CHEMICAL THERMODYNAMICS AND ENERGETIC

Physical Chemistry

Thermodynamics

- Thermodynamics (**Greek word thermo means heat and dynamics means motion**) is the branch of science which deals with the study of different forms of energy and the quantitative relationships between them.

- The complete study of thermodynamics is based upon three generalizations called first, second and third law of thermodynamics.

Study of Thermodynamics

We can predict feasibility of the reaction that is if two substances are mixed then the reaction between them will takes place or not.

If reaction does take place then what are the energy changes involved during the reaction.

If in a chemical reaction, equilibrium is going to get attained then what will be the equilibrium concentrations of different reactants & products, can be calculated with thermodynamics.

Terminology

System : Part of the universe which is under study for energy changes.

Surrounding : Rest of the universe.

**Universe :** Universe = System + Surroundings
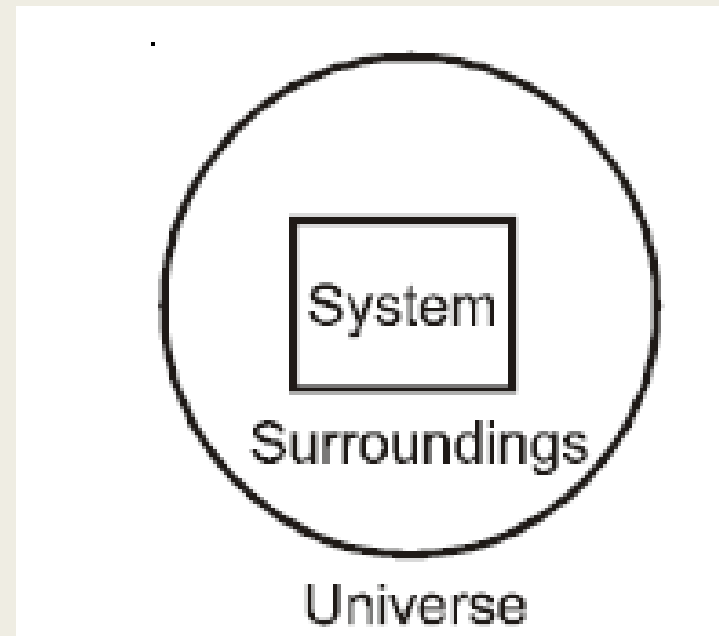
Boundary : Anything which separates system & surroundings is called boundary.

- Boundary can be real or imaginary.
- Boundary can be flexible or rigid

Boundary can be adiabatic(non-conducting) or diathermic(conducting).

Type of System

- **Open system :** System which can exchange energy & matter both with the surroundings. e.g. : Living systems(any living organism) are open systems, air in an open room

Open System
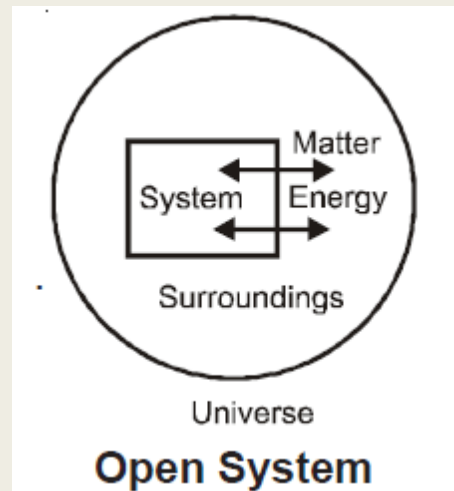
Closed system : System which can exchange only energy but cannot exchange matter with the surroundings is called closed system.

e.g. : any matter in a closed container.

Isolated system : System which cannot exchange energy and matter both with the surroundings.

e.g. : Water in thermos flask.(Though not a perfectly isolated system but can be taken as, for small interval of time as the energy exchanges are negligible).

Close System

Isolated system
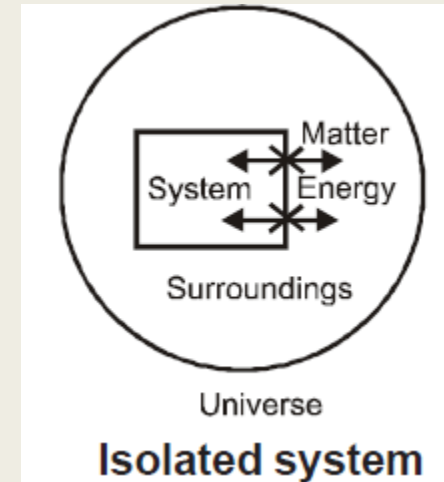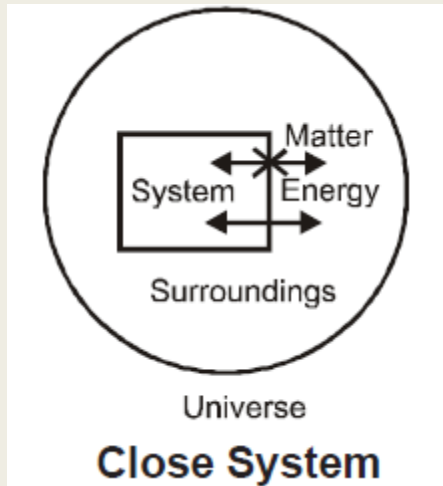
State function..

- It means the condition in which the system is present.
  It can be specified/defined by measuring/ specifying some observable/measurable properties of the system like pressure, volume, temperature, amount of substance, elasticity, heat capacity etc.

State function :

- Property of a system which is dependent only on the state of the system i.e. it is a point function
- It is independent of the path adopted to attain a particular state.

  e.g. In Mechanics, Displacement of any object will a state function but distance travelled by the object will be a path function.
  For any thermodynamic system,
  Temperature, Pressure, Volume, Total internal energy (E or U), Enthapy(H), Gibbs free energy (G), Entropy (S) are all state functions.

Path function :

- Quantities which are dependent on the path/way the system has achieved a particular state. e.g. Heat, work, Heat capacities(Molar heat capacities, specific heat capacities etc.).
- These quantities are define when there is a process going on.
- These can not have any definite (particular) value in any particular state of the system.

Thermodynamic Equilibrium

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

The criterion for thermodynamic equilibrium requires that the following three types of equilibrium exist simultaneously in a system,

(i) *Chemical Equilibrium* : A system in which the composition of the system remains fixed and definite.

(ii) *Mechanical Equilibrium* : No chemical work is done between different parts of the system or between the system and surrounding. It can be achieved by keeping pressure constant.

(iii) *Thermal Equilibrium* : Temperature remains constant *i.e.* no flow of heat between system and surrounding.

Extensive & Intensive Properties

Extensive properties :

- Functions or properties of the system which are dependent on mass or on size of the system are called Extensive Properties .

- Extensive functions are additive in nature(The addition of the volumes of the two parts equals the volume of the whole of the room.)
  e.g. Volume, Mass, Total heat capacity, Total internal energy (E), Enthalpy(H), Gibbs Free Energy(G), Entropy(S).

Intensive properties :

- Functions or properties which are not mass dependent or size dependent are called intensive function.
- Intensive properties are not additive in nature.

  eg. Temperature, pressure, molar heat capacity, specific heat capacity, density,concentration, vapour pressure.

Types of Thermodynamics process

Thermodynamic process : Any method/process by which system can change its state from one state of thermodynamic equilibrium to another state of thermodynamic equilibrium.

There can be infinite type of thermodynamic processes, out of these the following are important ones:

1.   **Isothermal process :** T = constant
   $dT = 0$
   $\Delta T = 0$

2.   **Isochoric process :** V = constant
   $dV = 0$
   $\Delta V = 0$

3.   **Isobaric process :** P = constant
   $dP = 0$
   $\Delta P = 0$

4.   **Adiabatic process :** q = constant
   or heat exchange with the surrounding = 0(zero)

Reversible & Irreversible process

Reversible process :

The process that can be reversed by a very small change is known as reversible process.

If a process is carried out in such a manner so that the system is always in thermodynamic equilibrium at every stage of the process.

If the process is carried out such that the difference in driving force and opposing force is infinitesimally small so that process takes place at infinitesimally slow rate.

An ideal reversible process will take infinite time to get completed.

It is carried out infinitesimally slowly.

Irreversible process : The process can not be reversed by a small change is known as irreversible.

If a process is carried out in such a manner so that the system is in thermodynamic equilibrium

(I) Only at initial & final state of the process but not at the intermediate stages.

(II) System may be in thermodynamic equilibrium state at some finite number of intermediate

stages only - for example - n step irreversible expansion of a gas

If during the process there is a finite difference in driving force and opposing force so that process takes place with a finite rate.

Irreversible processes will get completed in finite time.

At intermediate stages of the irreversible process, different state function such as Pressure, temperature etc. are not defined.

All real process are irreversible.

Work and Heat

These are two ways by which a system can interact or can exchange energy with its surroundings.
(i) Heat & (ii) Work
Heat & Work both are forms of energy.

Heat : When the energy transfer takes place because of temperature difference between system & surroundings. It is known as heat.

Work : Energy transfer which is not heat or which is not because of temperature difference is called work.
Work can be of many types : Mechanical work, Electrical work, Magnetic work, Gravitational work etc.

Sign convention of Heat & work

Any energy given to system is taken positive so heat given to system = positive
heat given out from system / taken out from system = Negative
Work done on the system = Positive
Work done by the system = Negative
The sign convention is different from physics, but the meaning always comes out to be same only in equation we have to use a different sign convention for work.
So if in any problem, w = – 10 J
It means system has done work of 10 Joule on surroundings.

IUPAC convention of Heat
1. Heat given to the system = +ve
2. Heat coming out of the system = –ve
3. Work done on the system = +ve
4. Work done by the system = –ve

Internal energy

Internal Energy (E, also denoted by U)

Every system having some quantity of matter is associated with a definite amount of energy, called internal energy .

It is the sum of all forms of energies present in the system.

$E = E_{Translational} + E_{Rotational} + E_{Vibrational} + E_{bonding} + \ldots$

$\Delta E = E_{Final} - E_{Initial}$.

It is an extensive property & a state function . It is exclusively a function of temperature.

If $\Delta T = 0$; $\Delta E = 0$ as well.

Heat (q) & Heat capacity

- Heat is a path function and is generally calculated indirectly using Ist Law of thermodynamics
- First calculate ΔE and W & then q or heat can be calculated if heat capacity of any process is given to us.
- Heat capacity is a path function and different type of heat capacities are defined

Total Heat Capacity (C_T)

Heat required to raise the temperature of system by 1°C under the given process is known as total heat capacity.

Mathematically, $C_T = \dfrac{\Delta q}{\Delta T} = \dfrac{dq}{dT}$ J/°C

It is extensive properties and path function.

So, $dq = C_T dT$

on integrating $\quad q = \int C_T dT$

Molar heat capacity (C_M/C)

Molar heat capacity (C)

Heat required to raise temperature of 1 mole of a subtance by 1°C

Mathematically, $C = \dfrac{\Delta q}{n\Delta T} = \dfrac{dq}{ndT}$ J mole^{-1}K^{-1}

So, $dq = nCdT$

$q = \int nCdT = nC\Delta T$

C is intensive path function.

C_p is molar heat capacity at constant pressure

C_V is molar heat capacity at constant volume

C_p and C_V are intensive but not a path function

Relation between C$_P$ and C$_V$

(i) $C_p - C_v = R = 2\,calories = 8.314\,J$

(ii) $C_v = \dfrac{3}{2}R$ (for monoatomic gas) and $C_v = \dfrac{3}{2} + x$ (for *di* and polyatomic gas), where x varies from gas to gas.

(iii) $\dfrac{C_p}{C_v} = \gamma$ (Ratio of molar capacities)

(iv) For monoatomic gas, $C_v = 3\,calories$ whereas, $C_p = C_v + R = 5\,calories$

(v) For monoatomic gas, $(\gamma) = \dfrac{C_p}{C_v} = \dfrac{\dfrac{5}{2}R}{\dfrac{3}{2}R} = 1.66$

(vi) For diatomic gas $(\gamma) = \dfrac{C_p}{C_v} = \dfrac{\dfrac{7}{2}R}{\dfrac{5}{2}R} = 1.40$

(vii) For triatomic gas $(\gamma) = \dfrac{C_p}{C_v} = \dfrac{8R}{6R} = 1.33$

Specific Heat capacity (S)

Heat required to raise temperature of unit mass (generally 1 g) of a substance by 1°C

$$S = \frac{\Delta q}{m\Delta T} = \frac{dq}{mdT} \quad Jg^{-1} K^{-1}$$

So, $\quad dq = msdT$

$$q = \int dq = \int ms\, dT = ms\Delta T$$

S is intensive path function

S_P is specific heat capacity at constant pressure

S_V is specific heat capacity at constant volume

S_P & S_V are intensive but not a path function

Relation between C_T, C_M/C& S

Total heat capacity, molar heat capacity & specific heat capacity of a process on a substance are related as

$$C_T = nC = ms \qquad \& \qquad C = Ms$$

Where m – weight of substance

  M – molar mass of substance

  n – no. of moles of the substance

For isothermal process $C = \pm \infty$ For isobaric process $C = C_p$

For isochoric process $C = C_v$ For adiabatic process $C = 0$

Heat capacity can have value from $-\infty$ to $+\infty$ depending on the process.

Laws of Thermodynamics

Zeroth law of Thermodynamics

- If a system A is in thermal equilibrium with a system C and if B is also in thermal equilibrium with system C, then A and B are in thermal equilibrium with each other whatever the composition of the system.

$$A \quad \rightleftharpoons \quad C \qquad\qquad B \quad \rightleftharpoons \quad C$$

$$A \quad \rightleftharpoons \quad B$$

First Law of Thermodynamics

Law of energy conservation :
Energy of total universe is always conserved.

or

Total energy of an isolated system is always conserved.

or

Hence absolute value of E can never be calculated only change in value of E can be calculated for a particular process.

Mathematical expression

If a system is intially in a particular state in which its total internal energy is E_1. Now q amount of heat is given to it and w amount of work is done on it so that in new state its total internal energy becomes E_2. Then according to 1st Law of thermodynamics.

$$E_2 = E_1 + q + w$$

so $$\Delta E = (E_2 - E_1) = q + w$$

Application of First Law

$$\Delta U = \Delta Q + \Delta W \qquad\qquad Since \qquad\qquad \Delta W = -P\ \Delta V$$

$$\therefore \qquad \Delta U = \Delta Q - P\Delta V$$

Question time..

At constant T and P, which one of the following statements is correct for the reaction, $CO(g) + \dfrac{1}{2} O_2(g) \rightarrow CO_2(g)$

(a) ΔH is independent of the physical state of the reactants of that compound

(b) $\Delta H > \Delta E$

(c) $\Delta H < \Delta E$

(d) $\Delta H = \Delta E$

Question

An ideal gas at constant temperature and pressure expands, then its

(a) Internal energy remains same

(b) Internal energy decreases

(c) Internal energy increases

(d) Entropy first increases and then decreases

Question

The work done during the expansion of a gas from a volume of $4\,dm^3$ to $6\,dm^3$ against a constant external pressure of $3\,atm$ is $(1L\,atm = 101.32\,J)$

(a) $+304\,J$

(b) $-304\,J$

(c) $-6\,J$

(d) $-608\,J$

Work Done

Energy that is transmitted from one system to another in such a way that difference of temperature is not directly involved is known as work. It is a **path function**.

This definition is consistent with our understanding of work as dw = Fdx. The force F can arise from electrical, magnetic, gravitational & other sources.

Units of heat and work :

These are related as, 1 *cal* = 4.184 *J*; 1*kcal* = 4.184*kJ*

The *S.I.* unit of heat is joule (*J*) or *kilojoule*. The Joule (*J*) is equal to *Newton – metre* (1 *J* = 1 *Nm*).

Work is measured in terms of ergs or joules. The *S.I.* unit of work is Joule.

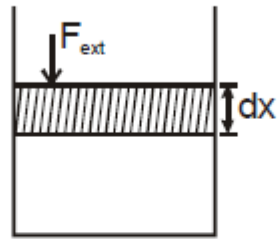$$1 \; Joule = 10^7 \; ergs = 0.2390 \; cal.$$

$$1 \; cal > 1 \; joule > 1 \; erg$$

Work done by Different types of process

P-V Work :

Assuming that under an external force F_x, the piston moves down by a distance 'dx'.

$$dW = \frac{F_{ext}}{A}(A\,dx) \quad \Rightarrow \quad dW = P_{ext}(dV) \Rightarrow W_{ext} = \int P_{ext}\,dV \;\&\; W_{gas} = -W_{ext} = -\int P_{ext}\,dV$$

As the work done in the above case by the external agent is +ve and as the expression conveys otherwise, hence a -ve sign is introduced.

$$\therefore \quad dW = -P_{ext}\cdot dV$$

Expansion of Gas & work done

(1) **Isothermal Expansion** : For an isothermal expansion, $\Delta T = 0$; $\Delta E = 0$.

According to first law of thermodynamics,

$$\Delta E = q + w \qquad \therefore q = -w$$

This shows that in isothermal expansion, the work is done by the system at the expense of heat absorbed.

Since for isothermal process, ΔE and ΔT are zero respectively, hence, $\Delta H = 0$
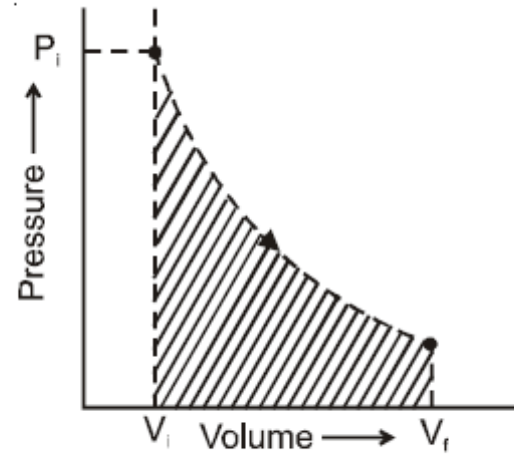
Work done in Isothermal Expansion

$$W = -nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$w = -nRT \log_e \frac{V_2}{V_1} \quad \text{or} \quad w = -2.303\,nRT \log_{10} \frac{V_2}{V_1}$$

At constant temperature, according to Boyle's law,

$$P_1V_1 = P_2V_2 \quad \text{or} \quad \frac{V_2}{V_1} = \frac{P_1}{P_2} \quad \text{So,} \quad w = -2.303\,nRT \log_{10} \frac{P_1}{P_2}$$

PV diagram Representation

In expansion work is done by system on the surroundings and $V_f > V_i$

$$W = -ve$$

Work = Area under the P–V diagram

Irreversible expansion

$$w = -\int_{V_1}^{V_2} P_{ext} \times dV = -P_{ext}(V_2 - V_1)$$

Work done in Adiabatic Expansion of gas

Adiabatic Expansion : In adiabatic expansion, no heat is allowed to enter or leave the system, hence, $q = 0$.

According to first law of thermodynamics,

$$\Delta E = q + w \qquad \therefore \quad \Delta E = w$$

Work done in reversible adiabatic expansion

Reversible adiabatic expansion : The following relationships are followed by an ideal gas under reversible adiabatic expansion.

$$PV^\gamma = \text{constant}$$

where, P = External pressure, V = Volume

$$\gamma = \frac{C_p}{C_v}$$

Irreversible adiabatic expansion

Irreversible adiabatic expansion : In free expansion, the external pressure is zero, *i.e,* work done is zero. Accordingly, ΔE which is equal to w is also zero. If ΔE is zero, ΔT should be zero. Thus, in free expansion (adiabatically), $\Delta T = 0$, $\Delta E = 0$, $w = 0$ and $\Delta H = 0$.

$$w = -P_{ext}(V_2 - V_1) = -P_{ext}\left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1}\right)$$

Limitations of the first law of thermodynamics

- All the limitations of the first law of thermodynamics can be remove by the second law of thermodynamics. This law is generalisation of certain experiences about heat engines and refrigerators. It has been stated in a number of ways, but all the statements are logically equivalent to one another.

Important points

Requirement : Ist law insufficient to Explain

Neutralization, Melting of ice > 0°

Combustion, Freezing of water < 0°

Fall of water , Boiling of water > 100° C

Cooling of a hot body, Free expansion of a gas, mixing of gases.

Spontaneous and Non spontaneous Process

■ A process which can take place by itself under the given set of conditions once it has been initiated if necessary, is said to be a *spontaneous process*. In other words, a spontaneous process is a process that can occur without work being done on it. The spontaneous processes are also called *feasible* or *probable processes*. It indicates that only exothermic reactions are spontaneous

■ On the other hand, the processes which are forbidden and are made to take place only by supplying energy continuously from outside the system are called *non-spontaneous processes*. In other words, non spontaneous processes can be brought about by doing work.

Examples

(1) The diffusion of the solute from a concentrated solution to a dilute solution occurs when these are brought into contact is spontaneous process.

(2) Mixing of different gases is spontaneous process.

(3) Heat flows from a hot reservoir to a cold reservoir is spontaneous process.

(4) Electricity flows from high potential to low potential is spontaneous process.

(5) Expansion of an ideal gas into vacuum through a pinhole is spontaneous process.

All the above spontaneous processes becomes non-spontaneous when we reverse them by doing work.

Entropy (S) and Entropy change ΔS

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

Entropy is represented by the symbol "S". It is difficult to define the actual entropy of a system. It is more convenient to define the change of entropy during a change of state.

Formula

$$\Delta S = S_{final} - S_{initial} = \frac{q_{rev}}{T}$$

If heat is absorbed, then $\Delta S = +ve$ and if heat is evolved, then $\Delta S = -ve$.

The entropy change of a system may be defined as the integral of all the terms involving heat exchanged (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly at constant temperature.

Characteristics of entropy

The important characteristics of entropy are summed up below-

(i) Entropy is an extensive property. Its value depends upon the amount of the substance present in the system.

(ii) Entropy of a system is a state function. It depends upon the state variables .

(iii) The change in entropy in going from one state to another is independent of the path.

(iv) The change in entropy for a cyclic process is always zero.

(v)   The total entropy change of an isolated system is equal to the entropy change of system and entropy change of the surroundings. The sum is called *entropy change of universe*.

Second Law of Thermodynamics

Entropy of the universe is constanlty inereasing.

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} > 0 \quad \text{for a spontaneous process.}$$

Where **(S)** = entropy is the measure of randomness or disorder. It is a state function and extensive property. Mathematically

$$ds = \frac{dq_{rev}}{T} \quad \text{or } \Delta S = \int \frac{dq_{rev}}{T}$$

$\frac{dq}{T}$ is state function only for reversible process

$$dS \propto dq_{rev} , \quad dS \propto \frac{1}{T}$$

At Higher T - entropy is already high. Therefore, heat addition will not introduce much change in the entropy.

Change of entropy for surrounding

Calculation of ΔS_{surrounding} : As the surrounding is an infinite heat reservoir hence, no. amount of heat given to the surrounding can cause turbulance in it, hence all heat exhanges with surroundings are considered to be reversible.

$$\Delta S_{surrounding} = \int \frac{dq_{surrounding}}{T}$$

For   surrounding T is constant

$$\therefore \quad \Delta S_{surr} = \frac{1}{T} \int dq_{surr} = \frac{q_{surrounding}}{T}$$

But according to the law of conservation of energy

$$q_{surr} = - q_{system}$$

$$\therefore \quad \Delta S_{surr} = \frac{-q_{system}}{T}$$

Entropy calculation for Ideal gas

(i) When T and V are two variables,

$$\Delta S = nC_v \ \ln \frac{T_2}{T_1} + nR \ \ln \frac{V_2}{V_1} \ . \text{ Assuming } C_v \text{ is constant}$$

(ii) When T and p are two variables,

$$\Delta S = nC_p \ \ln \frac{T_2}{T_1} - nR \ \ln \frac{p_2}{p_1} \ . \text{ Assuming } C_p, \text{ is constant}$$

(a) Thus, for an *isothermal process* (T constant),

$$\Delta S = nR \ \ln \frac{V_2}{V_1} \ or = -nR \ \ln \frac{p_2}{p_1}$$

Other formula of Entropy

(b) For *isobaric process* (*p* constant), $\Delta S = n C_p \ln\dfrac{T_2}{T_1}$

(c) For *isochoric process* (*V* constant), $\Delta S = n C_v \ln\dfrac{T_2}{T_1}$

(d) *Entropy change during adiabatic expansion* : In such process $q=0$ at all stages. Hence $\Delta S = 0$. Thus, reversible adiabatic processes are called *isoentropic process.*

Free energy (G) and Free energy change

- Gibb's free energy (*G*) is a *state function* and is a measure of maximum work done or useful work done from a reversible reaction at constant temperature and pressure.

Characteristics of free energy

(i) The free energy of a system is the enthalpy of the system minus the product of absolute temperature and entropy *i.e.,* $G = H - TS$

(ii) Like other state functions E, H and S, it is also expressed as ΔG. Also $\Delta G = \Delta H - T\Delta S_{system}$ where ΔS is entropy change for system only. This is *Gibb's Helmholtz equation.*

(iii) At equilibrium $\Delta G = 0$

(iv) For a spontaneous process decrease in free energy is noticed *i.e.,* $\Delta G = -ve$.

Gibbs energy and Equilibrium constant

$$\Delta G^o = -2.303 RT \log_{10} K,$$ where K is equilibrium constant.

(a) Thus if $K > 1$, then $\Delta G^o = -ve$ thus reactions with equilibrium constant $K>1$ are thermodynamically spontaneous.

(b) If $K<1$, then $\Delta G^o = +ve$ and thus reactions with equilibrium constant $K<1$ are thermodynamically spontaneous in reverse direction.

(2) **Criteria for spontaneity of reaction** : For a spontaneous change $\Delta G = -ve$ and therefore use of $\Delta G = \Delta H - T\Delta S$, provides the following conditions for a change to be spontaneous.

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