

## Energy changes and Thermodynamics

### Introduction:

Thermodynamics is a branch of natural science which deals with the energy transformation and the quantitative relation between various forms of energy.

The branch of chemistry which deals with the change in energy during a reaction is called chemical energetics.

### Some thermodynamical terms:

\* **System**: System may be defined as the any specified portion of matter under study which is separated from the rest of the universe with a boundary surface.

\* **Surrounding**: The rest of the universe which might be in a position to exchange matter as well as energy with the system.

### # Types of system:

\* **Open system**: A system which can exchange matter as well as energy to and from its surrounding is said to be an open system. For e.g. hot water in an open vessel.

\* **closed system**: A system which can exchange energy but not matter to and from its surrounding is said to be a closed system. For e.g. hot water in a closed vessel.

such as thermus, change in heat energy  $dQ = 0$

γ) Isobaric process: A system is said to be isobaric if pressure remains constant throughout the whole process. For e.g. heating of water to its boiling point.  
change in pressure,  $dp = 0$

δ) Isochoric process: A system is said to be isochoric if volume remains constant throughout the whole process. For e.g. heating a substance in non-expanding chamber.  
change in volume,  $dv = 0$

ε) 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 cyclic process.

change in internal energy,  $dE = 0$

change in enthalpy,  $dH = 0$

# Internal or intrinsic energy (U or E):

All matters (i.e. atoms, molecules or ions) possesses energy in the various forms. The total energy contained in a system due to its molecules is called internal energy or intrinsic energy.

The sum of all kinds of energy of a substance due to its chemical nature is called internal energy. It is denoted by  $E$  or  $U$ .

## # state of a system:

A thermodynamic system is said to be in a certain state when all the thermodynamic parameters are fixed. The quantities whose value determine the state of a system are called its thermodynamic variable or state variable. The most important state variables are mass, temperature, pressure and volume.

State function describes a thermodynamic state, any parameter whose value depends upon the initial and final state of the system only but not on the path followed by the change of state is called state function.

For e.g. internal energy, enthalpy, Gibbs's free energy, entropy etc.

## # Thermodynamic process: A thermodynamic process is path or an operation by which a system changes from one form to another.

a) Isothermal process: A process is said to be isothermal if the temperature of the system remains constant throughout the whole process. For e.g. A system is in a constant temperature bath. For an isothermal process change in temperature,  $dT = 0$ .

b) Adiabatic process: A process is said to be adiabatic if no heat is allowed to enter or leave the system during the whole process. For e.g. system in the isolated container.

i.e. Internal energy ( $E$ ) =  $E_r + E_v + E_n + E_e + E_t + \dots$

Internal energy is a state function hence it depends upon the initial and final state of state variable. i.e. temperature, pressure, and volume. Absolute value of internal energy cannot be determined. However the change in internal energy ( $\Delta E$ ) can be found experimentally by using bomb calorimeter.

\*

\* Enthalpy ( $H$ ): In an open system mechanical work ( $Pv$ ) done against expansion or contraction is to be added to internal energy. Therefore, the term internal energy is replaced by another thermodynamic term enthalpy or heat contained in an open system to express total energy of the system. Mathematically enthalpy is defined as

$$H = E + Pv$$

Enthalpy of the system may be defined as the heat absorbed or evolved at constant pressure.

Enthalpy is a state function and hence independent of the path by which the state is reached.

Suppose, a system changes from one state to another state at a constant pressure. Suppose at initial state the value of enthalpy, internal energy, volume of the system be  $H_1, E_1, V_1$  respectively. Similarly, enthalpy, internal energy, and volume of the system at final state are  $H_2, E_2, V_2$  respectively.

From the definition of enthalpy

$$H_1 = E_1 + PV_1 \text{ --- (i) [At initial state]}$$

$$H_2 = E_2 + PV_2 \text{ --- (ii) [At final state]}$$

Subtracting eq (i) from (ii)

$$H_2 - H_1 = E_2 + PV_2 - (E_1 + PV_1)$$

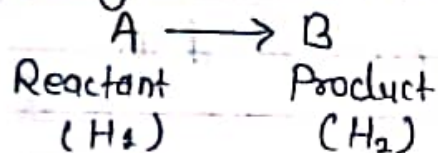
$$= E_2 + PV_2 - E_1 - PV_1$$

$$= \Delta E + P(V_2 - V_1)$$

$$\Delta H = \Delta E + P\Delta V \text{ --- (iii)}$$

This relationship is important because the absolute value of enthalpy and internal energy cannot be determined and only their change can be determined experimentally.

# Exothermic and Endothermic reaction in terms of enthalpy change: let us consider a hypothetical reaction.



Here, enthalpy of reactant  $H_1$  and enthalpy of product is  $H_2$ . Now, change in the enthalpy is given by:

$$\text{change in enthalpy } (\Delta H) = H_2 - H_1$$

Case (I)

$$\Delta H = -ve$$

$$\text{p.e. } H_2 < H_1$$

This is the condition for exothermic reaction in which the enthalpy of product is less than enthalpy of reactant.

p.e. heat is evolved during the reaction.

case (II)

$$\Delta H = +ve$$

p.e.  $H_2 > H_1$

This is the condition for endothermic reaction in which the enthalpy of product is greater than enthalpy of reactant. p.e. heat is absorbed during the reaction.

# Graphical representation of exothermic and endothermic reactions

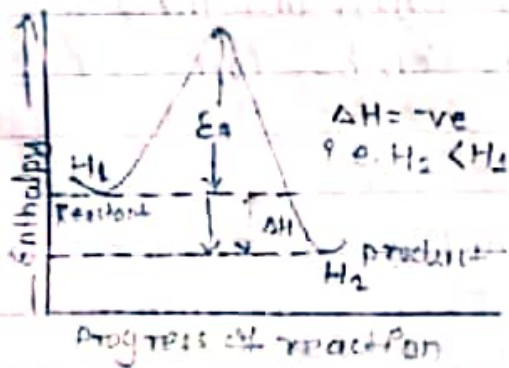


Fig: Energy profile diagram for exothermic reaction

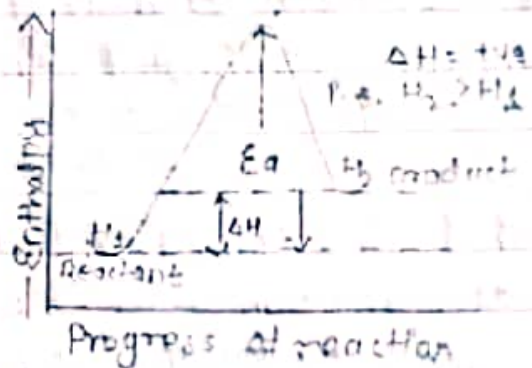


Fig:- Energy profile diagram for endothermic reaction

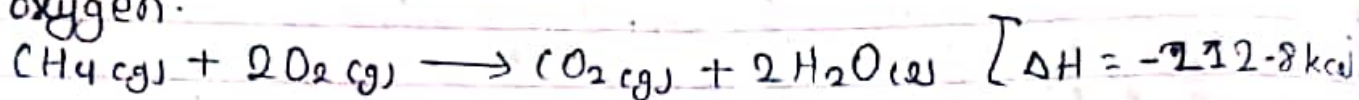
# Enthalpy of reaction (or Heat of reaction):

Enthalpy of reaction may be defined as the amount of heat evolved or absorbed during the chemical reaction when number of moles of reactants are converted into product.

# Different types of enthalpy of reaction.

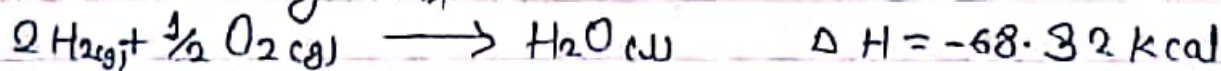
1. Enthalpy change in chemical changes:

b) Enthalpy of combustion ( $\Delta H_c$ ): Enthalpy of combustion is amount of heat liberated when one mole of substance is completely burnt in excess of air or oxygen. It is denoted by  $\Delta H_c$ . For e.g. when we burn methane in presence of oxygen.

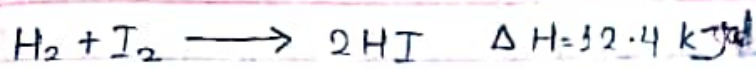


Since, 212.8 kcal of heat is released when one mole of  $\text{CH}_4$  is completely combusted, enthalpy of combustion of  $\text{CH}_4$  is -212.8 kcal.

c) Enthalpy of formation ( $\Delta H_f$ ): Enthalpy of formation or heat of formation is defined as the change in enthalpy involved when one mole of the compound is formed from its element. It is denoted by  $\Delta H_f$ .



Since, 68.32 kcal heat is released when one mole of water is formed from hydrogen and oxygen, enthalpy of formation of water is -68.32 kcal.

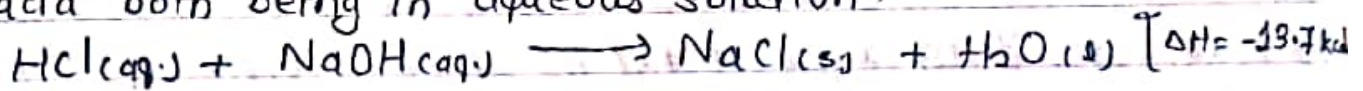


The value 12.4 kJ of heat does not represent the standard enthalpy of formation of hydrogen iodide because this is the amount of heat absorbed when 2 moles of hydrogen iodide is formed. Therefore, enthalpy of formation of hydrogen iodide will be 6.2 kJ.

iii) Enthalpy of neutralization: Enthalpy of neutralization may be defined as the change in enthalpy of the system when one mole of  $\text{H}^+$  ion is completely neutralized by a base in very dilute solution.

OR,

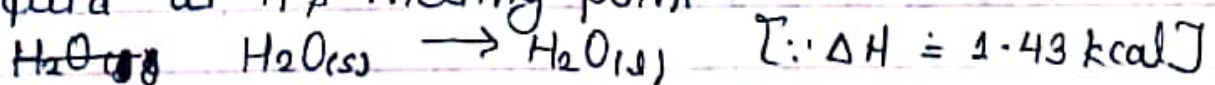
Enthalpy of neutralization of an acid or base is defined as enthalpy change when 1 gram equivalent of the acid or base is neutralized by 1 gram equivalent of a base or an acid both being in aqueous solution.



2. Enthalpy change in physical change:

i) Enthalpy of fusion:

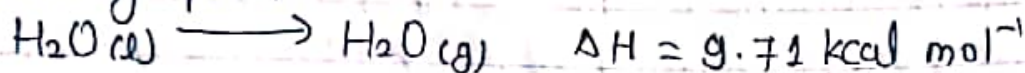
Enthalpy of fusion is defined as the change in enthalpy when one mole of a solid substance is converted into liquid at its melting point.





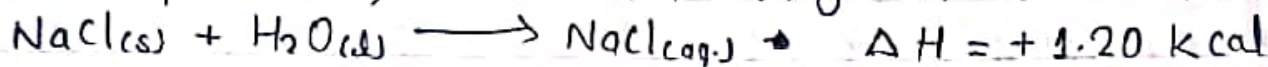
i) Enthalpy of vaporization:

Enthalpy of vaporization of a substance is defined as the change in enthalpy when one mole of liquid is converted into vapour or gaseous state at its boiling point.



ii) Enthalpy of solution:

Enthalpy of solution of a solute is defined as the enthalpy change when one mole of the solute is dissolved in excess of water that further addition of water to the solution produces no further change in heat contained.



iii) Enthalpy of sublimation:

Enthalpy of sublimation is the amount of heat required to change the one mole of solid substance into vapour state at a temperature below its melting point.

E.g. heat of sublimation of iodine is  $24.92 \text{ kcal mol}^{-1}$

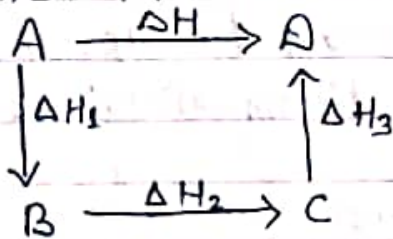


## Bond energy:

Bond energy may be defined as the average amount of energy required to dissociate all bonds of a particular type in one mole of the substance.

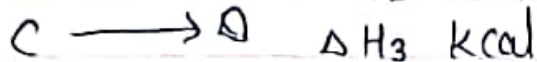
## Hess law of constant Heat summation:

This law was proposed by Germain Hess in 1840. This law can be verified experimentally and is also a direct consequence of the law of conservation of energy. It states that, "The amount of heat evolved or absorbed in a given chemical reaction is always the same regardless of whether the reaction is in one step or in several steps."



Suppose, that a substance 'A' can be changed to 'D' directly with the change in enthalpy ' $\Delta H$ ' by the first way. In the second way, 'A' can be changed into 'D' through the intermediate product formation 'B' and 'C'. And the total heat in the second way is given by  $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$  as shown in figure above.

The reaction involved



Now, According to Hess law,

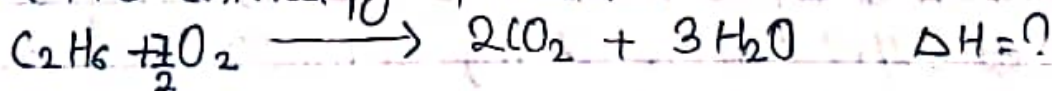
Total heat change in the 1<sup>st</sup> way should be equal to the heat in the 2<sup>nd</sup> way.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

# Application of Hess Law:

- i) Determination of heat of formation of substances.
- ii) Determination of heat of transition with the help of Hess law
- iii) Determination of <sup>enthalpy</sup> heat of reaction.
- iv) Determination of combustion of reaction
- v) Determination of formation of reaction.

Q. Find the enthalpy of reaction



Given the enthalpy of formation of  $C_2H_6$ ,  $CO_2$  and  $H_2O$  are  $-20 \text{ kcal}$ ,  $-90 \text{ kcal}$  and  $-70 \text{ kcal}$  respectively.

## # First law of thermodynamics:

1<sup>st</sup> law of thermodynamics is the basic law of nature which is directly related to the law of conservation of energy.

According to the law of conservation of energy to the thermodynamic system "the total energy of an isolated system is constant, energy can be transferred from one form to another form but can be neither created nor destroyed".

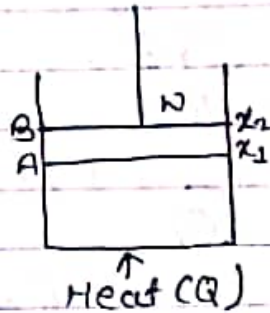
Mathematically it can be formulated as

$$dU = Q - W$$

where  $dU$  = Internal energy

$Q$  = amount of heat energy

$W$  = Mechanical work



Let us consider, a thermodynamic system when  $Q$  amount of heat is supplied to the system then internal energy of the system change from initial state 'A' to final state 'B' by performing mechanical work ( $W$ ). Therefore, total energy of the system remains constant:

$$U_2 = U_1 + Q - W$$

$U_1$  = Initial internal energy

$U_2$  = Final internal energy

$Q$  = Amount of heat supplied to the system

$W$  = <sup>mechanical</sup> work done by the system

$$U_2 - U_1 = Q - W$$

$$\therefore dU = Q - W \dots \textcircled{1}$$

Suppose, a system during expansion goes from the position A to the B, then the work done by the system is given by

$$\text{Mechanical work} = F \times \text{displacement}$$

$$= F \times (x_2 - x_1)$$

$$= F \times dx$$

$$= P \cdot A \times dx$$

$$\therefore W = Pdv$$

$\therefore$  Eqn (1) becomes  $dU = Q - Pdv \dots \textcircled{2}$

This is the mathematical formulation of 1<sup>st</sup> law of thermodynamics.

Case (I) for isochoric process  
(i.e. no change in volume)

There is no work of expansion i.e.  $w = 0$

Hence,  $dU = Q$

It implies that total amount of heat is used to increase in internal energy of the system.

case (II) For adiabatic process

No heat is used to increase in internal energy of the system i.e.  $Q=0$

$$dU = -PdV$$

$$PdV = -dU$$

This implies that work done by the system due to decrease in the internal energy of the system.

case (III) For cyclic process

$$\text{i.e. } dU=0$$

$$Q = PdV$$

$$Q = W$$

This implies that heat supplied in the cyclic process is equal to the amount of work done.

# Limitation of 1st law of thermodynamics

- 1) 1st law of thermodynamics does not explain why spontaneous or natural processes are unidirectional and why all naturally occurring processes always tend to change spontaneously in a direction which leads to equilibrium
- 2) It does not contradict the existence of heat engine of 100% efficiency.

iii) 1<sup>st</sup> law of thermodynamics cannot explain that while work can be completely converted into heat but heat cannot be completely converted into work without leaving permanent changes in the system or surrounding.

Spontaneous process:

Those process which occurs by themselves without any external support are called spontaneous process. For e.g. the fall of rain ~~at~~ clouds, flow of heat from a hotter body to colder body, rusting of iron, diffusion of gases, neutralization of acid and base.

Characteristics of spontaneous process

- i) Spontaneous process occurs by itself.
- ii) Spontaneous process may fast or slow.
- iii) Spontaneous process occurs till and equilibrium condition is reached.
- iv) All spontaneous process occurs in a definite direction.
- v) All spontaneous process occurs with decrease in free energy of a system.

Non-spontaneous process:

Non-spontaneous process occurs by supplying external energy to the system. For e.g. external energy is required to pump water from lower level to higher level.

## # 2nd Law of Thermodynamics:

In order to overcome the limitation of 1st law of thermodynamics, the 2nd law of thermodynamics came into the existence with the more detail concept about the work and energy <sup>at the</sup> system.

Thermodynamic function to express the randomness is called entropy. It is represented by  $S$ . Therefore, entropy is a thermodynamic function which measures the degree of randomness or disorderness of the system. It is the state function and an extensive property.

Mathematically, the change in entropy is

$$\Delta S = \frac{Q}{T} \quad \text{where, } \Delta S = \text{Entropy change}$$

$T = \text{absolute temp}$

$Q = \text{Amount of heat absorbed or emitted.}$

Unit of entropy

$$\Delta S = \frac{J}{K} = J K^{-1}$$

$$\text{or } \Delta S = \frac{Cal}{K} = Cal K^{-1}$$

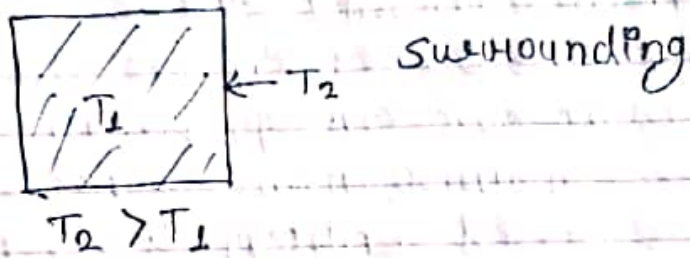
For 1 mole

$$\begin{aligned} \Delta S &= J K^{-1} mol^{-1} \\ &= Cal K^{-1} mol^{-1} \end{aligned}$$

$$S_{gas} > S_{liquid} > S_{solid}$$



Higher the randomness greater is the value of entropy and vice-versa.



Let us consider, a system at temp<sup>r</sup>  $T_1$  and surrounding temperature  $T_2$ . Let  $T_2 > T_1$ , so flow of heat will occur spontaneously from surrounding side to system side. Let  $\Delta H$  is the amount of heat transferred.

So,

$$\Delta S_{\text{system}} = \frac{\Delta H}{T_1} \quad \text{--- (i)}$$

$$\text{and } \Delta S_{\text{surrounding}} = -\frac{\Delta H}{T_2} \quad \text{--- (ii)}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$\Delta S_{\text{universe}} = \frac{\Delta H}{T_1} - \frac{\Delta H}{T_2}$$

$$\Delta S_{\text{universe}} = \Delta H \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\therefore \Delta S_{\text{universe}} = \text{+ve} \quad [ \because T_2 > T_1 ]$$

Statement: "All spontaneous process accompanied by increasing entropy of universe." This is the 2<sup>nd</sup> law of thermodynamics and can be also stated as "The entropy of universe is continuously increasing."

OR,

"There is no heat engine which can convert all the heat into the work."

OR,

"No heat engine has 100% efficiency."

\*\*\*\*

# Criteria of spontaneity in light of entropy changes.

- i) If  $\Delta S_{total} > 0$  i.e. +ve, then the process is spontaneous.
- ii) If  $\Delta S_{total} < 0$  i.e. -ve then the process is non-spontaneous.
- iii) If  $\Delta S_{total} = 0$  then the process is in equilibrium condition.

# Entropy change in phase transition:

1. Entropy of melting / Fusion: It is defined as the entropy change when one mole of solid substance changes into liquid form at its melting point.

$$\text{So, } \Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}}$$

Since,  $\Delta H_f$  is always positive quantity. So, entropy

of the system during melting is also a positive.

2. Entropy of vaporization:

It is defined as the entropy change when one mole of liquid changes into vapour at its boiling point.

$$\text{So, } \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{b.p.}}}$$

Since,  $\Delta S_{\text{vap}}$  is always a positive quantity. So entropy change in this process is also positive.

3. Entropy of sublimation:

It is defined as the entropy change when one mole of solid changes into vapour at a particular temperature.

$$\text{So, } \Delta S_{\text{sub}} = \frac{\Delta H_{\text{sub}}}{T}$$

Since, enthalpy of sublimation is positive quantity. So, entropy change in this process is also positive.

#### 4. Entropy of condensation:

It is defined as the entropy change when one mole of gas changes into liquid at its boiling point ~~point~~

$$\Delta S_{\text{condensation}} = \frac{\Delta H_{\text{condensation}}}{T_{\text{b.p.}}}$$

Since,  $\Delta H_{\text{condensation}}$  is always negative quantity so entropy change of system is decreases during the condensation.

#### 5. Entropy of freezing:

It is defined as the entropy change when one mole of liquid water is changes into ice.

$$\Delta S_{\text{freezing}} = \frac{\Delta H_{\text{freezing}}}{T_{\text{freezing}}}$$

since,  $\Delta H_{\text{freezing}}$  is always negative quantity so the entropy change during freezing process is decreases.

#### \* Entropy change in chemical reaction:

Entropy change in chemical reaction depends on the stoichiometry of the reaction.

i.e.  $\Delta S = \text{Sum of entropies of product} - \text{Sum of entropies of reactant}$

$$\Delta S = \sum S_{\text{products}} - \sum S_{\text{reactant}}$$

For a given reaction



$$\Delta S = (cS_C + dS_D) - (aS_A + bS_B)$$

(5 marks)  
VVVV

## # Gibbs's Free Energy ( $G$ ):

J. Willard Gibbs introduced a function called Gibbs's free energy ( $G$ ), this function accounts for enthalpy and entropy change in a system and is denoted by ' $G$ ' =  $H - TS$

where,  $G$  = Free energy of the system

$H$  = Enthalpy of the system

$T$  = Absolute temp<sup>o</sup>

$G$  is the also state function and defined as the amount of energy available for doing useful work at constant temp<sup>o</sup> & pressure.

Suppose, a system changes from one state to another state, say at initial state free energy, enthalpy and entropy of a system be  $G_1$ ,  $H_1$  &  $S_1$  respectively. Similarly, suppose free energy, enthalpy and entropy of a system at final state are  $G_2$ ,  $H_2$  and  $S_2$  respectively. If the change is carried out at constant temp<sup>o</sup>.

At initial state

$$G_1 = H_1 - TS_1 \quad \text{--- (i)}$$

At final state

$$G_2 = H_2 - TS_2 \quad \text{--- (ii)}$$

Now, subtracting equation (i) from (ii) we get,

$$G_2 - G_1 = H_2 - TS_2 - (H_1 - TS_1)$$

$$\Delta G = H_2 - TS_2 - H_1 + TS_1$$

$$\Delta G = H_2 - H_1 - TS_2 + TS_1$$

$$= \Delta H - T(S_2 - S_1)$$

$$\Delta G = \Delta H - T\Delta S \quad \text{--- (iii)}$$

This is called Gibbs's Helmholtz equation which is applied by predicting spontaneity in light of free energy change of the system.

Free energy change and spontaneity:

we have,

Gibbs's Helmholtz equation

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

where,  $\Delta G$  = Gibbs's free change of the system

$\Delta H$  = Enthalpy change of the system

$T$  = Absolute temp<sup>o</sup>

$\Delta S$  = Entropy change of the system

Suppose, enthalpy change of a system is  $\Delta H$  by the exchange of 'q' amount of heat then enthalpy change of the surrounding will be  $-\Delta H$ .

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T} \quad \left[ \because \Delta S = \frac{q}{T} \right]$$

$$\Delta S_{\text{total}} = \frac{T \Delta S_{\text{system}} - \Delta H_{\text{system}}}{T}$$

$$T \Delta S_{\text{total}} = T \Delta S_{\text{system}} - \Delta H_{\text{system}} \\ = - (\Delta H_{\text{system}} - T \Delta S_{\text{system}})$$

$$T \Delta S_{\text{total}} = - \Delta G_{\text{system}} \quad \text{--- (ii)}$$

This relation is employed in predicting the spontaneity by taking free energy change of the system.

- i) If  $\Delta G_{\text{system}}$  is +ve then  $\Delta S$  is -ve. Therefore, the process becomes non-spontaneous.
- ii) If  $\Delta G_{\text{system}}$  is -ve then  $\Delta S_{\text{total}}$  is +ve. Therefore, the process is spontaneous.
- iii) If  $\Delta G_{\text{system}}$  is zero (0) then  $\Delta S_{\text{total}}$  is also zero. Therefore, the process will be in equilibrium.

# Spontaneity in light of entropy change and enthalpy change of a system:

we have, Gibbs Helmholtz equation:

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T \Delta S_{\text{system}}$$

- i) when  $\Delta H$  is +ve and  $\Delta S$  is -ve then  $\Delta G$  +ve. Therefore the process is non-spontaneous.
- ii) when  $\Delta H$  is -ve and  $\Delta S$  is +ve then  $\Delta G$  -ve. Therefore, the process is spontaneous.
- iii) when  $\Delta H$  and  $\Delta S$  both are +ve then

- a) If  $\Delta H > T\Delta S$  then  $\Delta G$  is +ve. Therefore, the process is non-spontaneous.
- b) If  $\Delta H < T\Delta S$  then  $\Delta G$  is -ve. Therefore, the process is spontaneous.
- ii) When  $\Delta H$  and  $\Delta S$  both are -ve then
- a) If  $\Delta H < T\Delta S$  then  $\Delta G$  is -ve. Therefore, the process is spontaneous.
- b) If  $\Delta H > T\Delta S$  then  $\Delta G$  is +ve. Therefore, the process is non-spontaneous.

→ For exothermic reaction, enthalpy change  $\Delta H$  is always -ve.

- a) If  $\Delta H$  is +ve i.e.  $T\Delta S$  is +ve then the value of  $\Delta G = (-) - (+)$  and hence process is spontaneous  
 $\Delta G = -ve$  at all temp<sup>n</sup>.
- b) If  $\Delta S$  is -ve i.e.  $T\Delta S$  is -ve then the value of  $\Delta G = (-) - (-)$   
 $\Delta G = +ve$  or  $-ve$

At high temp<sup>n</sup>,  $\Delta G = +ve$  [ $\because \Delta T\Delta S > \Delta H$ ]

At low temp<sup>n</sup>,  $\Delta G = -ve$  [ $\because \Delta T\Delta S < \Delta H$ ]

Therefore, at high temp<sup>n</sup>, the process is non-spontaneous and at low temp<sup>n</sup> the process is spontaneous. Hence, the exothermic reaction is favoured at low temp<sup>n</sup>.



$$\Delta W = \Delta E + P\Delta V - \frac{T \cdot q_{rev}}{T}$$

$$\Delta W = \Delta E + P\Delta V - q_{rev} \quad \text{--- (P)}$$

From 1<sup>st</sup> law of thermodynamics,

$$q_{rev} = \Delta E + W_{rev} \quad \text{then eqn (P)}$$

becomes,

$$\Delta W = \Delta E + P\Delta V - (\Delta E + W_{rev})$$

$$= \Delta E + P\Delta V - \Delta E - W_{rev}$$

$$\Delta W = P\Delta V - W_{rev}$$

$$\Delta W = -(W_{rev} - P\Delta V)$$

$$\Delta W = -W_{useful\ work} \quad \text{--- (Q)}$$

This means decrease in free energy of a system is equal to useful work. Therefore, free energy can be defined as energy available for doing useful work at constant temp<sup>r</sup> and pressure.

standard entropy: The entropy value measured at 25°C and 1 atm when the substance is in the most stable and purest form is called standard entropy.

standard free energy: It is the free energy value measured at 298 K and 1 atm pressure when the substance is in the most stable and purest form.

## Entropy and Temperature:

As the temp<sup>r</sup> increases the molecular randomness also increases. This means at lower temp<sup>r</sup> the absolute entropy of a substance becomes lower. This is still lower for a crystalline solid substance. Hence, the absolute entropy of a perfectly crystalline substance is zero at absolute zero. This is called 3<sup>rd</sup> law of thermodynamics.

## # Standard free energy change and equilibrium constant:

The free energy change at non-standard condition is  $\Delta G$  and that at standard condition is  $\Delta G^\circ$  can be related as

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

where,  $K$  = equilibrium constant

$R$  = Universal gas constant

$T$  = absolute temp<sup>r</sup>

At equilibrium condition

$$\Delta G = 0$$

Then above eq<sup>n</sup> becomes,

$$0 = \Delta G^\circ + RT \ln K$$

$$\Delta G^\circ = -RT \ln K$$

$$\text{Or } \Delta G^\circ = -2.303 RT \log K \quad \text{--- (ii)}$$

Special cases:

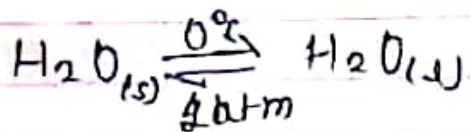
- i) If  $k=1$  then  $\Delta G^\circ = 0$  the process is in equilibrium  
ii) If  $k < 1$  then  $\Delta G^\circ > 0$  then the process is non-spontaneous.  
iii) If  $k > 1$  then  $\Delta G^\circ < 0$  then the process is spontaneous.

Q. What will  $\Delta S$  and  $\Delta G$  for conversion of ice into water when they are in equilibrium?  $\Delta H = 6 \text{ kJ/mole}$

At equilibrium condition

$$\Delta G = 0$$

$$\Delta H = 6 \text{ kJ/mole}$$



$$T = 0^\circ\text{C} = 273 \text{ K}$$

$$\Delta S = ?$$

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

$$0 = 6 - 273 \Delta S$$

$$\therefore \Delta S = \frac{6}{273}$$

$$\therefore \Delta S = 0.022 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

v) For endothermic reaction, the enthalpy change is always +ve.

a) If  $\Delta S$  is -ve i.e.  $T\Delta S$  is -ve then  $\Delta G = (+) - (-) = +ve$

Therefore, the process is non-spontaneous at all temp.

b) If  $\Delta S$  is +ve i.e.  $T\Delta S$  is +ve then  $\Delta G = (+) - (+)$   
 $= +ve \text{ or } -ve$

• At high temp,  $\Delta G = -ve$  [ $\because T\Delta S > \Delta H$ ]

• At low temp,  $\Delta G = +ve$  [ $\because T\Delta S < \Delta H$ ]

Hence, endothermic reaction is spontaneous at high temp and non-spontaneous at low temp.

# Free energy change and useful work:

We have, by Helmholtz equation,

$$\Delta G = \Delta H - T\Delta S \quad \text{--- (i)}$$

$$\text{Also, } \Delta H = \Delta E + P\Delta V \quad \text{--- (ii)}$$

where,  $\Delta E$  = change in internal energy of the system

$\Delta V$  = change in volume

$\Delta H$  = change in enthalpy of the system

$P$  = constant pressure.

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

$$\Delta G = \Delta E + P\Delta V - T\Delta S \quad \text{--- (iii)}$$

If  $q_{rev}$  amount of heat exchanged reversibly then,

$$\Delta S = \frac{q_{rev}}{T} \quad \text{then eq (iii) becomes}$$