



Syllabus

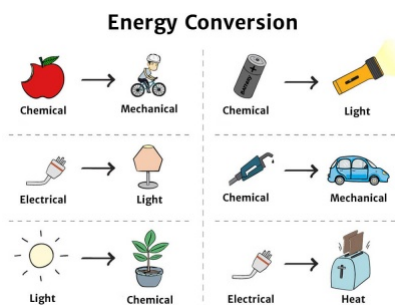
Module No. & Name	Topics to be covered
3 Thermodynamics	Intensive and extensive variables, state and path functions, Laws of Thermodynamics (First law and enthalpy; second law and entropy, spontaneity, and equilibrium; third law and absolute entropy) free energy, Gibbs and Maxwell's relations, Ideal and real gases

Energy is one of the important factor which has significant contribution in our living standards.

The 03 primary sources of energy are solar energy, nuclear energy & chemical energy.

All the chemical reactions are associated with energy changes appearing in different forms like heat energy, light energy, mechanical energy, electrical energy etc.

Thermodynamics is a branch of science which deals with the quantitative relationship between **heat and other forms of energies**.



Scope of Thermodynamics:

Energy Prediction: It helps in the prediction of maximum efficiency of various types of heat energies and maximum work obtained from a given fuel/source of energy.

Predicts feasibility of chemical reaction: Helps in predicting the feasibility a chemical reaction under given set of conditions.

Predicts extend of chemical reaction: Helps in predicting the extend to which the chemical reaction can occur before the equilibrium is attained.

Limitation of Thermodynamics:

- Thermodynamics helps to predict the feasibility of a process but doesn't about the rate of reaction or time required for completion of process.
- It don't throw light on the mechanism of a process.
- Laws of Thermodynamics are not applicable microscopic system (Atom, Molecule) but are applicable to macroscopic system (i.e. The matter in bulk).

Basic concept of Thermodynamics

- **System:** A part of universe which is under investigation.

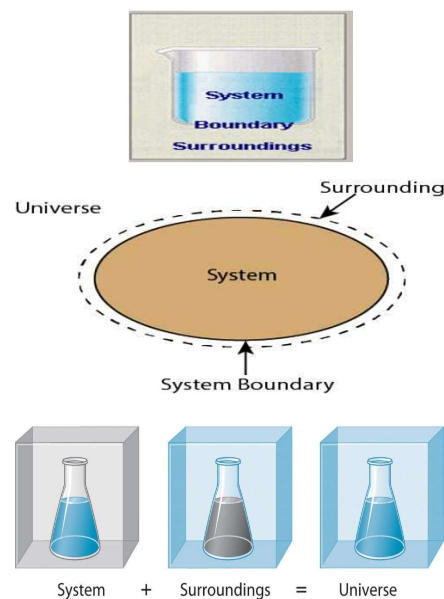
For e.g.: Effect of temperature on the properties of water then water will be considered as system.

- **Surrounding:** Its a part of universe other than system.

- **Universe:** System and surrounding together constitute the universe.

$$\text{Universe} = \text{System} + \text{Surrounding}$$

- **Boundary:** The wall (imaginary / real) which separates the system from the surrounding is called boundary.

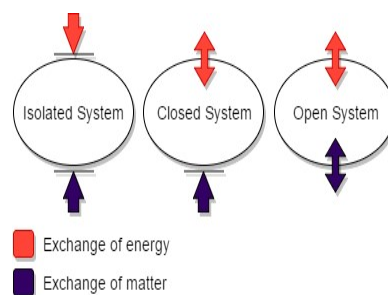


Types of Systems

- ✓ **Isolated System:** A system which neither exchange energy not mass with the surrounding.

For e.g.- Reaction taking place in closed & insulated vessel.

- ✓ **Open System:** A system which can exchange mass as well energy with the surrounding.



For e.g.- Calcination of CaCO_3 in a open bulb: On heating CaCO_3 decomposes into CaO & CO_2 but CO_2 escape to the surrounding.



- ✓ **Closed System:** A system which can exchange energy with the surrounding but not the mass.

For e.g.- Calcination of CaCO_3 in a sealed bulb: On heating CaCO_3 decomposes into CaO & CO_2 but CO_2 doesn't escape to the surrounding.



➤ *Macroscopic System:*

A system containing large number of chemical species (atom, molecule or ions) is called as macroscopic system. The properties of the system arises from the collective behavior of large number of chemical species are called macroscopic property.

For e.g. – To determine the temperature of water we don't deal with individual molecules but we consider the molecules in bulk.

For e.g. – Pressure, Temperature, Volume, Density, Composition, Refractive Index, Surface tension etc.

➤ *Extensive and Intensive Property:*

Various properties of the system may be classified into 02 types: -

- ✓ Extensive Property
- ✓ Intensive Property

Extensive Property

The properties of the system which depends upon the quantity of matter or the size of the matter present in it are called extensive property.

For e.g.- *Mass, Volume, Energy, Heat Capacity*

Intensive Property

The properties of the system which are independent of the quantity of matter or the size of the matter present in it are called intensive property.

For e.g.- *Temperature, Pressure, Viscosity, Refractive Index, Density, Specific Heat.*

➤ *State of the System:*

State of the system means the condition of existence of the system when its macroscopic properties have definite values. If any of the macroscopic property changes, the system undergoes change in its state.

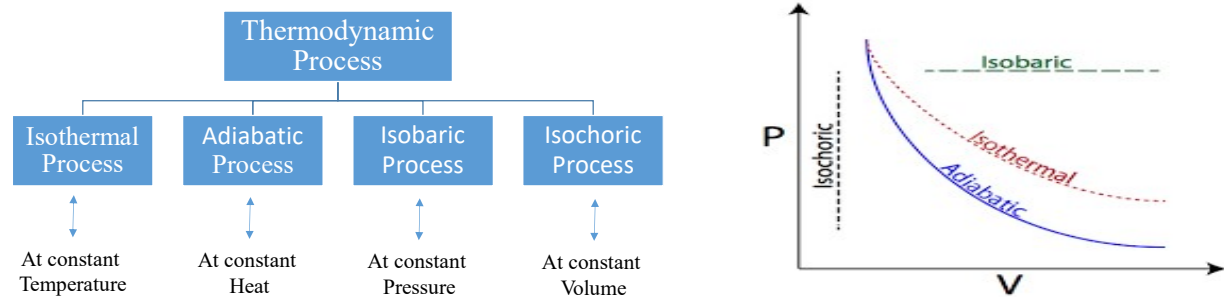
For e.g. – Temperature, Pressure, Volume and Concentration.

For e.g. – Let us consider system of fundamental molecule water in liquid state at 25°C and 1 atm. Pressure then all the macroscopic properties will have definite value. If any of the macroscopic property changes (like temperature) then all the other macroscopic property will also change and water will constitute another state of system.

The macroscopic property of the system are also called state variable / state function.

➤ *Thermodynamic Process:*

The process / operation which bring about the change in the state of the system is known as Thermodynamic process.



➤ *Reversible and Irreversible Process:*

Reversible Process: A process which carried out so slowly that system always remain in a state of equilibrium at every stage is called reversible process. Such type of process can be reversed by infinitely small change.

The reversible process are ideal process and can't be realized in actual practice.

Irreversible Process: A process which carried out very rapidly and system don't remain in the state of equilibrium at every stage is called irreversible process. Such type of process can be reversed with the help of external agency/changing reaction conditions.

Internal Energy & Internal Energy Change (ΔE)

Every substance is associated with a definite amount of energy which depends upon its chemical nature and state of existence. This energy is called internal energy or intrinsic energy of the substance and denoted by ' E '. Unit – Joules or Ergs ($1\text{J} = 10^7\text{Ergs}$)

Internal energy or intrinsic energy is the energy possessed by all constituents of the molecule. The various forms of energy which contribute towards the energy of the molecule are translations energy, rotational energy, vibrational energy, electronic energy, nuclear energy of constituent atoms and potential energy due to interaction with the neighboring molecule.

Internal energy is a state property i.e. its value depends upon the state of the substance but doesn't depend upon how that state is achieved.

Internal energy is a extensive property i.e. its value depends upon the quantity / size of the matter.

Absolute value of Internal energy can't be determined but the change in internal energy (ΔE) accompanying a chemical / physical process is measurable.

$$(\Delta E) = \sum E_{\text{Product}} - \sum E_{\text{Reactant}}$$

For Isothermal Process: At Temperature ~ Constant

$$(\Delta E) = 0$$

Heat (q)

Heat is another mode of changing the internal energy of the system. If heat is absorbed by the system then internal energy increases whereas if the heat is given out of the system the internal energy decreases.

Heat is another mode of changing the internal energy of the system. Exchange of energy between system & surrounding is possible only if temperature difference exists between them.

Heat absorbed by the system = + ive ($q > 0$)

Heat given out by the system = - ive ($q < 0$)

Work (w)

Work is the product of force and displacement but in thermodynamics work can be of 02 types

(1) Pressure – Volume Work

(2) Electrical Work

Pressure – Volume Work:

When pressure is applied on a gaseous system then there is change in the volume of gas. It is also known as Expansion Work.

If 'P' is the pressure applied on the gaseous system and the volume of gas changes from V_1 to V_2 then

$$W = P (V_2 - V_1) = \pm P \Delta V$$

Electrical Work (Non Expansion Work):

In electrochemical cell where redox reaction takes place and the charge is transferred through external circuit.

In this type of work the force refers to the potential difference and displacement refers to the quantity of charge transferred / flowing through conductor.

If 'Q' is the charge flowing across the conductor & 'E' is the potential difference across the conductor then

$$W_{\text{elec.}} = \pm EQ$$

Unit: In CGS – Ergs

In S.I. Units – Joules

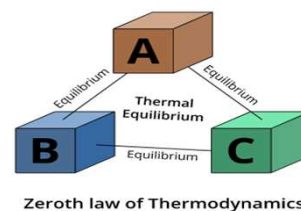
(1 J = 10^7 ergs = 1 Nm = 1 Kg m² s⁻²)

Work done on the system = +ive (**Work has been done on the system by the surrounding & increases the internal energy**).

Work done on the system = -ive (**Work has been done by the system by the surrounding & decreases the internal energy**).

Zeroth Law of Thermodynamics

If two bodies (B & C) are in thermal equilibrium with another body 'A' then bodies B & C will also be in thermal equilibrium with each other.



First Law of Thermodynamics

Energy can neither be created nor destroyed but it can be converted from one form to another. In other words the energy of the universe is constant.

Let us consider a system having internal energy ' E_1 ' and absorbs certain amount of heat energy ' q ' then internal energy of the system ' E_2 ' will be

$$E_2 = E_1 + q$$

If ' W ' amount of work is done on the system then final internal energy will be

$$E_2 = E_1 + q + W$$

$$E_2 - E_1 = q + W \quad \text{-----equ}^n 1$$

$$\Delta E = q + P\Delta V$$

$W = +P\Delta V$; When work done **on** the system

$$\Delta E = q - P\Delta V \quad \text{-----equ}^n 2$$

$W = -P\Delta V$; When work done **by** the system

q and W are not state function (i.e. don't depend on the condition of existence of system) but their addition is a state function (i.e. ΔE).

Significance of ΔE :

For Isothermal Process $\Delta E = 0$ then putting the value in equⁿ 1

$$\Delta E = q + P\Delta V$$

$$P\Delta V = -q \quad \therefore \Delta E = 0$$

For Adiabatic Process $q = 0$ then work is done by the system. Putting the value in equⁿ 2

$$\Delta E = q + P\Delta V$$

$$\Delta E = -P\Delta V$$

For Isochoric Process $\Delta V = 0$ then work done $P\Delta V = 0$. Putting the value in equⁿ 1

$$\Delta E = q$$

Enthalpy or Heat Content (H)

Enthalpy is the total energy associated with a system which includes its internal energy 'E' and energy due to the environmental factors such as Pressure & Volume conditions. It's denoted by 'H'.

$$H = E + PV$$

Enthalpy is a state function (Depends on the condition of existence of the system when macroscopic properties have definite value) i.e. it has definite value depending upon the state of the system.

Enthalpy is not a path function i.e. It's independent of the path by which state of the system is achieved.

It's not possible to determine the absolute value of enthalpy of the system as absolute value of internal energy 'E' is not known but we can find out change in enthalpy.

Change in Enthalpy (ΔH) :

$$\Delta H = \Delta E + P\Delta V$$

Change in enthalpy for a process in which initial (reactants) and final (products) are in their standard states.

First Law of Thermodynamics in terms of ΔH

By first law of thermodynamics
when work is done by the system

$$\Delta E = q - P\Delta V \quad \text{-----equ}^n 1$$

Change in enthalpy

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta E = \Delta H - P\Delta V \quad \text{-----equ}^n 2$$

From equⁿ (1) & (2)

$$\Delta H - \cancel{P\Delta V} = q - \cancel{P\Delta V}$$

$$\Delta H = q$$

Change in enthalpy (ΔH) is the measure of heat evolved or absorbed in a reaction at constant Temperature & Pressure.

Relationship between ΔH & ΔE

Let us consider a reaction in gaseous phase at constant temperature (T) and constant pressure (P). If V_A and V_B are the total volume of gaseous reactants and products respectively. If n_A and n_B are the number of moles of gaseous reactants and products respectively then



By Ideal Gas Equation

$$P V_A = n_A RT \quad \text{-----equ}^n 1$$

$$P V_B = n_B RT \quad \text{-----equ}^n 2$$

Subtracting equⁿ (1)
from (2)

$$P V_B - P V_A = n_B RT - n_A RT$$

$$P (V_B - V_A) = (n_B - n_A) RT$$

$$P \Delta(V) = \Delta(n) RT \quad \text{-----equ}^n 3$$

Change in enthalpy is defined as

$$\Delta H = \Delta E + P\Delta V \quad \text{-----equ}^n 4$$

From equⁿ (3) & (4)

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

Significance of ΔH :

If $\Delta n = 0$ then $\Delta H = \Delta E$

If $\Delta n = +ive$ then $\Delta H > \Delta E$

If $\Delta n = -ive$ then $\Delta H < \Delta E$

Numerical based on ΔH , ΔE and Δn and First Law of Thermodynamics

Heat Capacity of a system (C)

The heat (q) absorbed by the system is directly proportional to the rise in temperature (ΔT).

$$q \propto \Delta T \quad \longrightarrow \quad q = C\Delta T \quad \longrightarrow \quad C = q / \Delta T$$

For infinitely small change, if (dq) heat required to rise the temperature from T to (T+dT) then

$$C = dq / dT$$

Heat Capacity of a system is the quantity of heat required to raise the temperature through 1°C.

Specific Heat Capacity of a system is the quantity of heat required to raise the temperature of unit mass through 1°C.

$$\text{Specific Heat Capacity (c)} = C / m \quad \text{Where } C = q / \Delta T$$

$$\text{Specific Heat Capacity (c)} = q / m \Delta T$$

Heat capacity is not a state function but it depends on the path i.e it's a path function.

Molar heat capacity at constant volume (C_V): It is defined as the rate of change of internal energy with temperature at constant volume.

$$\text{Heat Capacity at constant volume } (C_V) = (\partial E / \partial T)_V$$

Molar heat capacity at constant pressure (C_P): It is defined as the rate of change of enthalpy with temperature at constant pressure.

$$\text{Heat Capacity at constant pressure } (C_P) = (\partial H / \partial T)_P$$

Relationship between C_P & C_V

At constant volume the heat absorbed the system is completely utilized in increasing the internal energy of the system and no work is done.

At constant pressure the heat absorbed the system is utilized in increasing the internal energy and work done.

Rise in temperature of the system at constant pressure and volume remain same but some extra heat is required for doing work of expansion at constant pressure.

$$\therefore C_P > C_V$$

$$C_P - C_V = \left(\frac{\partial V}{\partial T} \right)_P \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right] \quad \text{-----equ}^n 1$$

Above equation is applicable to solids, liquids and gases and the term $\left(\frac{\partial V}{\partial T}\right)_P$ is the change in the volume due to the rise in temperature at constant pressure and multiplication with pressure 'P' converts it into work done.

The term $\left(\frac{\partial E}{\partial V}\right)_T$ is the change in the internal energy due to the change in volume at constant temperature and known as internal pressure.

The term Internal pressure $\left(\frac{\partial E}{\partial V}\right)_T$ is a measure of interaction between the molecules.

$$\left[\left(\frac{\partial E}{\partial V}\right)_T\right]_{\text{Solids}} > \left[\left(\frac{\partial E}{\partial V}\right)_T\right]_{\text{Liquids}} > \left[\left(\frac{\partial E}{\partial V}\right)_T\right]_{\text{Gases}}$$

For Ideal Gas

$$C_P - CV = nR$$

Kirchhoff's Equation

Kirchhoff's Equation: It states that variation in ΔH of a reaction with temperature at constant pressure is equal to variation in heat capacity at constant pressure ΔC_P

$$\left(\frac{\partial H}{\partial T}\right)_P = \Delta C_P$$

Similarly

$$\left(\frac{\partial E}{\partial T}\right)_V = \Delta C_V$$

Spontaneous Process or Irreversible Process

A process which proceeds by its own without any outside assistance is called a Spontaneous Process.

For e.g.- Flow of heat from hot body to cold body or two different gases enclosed in a vessel will mix with each other.

This tendency of the process to occur by its own is known as *Spontaneity*.

Criteria for Spontaneity

- ✓ It's unidirectional.
- ✓ For a unstable system (not in equilibrium), Spontaneous process is expected till the equilibrium state is attained.
- ✓ Increase in randomness (Maximum Entropy) favours Spontaneous process.

For e.g.- Melting of Ice, Flow of heat from hot body to cold body.

Second Law of Thermodynamics

Need for Second Law of Thermodynamics:

First Law of Thermodynamics don't tell about the feasibility of the process but it tells that there is exact equivalence between various forms of energy & heat gain is equal to the heat loss.

It don't tell about the direction in which energy can be transferred.

Second Law of Thermodynamics tells about the direction in which heat can transfer and also gives information whether the reaction can takes place spontaneously via a concept of entropy.

Various statement of Second Law of Thermodynamics:

- The complete conversion of heat into work is impossible without some effect elsewhere. [**Kelvin-Planks Statement**].
- It is impossible to construct a machine, functioning in cycle, which can convert heat into equivalent amount of work without producing changes elsewhere. [**Clausius Statement**].
- Without the use of external agency, heat can't by itself pass from colder body to hotter body.
- Entropy increases in irreversible process.

Entropy

Entropy is a measure of the randomness or disorder of the molecules of the system and denoted by 'S'.

Entropy is a thermodynamic state quantity i.e. $\Delta S = S_f - S_i$

S_f = Entropy of the final state
 S_i = Entropy of the initial state

For Spontaneous Process = $S_f - S_i > 0$ or $S_f > S_i$ or $\Delta S > 0$

Entropy Change:

For a reversible change taking place at a fixed temperature 'T', the change in entropy ΔS is equal to the heat energy absorbed or evolved divided by the temperature.

Entropy change is the ratio of heat absorbed or evolved to the temperature.

$$\Delta S = \int_i^f \frac{\Delta q_{rev}}{T}$$

Change in entropy is inversely proportional to the temperature at which the heat is absorbed or evolved or state change takes place.

Unit of Entropy

S.I. System	Jmole ⁻¹ K ⁻¹	~ EU	
CGS System	Cal mol ⁻¹ K ⁻¹	~ eu	∴ 1eu = 4.184 EU

Helmholtz Free Energy or Work Function

Helmholtz free energy or Work function is defined as

$$A = E - TS$$

From the above equation we can say that A is the total internal energy of the system (E) less the contribution that is stored Chaotically (Condition or place of great disorder) i.e. quantity 'TS'.

Chaotic energy can't be used to achieve the uniform motion in surrounding and only a part of internal energy i.e. E-TS is available for conversion into work.

Helmholtz free energy or Work function is a state function i.e. it depends on the initial & final state of the system and don't depends on the path by which final state of the system is achieved.

Change in Helmholtz Free Energy: $(\Delta A) = \Delta E - T\Delta S$

For cyclic process $\Delta E = 0$ and $\Delta S = 0$ then $\Delta A = 0$

Significance of Work Function or Helmholtz Free Energy:

$$dA = - (W_{\text{rev.}} + SdT)$$

For Isothermal process i.e $dT = 0$

$$dA = - (W_{\text{rev.}}) \quad \text{or} \quad W_{\text{rev.}} = -dA$$

- ✓ A decrease in work function at constant temperature gives maximum reversible work done by the system.

Arbeit is a German word for work, so symbol 'A' is used for work.

- ✓ Spontaneous change for Isochoric process i.e. $\Delta V = 0$; $\Delta A < 0$.
- ✓ Helmholtz free energy is applicable to the geochemical problem where huge pressure is involved at constant volume.

Variation of Work Function 'A' with Temperature & Volume

Following equation represents the variation of Work Function / Helmholtz free energy with temperature and volume.

$$\partial A = - nRT \quad A = \frac{\partial V}{V}$$

For Isothermal process, $\Delta T = 0$ and Change in volume is V_1 to V_2

$$\Delta A = -nRT \log \frac{V_2}{V_1}$$

For Isochoric process, $\Delta V = 0$ and Change in volume is V_1 to V_2

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

Gibb's - Helmholtz Equation in terms of Work Function

$$\Delta A = \Delta E + T \left(\frac{\partial \Delta A}{\partial T}\right)_V$$

Gibb's Free Energy Function (G)

Gibb's free energy can be defined as the maximum amount of energy available to system which can be put into useful work. It is denoted by 'G'.

$$G = H - TS$$

Where
H = Enthalpy, T = Temperature
S = Entropy

Gibb's free energy is a state function i.e. it depends on the initial and final state of the process and it's not a path function (i.e. don't depend on the path by which final state is achieved).

We can't find out the absolute value of Gibb's free energy at any point in the process as the absolute value of 'H' is not known hence we can only find out the change in Gibb's Free Energy.

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

Gibb's free energy is an extensive property which depends on the quantity of matter or the size of the system.

For Cyclic process Gibb's free $\Delta G = 0$

For cyclic process: $\Delta H = \text{Enthalpy} = 0$
 $\Delta S = \text{Entropy} = 0$

The value $\Delta G = 0$ means the state of equilibrium.

Significance of Gibb's Free Energy (Free Energy Change & Spontaneity)

ΔH	ΔS	ΔG	Conclusion	Example
- ive	+ ive	- ive	Reaction will be spontaneous	
- ive	- ive	- ive	(if $\Delta H > \Delta S$) Reaction will be spontaneous	$\text{H}_2\text{O (g)} \longrightarrow \text{H}_2\text{O (l)}$
- ive	- ive	+ive	(if $\Delta H < \Delta S$) Reaction will not takes place	$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{SO}_3(\text{g})$
+ive	+ive	+ive	(if $\Delta H > \Delta S$) Reaction will not takes place	$\text{NH}_4\text{Cl (s)} \longrightarrow \text{NH}_3(\text{g}) + \text{HCl (g)}$
+ive	+ive	- ive	(if $\Delta H < \Delta S$) Reaction will takes place	$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g})$
+ ive	- ive	+ive	<ul style="list-style-type: none"> For exothermic reaction $\Delta H = +\text{ive}$ and for endothermic reaction $\Delta S = -\text{ive}$. Both the factors are unfavorable and make $\Delta G = +\text{ive}$ Reaction will not takes place 	Exothermic reaction involving decrease in entropy i.e. S will never occur

Standard Gibb's Free Energy (ΔG°)

The free energy change for a process at a specified temperature in which reactants in their standard state (At Temperature = 298 K & Pressure = 1 atm.) are converted into product in their standard state.

$$\Delta G^\circ = \sum \text{Standard free energies of formation of product} - \sum \text{Standard free energies of formation of reactant}$$

Partial Molar Gibb's Free Energy or Chemical Potential (μ)

The Partial Molar Gibb's free energy is defined by following expression -

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j}$$

The Partial Molar Gibb's free energy (μ) is the increase in Gibb's free energy per mole when temperature, pressure and composition is kept constant.

‘ μ ’ is intensive property (independent of quantity of matter) and has same value throughout the system at equilibrium.

Chemical Potential ‘ μ ’ of a component is the measure of its ability to bring about the chemical change.

Gibb's – Duhem Equation

If n_A and n_B are the number of moles and μ_A & μ_B are the chemical potential of components A & B respectively then Gibb's Duhem Equation is defined as

$$n_A d\mu_A + n_B d\mu_B = 0 \quad \text{Or} \quad d\mu_B = -\frac{n_A}{n_B}(d\mu_A)$$

Significance

The chemical composition of one component of mixture can't change independently the chemical potential ‘ μ ’ of other component.

Numerical on Gibb's Free Energy (G)