C_v = \frac{n_1C_{v_1} + n_2C_{v_2}}{n_1 + n_2}$

$\gamma$ for the mixture $\frac{n_1 + n_2}{\gamma - 1} = \frac{n_1}{\gamma_1 - 1} + \frac{n_2}{\gamma_2 - 1}$

**(6)** Kirchoff's equation

$$\frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = \Delta C_V \qquad \frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = \Delta C_P$$

**(7)** $T_i = \frac{2a}{Rb}$

[$T_i$ = inversion temperature $a$, $b$ = van der Waal's constant]

**(8)** $\Delta H = \Sigma\Delta H$ (Product) – $\Sigma\Delta H$ (Reactant)

If $\Delta H_P > \Delta H_R$, $\Delta H$ = +ve, endothermic

If $\Delta H_P < \Delta H_R$, $\Delta H$ = –ve, exothermic

**(9)**

$$\Delta S = \frac{\delta q_{rev}}{T},$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$$

$\Delta S = S_f - S_i$  $S_f$ = Entropy of final state

$S_i$ = Entropy of initial state

If $\Delta S$ = +ve, randomness increases

$\Delta S$ = –ve, randomness decreases

**(10)** For spontaneous process;

$$\Delta S_{syst} + \Delta S_{surr} > 0$$

**(11)** Entropy change for $n$ moles of an ideal gas during reversible expansion.

$$\boxed{\Delta S = nC_p \ln\frac{T_2}{T_1} + nR \ln\frac{P_1}{P_2}}$$

$$\boxed{\Delta S = nC_v \ln\frac{T_2}{T_1} + nR \ln\frac{V_2}{V_1}}$$

For isothermal reversible process;

$$\boxed{\Delta S = 2.303 nR\log\frac{V_2}{V_1} = 2.303 nR\log\frac{P_1}{P_2}}$$

For isobaric process;

$$\boxed{\Delta S = nC_p \ln\frac{T_2}{T_1}}$$

For isochoric process;

$$\boxed{\Delta S = nC_v \ln\frac{T_2}{T_1}}$$

**(12)** Entropy of mixing $\Delta S_{mx}$

$$= -n_i R\sum X_i \ln x_i$$

Where $n_i$ = total number of moles of gas

$x_i$ = mole fraction of ith gas

**(13)** Thermodynamic efficiency ($\eta$) = $\frac{W}{Q_2} = \frac{T_2 - T_1}{T_2}$

**(14)** Heat of neutralisation of strong acid and strong base = –57.6 kJ $mol^{-1}$

**(15)** Gibb's free energy

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

$$\Delta G = -W = 2.303\, RT \log\frac{V_2}{V_1}$$

$$\Delta G = \Delta G^o + 2.303\ RT \log Q$$

At equilibrium $\Delta G^o + 2.303\ RT \log K$

**(16)** Clausius-Clapeyron equation (integrated form)

$$\text{In}\frac{P_2}{P_1} = \frac{\Delta H_v}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$P_1$, $P_2$ are vapour pressures of a liquid at temperatures $T_1$ and $T_2$.

**(17)** Residual entropy can be calculated from 3rd law of thermodynamics

$S_R = k \ln w$

w = Thermodynamic probability

k = Boltzmann constant

KN = R (Universal gas constant)

**(18)** Debye equation $C_v = aT^3$

$a$ = Constant for a substance, from this equation $C_v$ can be calculated at absolute zero temperature using the extrapolate technique.

●●