Thermodynamics

The study of the flow of heat or any other form of energy into or out of a system as it undergoes a physical or chemical transformation is called Thermodynamics.

Scope of Thermodynamics:

(1) Most of the important laws of Physical Chemistry, including the van't Hoff law of lowering of vapor pressure, the Phase Rule, and the Distribution Law, can be derived from the laws of thermodynamics.

(2) It tells whether a particular physical or chemical change is feasible or not under a given set of conditions of temperature, pressure, and concentration.

(3) It also helps in predicting how far a physical or chemical change can proceed, until the equilibrium conditions are established.

Limitations of Thermodynamics

(1) **Thermodynamics is applicable to macroscopic systems** consisting of matter in bulk and not to microscopic systems of individual atoms or molecules. **It ignores the internal structure of atoms and molecules.**

(2) Thermodynamics does not bother about the time factor. That is, it does not tell anything regarding the rate of a physical change or a chemical reaction. **It is concerned only with the initial and the final states of the system.**

Thermodynamic terms and basic concepts

An important part of the study of thermodynamics is a few terms and definitions which must be understood clearly.

The system, Boundary, and Surroundings:

A system is that part of the universe which is under thermodynamic study and the rest of the universe is its surroundings.

The real or imaginary surface separating the system from the surroundings is called the **boundary**. In experimental work, a specific amount of one or more substances constitutes the system. Thus 200 g of water contained in a beaker constitutes a thermodynamic system. The beaker and the air in contact are the **surroundings**.

Similarly, one mole of oxygen confined in a cylinder fitted with a piston, is a thermodynamic system. The cylinder and the piston and all other objects outside the cylinder, form the surroundings. Here the boundary between the system (oxygen) and the surroundings (cylinder and piston) is clearly defined.

Types of thermodynamic systems:

There are three types of thermodynamic systems depending on the nature of the boundary. If the boundary is closed or sealed, no *matter* can pass through it. If the boundary is insulated, no *energy* (say heat) can pass through it.

(1) **Isolated System:** When the boundary is both sealed and insulated, no interaction is possible with the surroundings. Therefore, *an isolated system is one that can transfer neither matter nor energy to and from its surroundings*.

A substance, say boiling water, contained in a *thermos flask,* is an example of an isolated system.

(2) **Closed System:** Here the boundary is sealed but not insulated. Therefore, *a closed system is one which cannot transfer matter but can transfer energy in the form of heat, work and radiation to and from its surroundings*. A

specific quantity of hot water contained in a sealed tube, is an example of a closed system. While no water vapour can escape from this system, it can transfer heat through the walls of the tube to the surroundings.

A gas contained in a cylinder fitted with a piston constitutes a closed system. As the piston is raised, the gas expands and transfers heat (energy) in the form of work to the surroundings.

(3) **Open System:** In such a system the boundary is open and un-insulated. Therefore, *an open system is one which can transfer both energy and matter to and from its surroundings*. Hot water contained in a beaker placed on laboratory table is an open system. The water vapour (matter) and also heat (energy) is transferred to the surroundings through the imaginary boundary.

Intensive and extensive properties:

The macroscopic or bulk properties of a system (volume, pressure, mass, etc.) can be divided into two classes:

(*a*) Intensive properties (*b*) Extensive properties

Intensive Properties:

A property that does not depend on the quantity of matter (amount of mass) present in the system is known as **Intensive Property**.

Some examples of intensive properties are *pressure, temperature, density*, and *concentration*. If the overall temperature of a glass of water (our system) is 20ºC, then any drop of water in that glass has a temperature of 20ºC. Similarly, if the concentration of salt, NaCl, in the glass of water is 0.1 mole/litre, then any drop of water from the glass also has a salt concentration of 0.1 mole/litre.

Extensive Properties:

A property that does depend on the quantity of matter (amount of mass) present in the system is called an **Extensive Property**.

Some examples of extensive properties are *volume, number of moles, enthalpy, and Gibbs' free energy*.

By definition, the extensive properties are additive while intensive properties are not. Let us consider the system 'a glass of water'. If we double the mass of water, the volume is doubled and so are the number of moles and the internal energy of the system.

Intensive properties		Extensive properties
Temperature	Surface tension	Mass
Pressure	Refractive index	Volume
Density	Viscosity	Internal energy
Boiling point	Freezing point,	Enthalpy

Thermodynamic Equilibrium and non–equilibrium states:

A system in which the state variables have constant values throughout the system is said to be in a state of thermodynamic equilibrium.

Suppose we have a gas confined in a cylinder that has a frictionless piston. If the piston is stationary, the state of the gas can be specified by giving the values of pressure and volume. The system is then in a *state of equilibrium*.

A system in which the state variables have different values in different parts of the system is said to be in a non-equilibrium state.

If the gas contained in a cylinder, as stated above, is compressed very rapidly by moving down the piston, it passes through states in which pressure and temperature cannot be specified, since these properties vary throughout the gas. The gas near the piston is compressed and heated and that at the far end of the cylinder is not. The gas then would be said to be in a non-equilibrium state.

Thermodynamics is concerned only with equilibrium states.

Thermodynamic processes:

When a thermodynamic system changes from one state to another, the operation is called a **Process.** These processes involve the change of conditions (temperature, pressure and volume). The various types of thermodynamic processes are:

(1) **Isothermal Processes:** Those processes, in which the temperature remains fixed, are termed isothermal processes. This is often achieved by placing the system in a thermostat (a constant temperature bath).

For an isothermal process $dT = 0$

(2) **Adiabatic Processes:** Those processes in which no heat can flow into or out of the system are called adiabatic processes. Adiabatic conditions can be approached by carrying the process in an insulated container such as 'thermos' bottle. High vacuum and highly polished surfaces help to achieve thermal insulation.

For an adiabatic process $dq = 0$

(3) **Isobaric Processes:** Those processes which take place at constant pressure are called isobaric processes. For example, heating of water to its boiling point and its vaporization take place at the same atmospheric pressure. These changes are, therefore, designated as isobaric processes and are said to take place isobarically.

For an isobaric process $dp = 0$

(4) **Isochoric Processes:** Those processes in which the volume remains constant are known as isochoric processes. The heating of a substance in a non-expanding chamber is an example of isochoric process.

For isochoric processes $dV = 0$.

(5) **Cyclic Process:** When a system in a given state goes through a number of different processes and finally returns to its initial state, the overall process is called a cycle or cyclic process.

For a cyclic process $dE = 0$, $dH = 0$.

Reversible and irreversible processes:

A thermodynamic reverse process is one that takes place infinitesimally slowly and its direction at any point can be reversed by an infinitesimal change in the state of the system.

In fact, a reversible process is considered to proceed from the initial state to the final state through an infinite series of infinitesimally small stages. At the initial, final and all intermediate stages, the system is in equilibrium state. This is so because an infinitesimal change in the state of the system at each intermediate step is negligible.

When a process goes from the initial to the final state in a single step and cannot be carried in the reverse order, is known as an irreversible process. Here the system is in an equilibrium state in the beginning and at the end, but not at points in between.

	Reversible Process	Irreversible Process
1	It takes place in infinite number of infinitesimally small steps and it would take *infinite time* to occur.	It takes *finite time* for completion.
2	It is *imaginary* as it assumes the presence of frictionless and weightless piston.	It is *real* and can be performed actually.
3	It is in equilibrium state at *all stages* of the operation.	It is in equilibrium state only at the *initial and final stages* of the operation.
4	All changes are *reversed* when the process is carried out in reversible direction.	After this type of process has occurred all changes *do not return* to the initial state by them.
5	It is extremely slow.	It proceeds at *measurable speed*.
6	Work done by a reversible process is *greater* than the corresponding irreversible process.	Work done by an irreversible process is *smaller* than the corresponding reversible process.

Nature of heat and work:

When a change in the *state* of a system occurs, energy is transferred to or from the surroundings. This energy may be transferred as heat or mechanical work.

Heat: *Heat is the process of energy transfer as a result of a temperature difference between the system and its surroundings.*

Walls that permit heating as a mode of transfer of energy are called **diathermic**. A metal container is diathermic.

Walls that do not permit heating even though there is a difference in temperature are called **adiabatic** (from the Greek words for 'not passing through'). The double walls of a vacuum flask are adiabatic to a good approximation.

Units of Heat: The unit of heat, which was used for many years, is **calorie** (cal). A calorie is defined as the quantity of heat required to raise the temperature of 1 gram of water by 1º C in the vicinity of 15ºC. Since heat and work are interrelated, **SI unit of heat is the joule (J).**

1 joule = 0.2390 calories; 1 calorie = 4.184 J; or 1 kcal = 4.184 kJ

Pressure–Volume Work:

In physics, mechanical work is defined as force multiplied by the distance through which the force acts. In elementary thermodynamics the only type of work generally considered is the work done in expansion (or compression) of a gas. This is known as **pressure-volume work** or **PV work** or **expansion work.**

Consider a gas contained in a cylinder fitted with a frictionless piston. The pressure (force per unit area) of the gas, P, exerts a force on the piston. This can be balanced by applying an equal but opposite pressure from outside on the piston. Let it be designated as P_{ext}. It is important to remember that it is the external pressure, P_{ext}, and not the internal

pressure of the gas itself which is used in evaluating work. This is true whether it be expansion or contraction. If the gas expands at constant pressure, the piston would move, say through a distance *l*.

We know that $\qquad$ *work = force × distance* (by definition)

$$W = f \times l \dots\dots\dots\dots\dots\dots(1)$$

Since pressure is force per unit area,

$$f = P_{ext} \times A \dots\dots\dots\dots\dots\dots(2)$$

where A is the cross-section area of the piston.

From (1) and (2), we have $\qquad W = P_{ext} \times A \times l$

$$= P_{ext} \times \Delta V$$

(Area x distance = Volume)

During the process volume of the gas changes from initial volume V₁ and to final volume V₂.

$$\therefore W = \int_{V_1}^{V_2} P dV$$

$$W = P(V_2 - V_1)$$

$$W = P\Delta V$$

When work is done by the system W is +ve., i.e., $V_2 > V_1$. ΔV is positive, expansion takes place.

When work in done on the system by surroundings W is –ve. i.e., $V_2 < V_1$, compression takes place.

It may be noted that **the work done by a system is not a state function.** This is true of the mechanical work of expansion. We shall show presently that the work is related to the process carried out rather than to the internal and final states. This will be evident from a consideration of the reversible expansion and an irreversible process.

Figure. 1. Pressure volume work of a system (gas) confined by a frictionless piston.

Units of Work

In CGS system the unit of work is erg which is defined as the work done when a resistance of 1 dyne is moved through a distance of 1 centimeter. Since the erg is so small, a bigger unit, the **joule (J)** is now used.

1 joule = 10^7 ergs or 1 erg = 10^{-7} J. We often use **kilojoule** (kJ) for large quantities of work; 1 kJ = 1000 J

Internal Energy (E):

Internal energy is the heat content of the system measured at constant volume and temperature.

It is defined as sum of all energies possessed by the system.

E = K.E + P.E

K. E= Translational energy + rotational energy + Vibrational energy + Electronic energy

P.E = Intermolecular attractions + Interatomic attractions + attraction between Electrons and the nucleus
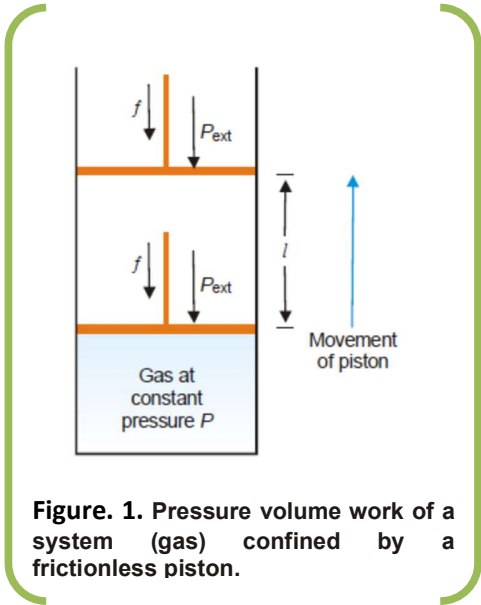
Internal energy is an extensive property and a state function. Absolute values of it cannot be calculated. Since it is difficult to calculate translational and rotational energies. However, change in internal energy (ΔE) can be calculated

First Law of Thermodynamics: Statements:

(1) The energy can be neither created nor destroyed, although it is converted from one form to another.

(2) The total energy of an isolated system or universe remains constant.

(3) Whenever a quantity of energy of a particular type disappears equivalent amount of another type must be produced.

(4) Total energy of system and surroundings remains constant (or conserved)

(5) It is impossible to construct a perpetual motion machine that can produce work without spending energy on it.

When a system is changed from state A to state B, it undergoes a change in the internal energy from E_A to E_B. Thus, we can write

$$\Delta E = E_B - E_A$$

This energy change is brought about by the evolution or absorption of heat and/or by work being done by the system. Because the total energy of the system must remain constant, we can write the mathematical statement of the First Law as:

$$\Delta E = q - w$$

where q = the amount of heat supplied to the system, w = work done by the system

Some Special Forms of the First Law of Thermodynamics: Mathematical statement of the First Law of Thermodynamics is

$$\Delta E = q - w$$

Case 1: For a cyclic process involving isothermal expansion of an ideal gas

$$\Delta E = 0 \qquad \therefore q = w$$

Case 2: For an isochoric process (no change in volume) there is no work of expansion *i.e.* $w = 0$. Hence

$$\Delta E = q_v$$

Case 3: For an adiabatic process there is no change in heat gained or lost *i.e.* $q = 0$. Hence

$$\Delta E = - w$$

In other words, the decrease in internal energy is exactly equal to the work done on the system by surroundings.

Case 4: For an isobaric process there is no change in pressure, *i.e.* P remains constant. Hence

$$\Delta E = q - w \text{ or } \Delta E = q - P\Delta V$$

Limitations of First law:

Although the first law of thermodynamics is exact, but has certain limitations.

1) According to 1st law of thermodynamics energy of one form can be converted to another form but total energy always remains constant but 1st law does not indicate whether a given process is spontaneous or not and if so in which direction.

2) First law does not account whether heat can flow from colder body to hotter body, whether gas can diffuse from low to high pressure. All that 1st law is heat energy gained by one end is exactly equal to heat energy lost by the other end.

3) According to 1st law, the energy of one form should be converted into an exactly equivalent amount of other forms of energy. Although various forms of energy are converted into one another, it is observed that no heat engine can convert all the heat absorbed into exactly the equivalent amount of work without any loss.

The above limitations of 1st law were explained on the basis of the 2nd law of thermodynamics.

The second law of thermodynamics: Some of the statements of the 2nd law are,

1) All spontaneous processes are thermodynamically irreversible.

2) Without the help of external work heat cannot flow on its own from a colder to a hotter body.

3) It is impossible for any heat engine to convert all the heat absorbed into equivalent work without producing changes elsewhere.

One of the statements of the 2nd law given by Kelvin, states that;

"It is impossible for a cyclic process to take heat from a hotter reservoir and convert it into an equivalent work without transferring a part of heat to a colder reservoir."

This statement recognizes the fact that no heat engine is 100% efficient.

Statement for 2nd law given by Clausius:

"It is impossible for any cyclic process to transfer heat from a system at lower to a system at a higher temperature without applying some work."

This statement recognizes the fact that heat flows spontaneously.

Entropy:

Definition of entropy:

Entropy is a thermodynamic state quantity that is a measure of the randomness or disorder of the system.

Entropy is a measure of disorderliness or randomness of a system. More is the disorder of the system; greater will be its entropy. An increase in disorderliness during a physical or chemical process indicates an increase of entropy.

Consider a molecular system existing in two states A and B. In the state A the molecules are regularly arranged in an orderly fashion and its entropy is low.

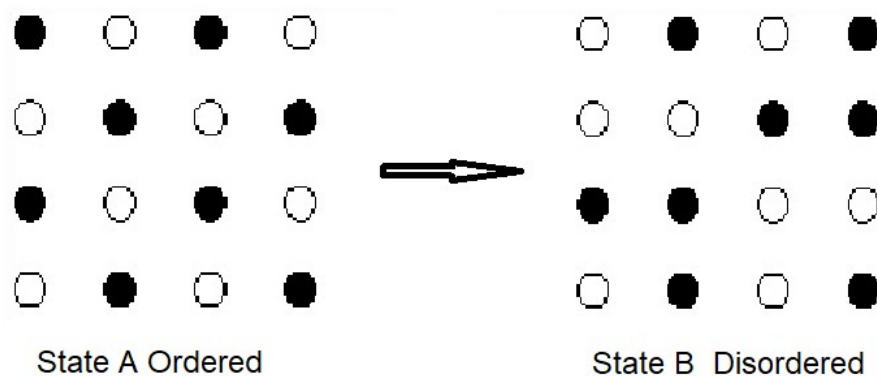While in state B the molecules are randomly arranged and its entropy is high.

State A Ordered   State B Disordered

Figure 6 (a) State A is highly ordered, low entropy and less probable;

   (b) State B is highly disordered high entropy and more probable.

Change of state A (regular arrangement) to state B (disorder) leads to an increase of entropy.

According to the law of probability, state A is less probable than state B. As a result of state A changing to state B is spontaneous.

On this basis, it can be stated that ***"any change which can be accompanied by an increase of entropy tends to be spontaneous".***

Units of Entropy: Since entropy is equal to heat energy divided by absolute temperature, therefore it is measured in entropy units (**eu**) which are Cal.deg^{-1}.K^{-1}. (Or) Cal.K^{-1}.mol^{-1}.

In the SI system, the units are J.mol^{-1}.deg^{-1}. (Or) J.mol^{-1}.K^{-1}., these are represented by **eu.**

Entropy change for a reversible process:

A reversible process is the one, when heat is absorbed by the system reversibly and at the same time heat is lost by the surroundings also reversibly.

In a reversible process

$$\Delta S_{sys} = \frac{Q_{rev}}{T}$$

$$\Delta S_{surr} = -\frac{Q_{rev}}{T}$$

Net change of entropy

$$\Delta S_{sys} + \Delta S_{surr} = \frac{Q_{rew}}{T} - \frac{Q_{rew}}{T} = 0$$

$$\therefore \quad \Delta S_{sys} + \Delta S_{surr} = 0$$

For a thermodynamically reversible process, the net entropy changes of the combined system and surroundings taken together is zero.

Entropy change for an irreversible process:

If any small part of a reversible process is carried out rapidly then the entire process becomes irreversible.

Even in such irreversible process, ΔS of the system will not depend upon the actual heat absorbed but it depends upon heat absorbed reversibly.

$$\Delta S_{sys} = \frac{Q_{rev}}{T}$$

If –Q$_{irr}$ is the heat lost by the surroundings at temperature T, then ΔS of the surroundings in an irreversible process is given as

$$\Delta S_{surr} = -\frac{Q_{irr}}{T}$$

Net change of entropy

$$\Delta S_{sys} + \Delta S_{surr} = \frac{Q_{rew}}{T} - \frac{Q_{irr}}{T}$$

It is known that the work done a reversible process is greater than irreversible.

$$W_{rev} > W_{irrev}$$

According to first law of thermodynamics

$$w \propto Q$$
$$Q_{rev} > Q_{irr}$$
$$\frac{Q_{rew}}{T} - \frac{Q_{irr}}{T} > 0$$
$$\therefore \quad \Delta S_{sys} + \Delta S_{surr} > 0$$

For a thermodynamically irreversible process, the net entropy change for the combined system and surroundings together always greater than zero. For an irreversible process, the total entropy always increases.

The combined equation for entropy change is,

$$\Delta S_{sys} + \Delta S_{surr} \geq 0$$
$$\Delta S_{sys} + \Delta S_{surr} = 0 \ (for \ reversible \ process)$$
$$\Delta S_{sys} + \Delta S_{surr} > 0 \ (for \ irreversible \ process)$$

Based on this another statement for second law given as *"All spontaneous processes are accomplished by increase of entropy".*

Physical significance of Entropy:

Entropy is a measure of disorder or randomness of a system. The entropy of the system increases if it goes from more orderly state to less orderly state and vice–versa. This concept of entropy has led to the conclusion that *all substances in their normal crystalline state at absolute zero would be the most ordered state with zero entropy.* At this state, all motion ceases. In case of a perfect crystal the entropy is zero. **This is third law of Thermodynamics**

Entropy change in Universe:

Most of the processes occurring in nature are spontaneous and irreversible due to which the entropy of the universe is continuously increasing.

The essentials of first law and second law of thermodynamics were combined by Clasius and stated as *"energy of the universe remains constant but entropy of the universe is continuously increasing and it tends to maximum".*

Entropy change-Phase change:

Change of phase occurs during the following processes:

1) When solid melts to liquid or when liquid freezes to solid
2) When liquid evaporates to vapour or when vapour condenses to liquid.

Temperature remains constant as long as phase changes completely. Phase change occurs at constant temperature.

The heat evolved or absorbed during phase change at constant temperature is called latent heat (ΔHL)

Entropy change (ΔS) for any process is

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

Entropy changes for melting

$$\Delta S_m = \frac{\Delta HL_m}{T}$$

Entropy change for vapourisation

$$\Delta S_V = \frac{\Delta HL_V}{T}$$

The process of melting and vapourization involve absorption of heat. They show increase in entropy and hence ΔS for these processes is +ve.

The process of freezing and condensation involve evolution of heat, therefore they show decrease of entropy and hence ΔS is –ve.

Gibbs free energy function (G):

➢ The amount of energy available to do useful work is known as Gibbs free energy.

➢ All spontaneous reactions are unidirectional and proceed in the direction where ΔG is negative.

➢ During a physical or chemical process spontaneous nature is decided by useful form of work. [except mechanical work i.e. expansion or compression]

➢ Greater the amount of useful work more will be the decrease in ΔG and the process will be more spontaneous.

Gibbs free energy function G is expressed as G = H – TS …………………..(1)

Enthalpy (H), Entropy (S) are state functions, therefore function G is also a state function.

On applying initial and final states to equation (1), we get

$$G_1 = H_1 - TS_1 \text{ and } G_2 = H_2 - TS_2$$

The change in the free energy (ΔG) on moving from initial state to final state under isothermal conditions

$$\Delta G = G_2 - G_1$$

On substituting above equations

$$\Delta G = (H_2 - TS_2) - (H_1 - TS_1)$$

$$\Delta G = \Delta H - T\Delta S \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

From definition of entropy $T\Delta S = Q_{rev}$ ……………………….……….i

From definition of enthalpy $\Delta H = \Delta E + PdV$……………………….ii

Substituting equations i and ii in equation (2)

$$\Delta G = \Delta E + PdV - Q_{rev}\ldots\ldots\ldots\ldots(3)$$

From the first law of thermodynamics $\Delta E = Q - W$

Applying this equation to a reversible process, we get

$$\Delta E = Q_{rev} - W_{max}$$

$$\Delta E - Q_{rev} = -W_{max}\ldots\ldots\ldots\ldots\text{iii}$$

Substituting equation (iii) in equation (3) $\Delta G = -W_{max} + PdV$

$$-\Delta G = W_{max} - PdV$$

$$-\Delta G = \text{Net Work.}$$

For a process carried out at constant pressure, the decrease of function (G) gives the maximum work obtained from system other than pressure-volume work (PV work).

In other words, the decrease of function (G) gives the network obtained from the system which can be electrical work (or) chemical work.

Variation of free energy (G) with temperature (T) and pressure (P)

By definition of free energy function (G)

$$G = H - TS \ldots\ldots\ldots\ldots\ldots(1)$$

By definition of enthalpy the equation (1) can be written as

$$G = E + PV - TS \ldots\ldots\ldots\ldots.(2)$$

On complete differentiation

$$dG = dE + PdV + VdP - TdS - SdT \ldots\ldots\ldots\ldots(3)$$

For an infinitesimal change in a reversible process, entropy change is given as

$$dS = \frac{Q_{rev}}{T}$$

From first law of thermodynamics

$$\delta Q_{rev} = dE + PdV \quad (\because \ dE = \delta Q - PdV)$$

$$\therefore \ dS = \frac{dE + PdV}{T}$$

$$TdS = dE + PdV$$

On substituting the above equation in equation (3)

$$dG = dE + PdV + VdP - (dE + PdV) - SdT$$

$$\therefore \ dG = VdP - SdT \cdots\cdots\cdots (i)$$

The above equation gives the change of free energy with pressure and with temperature.

$$dG = VdP - SdT$$

At constant temperature, dT = 0

$$(dG)_T = VdP$$

$$\left(\frac{dG}{dP}\right)_T = V \cdots\cdots\cdots (ii)$$

Equation II represents the change of free energy change with pressure at constant temperature.

$$dG = VdP - SdT$$

At constant pressure dP = 0

$$(dG)_P = -SdT$$

$$\left(\frac{dG}{dT}\right)_P = -S \cdots\cdots\cdots (iii)$$

Equation gives variation of free energy with temperature at constant pressure.

For an isothermal process, the change in free energy with pressure can be determined as follows.

Let G_1 and G_2 are quantities of free energy in initial state and final state. Let quantities of pressure by P_1 and P_2 in initial and final states.

Under isothermal conditions

$$(dG)_T = VdP$$

On integration of above equation within G_1 to G_2 and P_1 to P_2

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} VdP$$

From ideal gas equation $\qquad PV = nRT$

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

$$G_2 - G_1 = \int_{P_1}^{P_2} \frac{nRT}{P} \, dP$$

n, R, T are constants

$$\boxed{(\Delta G)_T = nRT \ln \frac{P_2}{P_1} \cdots \cdots \cdots \cdots (I)}$$

$$P_1 V_1 = P_2 V_2$$

$$\frac{P_2}{P_1} = \frac{V_1}{V_2}$$

$$\boxed{(\Delta G)_T = nRT \ln \frac{V_1}{V_2} \cdots \cdots \cdots \cdots (II)}$$

Equation I and II give the change of free energy with pressure at constant temperature for a finite process.

Gibbs-Helmholtz equation:

$$G = H - TS \cdots \cdots \cdots \cdots \cdots (i)$$

$$G = E + PV - TS \cdots \cdots \cdots \cdots (ii)$$

On complete differentiation

$$dG = dE + PdV + VdP - TdS - SdT \cdots \cdots \cdots (iii)$$

But we know from first law

$$dQ = dE + PdV \cdots \cdots \cdots (iv))$$

From equations (iii) and (iv)

$$dG = dQ + VdP - TdS - SdT \cdots \cdots \cdots (v)$$

From the entropy definition we know that

$$dS = \frac{dQ}{T}$$

$$TdS = dQ$$

Substituting the TdS value in equation (v)

$$dG = dQ + VdP - dQ - SdT \cdots \cdots \cdots (vi)$$

$$dG = VdP - SdT \cdots\cdots\cdots (vii)$$

At constant pressure dp=0, then

$$(dG)_P = -SdT$$

$$\left(\frac{dG}{dT}\right)_P = -S$$

Where dG and dT represent the infinitesimally small changes in free energy and temperature respectively. The above equation for the initial and final states can be written as below

$$\left(\frac{dG_1}{dT}\right)_P = -S_1 \cdots\cdots\cdots\cdots (viii) \; for \; initial \; state$$

$$\left(\frac{dG_2}{dT}\right)_P = -S_2 \cdots\cdots\cdots\cdots (ix) \; for \; final \; state$$

Subtracting the equation viii for ix

$$\left(\frac{dG_2}{dT}\right)_p - \left(\frac{dG_1}{dT}\right)_p = -(S_2 - S_1)$$

$$\left(\frac{\partial(\Delta G)}{dT}\right)_P = -\Delta S \cdots\cdots\cdots (x)$$

Let G_1, H_1, and S_1 be the free energy, enthalpy and entropy of the system in the initial state and G_2, H_2 and S_2 are the corresponding values in the final state brought about isothermally at temperature T. Thus

$$\Delta G = \Delta H - T\Delta S \cdots\cdots\cdots (xi)$$

Substituting the ΔG value form equation (x) in equation in (xi)

$$\boxed{\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{dT}\right)_P \cdots\cdots\cdots (xii)}$$

The above equation is the common form of **Gibbs-Helmholtz equation.** It is applicable to all processes occurring at constant pressure.

Applications of Gibbs-Helmholtz equation:

1) The most important application of the equation is in the study of galvanic cells (or electrochemical cells).

When a redox reaction, e.g., Zn + H_2SO_4 $\longrightarrow$ $ZnSO_4$ + H_2, is allowed to take place in a single beaker, heat is evolved. Earlier it was believed that when the same reaction is allowed to take in an electrochemical cell, the electrical energy produced was equivalent to heat evolved. However, later on it was not found to be correct in all cases.

According to Gibbs-Helmholtz the electrical energy produced was equal to the decrease in the free energy accompanying the cell reaction. If n is the number of electrons given out by one of the electrodes (e.g., Zn in the present case) or taken up by the other electrode. Then,

Quantity of electricity produced = nF

Let, E.M.F. of the cell = E

Decrease in free energy, ΔG = –nFE

Substituting the value of ΔG in equation (xii), we get

$$\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P \cdots\cdots\cdots \text{(xii)}$$

$$-nFE = \Delta H + T\left(\frac{\partial(-nFE)}{\partial T}\right)_P \cdots\cdots\cdots \text{(xii)}$$

$$nFE = -\Delta H + TnF\left(\frac{\partial E}{\partial T}\right)_P \cdots\cdots\cdots \text{(xii)}$$

Thus knowing the temperature coefficient of the EMF of the cell i.e., $(\partial E/\partial T)_P$, change in enthalpy can be calculated if EMF (i.e., E) of the cell is known or *vice-versa.*

Evidently, the electrical energy produced (nFE) is equal to heat evolved ($-\Delta H$) only when temperature coefficient of the EMF of the cell, i.e., $(\partial E/\partial T)_P$ is zero.

2) The Gibbs-Helmholtz equation is useful in predicting the feasibility of the process.

Criteria for feasibility (Spontaneous) of a Process:

We observed that the net entropy change for the combined system and the surroundings can be taken as criteria for the feasibility of spontaneity of a process.

If there is a net increase in the entropy of the system and the surroundings taken together

$$dS_{\text{system}} + dS_{\text{surroundings}} > 0$$

the process would proceed irreversibly. i.e., it would be thermodynamically feasible

If the there is no net change in the entropy of the system and the surroundings taken together

$$dS_{\text{system}} + dS_{\text{surroundings}} = 0$$

the process will be reversible. i.e., it will remain in a state of equilibrium and hence not possible.

However, the criterion of entropy change is not convenient as it requires the knowledge of entropy change of the system as well as that of surroundings. Hence, other thermodynamic quantities are preferred for knowing the criteria of feasibility of a process because in these quantities, knowledge of change of that particular thermodynamic quantity of only system is sufficient. These quantities are energy, enthalpy, work function and free energy.

The entropy change criteria for the feasibility of an infinitesimal process, can be written as below

$$dS_{\text{system}} + dS_{\text{surroundings}} \geq 0 \ldots\ldots\ldots\text{(1)}$$

If we assume the change in surroundings as reversible and surroundings evolve dq heat reversibly, at Temperature T

Then

$$dS_{surrounding} = -\frac{dQ}{T}\cdots\cdots\cdots \text{(2)}$$

From the first law of Thermodynamics

$$dQ_{rev} = dE + PdV \cdots\cdots\cdots\cdots \text{(3)}$$

Substituting the value of dQ_{rev} in equation (ii)

$$dS_{surrounding} = -\frac{dQ}{T} = -\frac{(dE + PdV)}{T}\cdots\cdots\cdots \text{(4)}$$

From equation (1) we get $dS_{\text{system}} + dS_{\text{surroundings}} \geq 0 \ldots\ldots\ldots\text{(1)}$

$$dS_{syst} - \frac{(dE + PdV)}{T} \geq 0$$

$$TdS \geq dE + PdV \cdots\cdots\cdots (5)$$

Note: The subscript 'system' has been omitted from dS for the sake of convenience.

In equation (5) the sign '>' (greater than) stands for the irreversible process, while the sign '=' (equal to) stands for reversible process.

The equation (5) is the basic equation which leads to a number of criteria for predicting the feasibility of a process.

1) Criterion in terms of change of entropy of the system:

If when E and V are constant, the $dE = 0$ and $dV = 0$ the equation (iii) reduces to

$$(dS)_{E,V} \geq 0 \ldots\ldots\ldots\ldots\ldots..(6)$$

or $\quad (dS)_{(E,V)} > 0$ for an irreversible change and the process is feasible

and $\quad (dS)_{(E,V)} = 0$ for a reversible change (equilibrium)

2) **Criterion in terms of change of internal energy of the system:**

When S and V are constant, Then $dS = 0$ and $dV = 0$

The equation (iii) reduces to

$$(dE)_{S,V} \leq 0 \ldots\ldots\ldots\ldots\ldots\ldots.(7)$$

or $\quad (dE)_{S,V} < 0$ for an irreversible change and the process is feasible

and $\quad (dE)_{S,V} = 0$ for a reversible change (equilibrium)

3) **Criterion in terms of free energy change of the system:**

By definition, the free energy (G) of a system is given by the following expression

$$G = H - TS$$

Or $\quad\quad\quad\quad G = E + PV - TS \; [\because H = E + PV]$

on differentiating we get

$$dG = dE + PdV + VdP - TdS - SdT$$

$$dE + PdV = dG - VdP + TdS + SdT$$

Substituting in equations (iii) we get

$$TdS \geq dE + PdV$$

$$TdS \geq dG - VdP + TdS + SdT$$

or $\quad\quad\quad\quad\quad\quad\quad dG - VdP + SdT \leq 0$

At constant pressure in an isothermal process (T is also constant) this equation reduces to

$$(dG)_{P,T} \leq 0 \ldots\ldots\ldots\ldots\ldots.(8)$$

or $\quad\quad\quad\quad\quad\quad\quad (dG)_{P,T} < 0$ for an irreversible change and the process is feasible

and $\quad\quad\quad\quad\quad\quad\quad (dG)_{P,T} = 0$ for a reversible change (equilibrium)

The equation (8) leads to the following conclusion.

If a process under constant conditions of temperature and pressure is accompanied by decrease in free energy (i.e., ΔG has a negative value), the process is irreversible; While if it occurs without change in free energy (i.e., ΔG=0), it is said to be reversible and if it occurs an increase in free energy (i.e., ΔG has a positive value), it is not feasible.

The criterion in terms of free energy change is the most useful criterion to decide between reversibility and irreversibility of a process because most of the processes take place at constant temperature and pressure.