Chemical Thermodynamics

Let us consider the following two reactions.

$N_2 + 3 H_2 \longrightarrow 2 NH_3$ $\Delta H = -22.4$ K Cal

$N_2 + O_2 \longrightarrow 2 NO$ $\Delta H = +43.2$ K Cal

In the given examples, the first reaction is an exothermic reaction and second reaction is an endothermic reaction. The branch of chemistry which deals with chemical reaction and energy change associated with it is called CHEMICAL THERMODYNAMICS.

Some Thermodynamic terms and definition

a. System : System is that part of universe which is under study. E.g. Hot water contained in a glass vessel.

b. Surrounding : The rest part of the universe except system which affects the system is called surrounding. E.g. All the factors that affect the hot water in a glass vessel.

c. Boundary : Anything that separates the system from surrounding is called boundary. E.g. Wall of glass vessel containing hot water.

Types of System

Depending upon the nature of interaction between system and surrounding , system can be classified into three types.

i. Open System: The system which can exchange both energy and matter with surrounding is called open system. Eg. Hot water contained in open vessel.

ii. Closed System : The system which can exchange only energy but not matter with surrounding is called closed system. Eg. Hot water contained in closed vessel.

iii. Isolated System : The system which can exchange neither energy nor matter with surrounding is called isolated system. Eg. Hot water contained in Thermos Flask.

Variables and Functions

State Variables : The thermodynamic properties which can define state of a system are called state variables. Eg. Pressure , Temperature , Volume , Mass , no. of moles etc.

Independent Variables :State variables which are independent upon other variables are called independent variables. Eg. Pressure, temperature, no. of moles etc.

Dependent Variables : State variables which are dependent upon other variables are called dependent variables. Eg. Volume

State Function : State variables which are dependent only upon the state of the system but not upon the path by which that state has been attained are called state function. E.g. Almost all state variables (except *work* and *heat* which are path function)

Extensive and Intensive Properties

The various properties or state variables can be classified into two types.

a. Extensive Properties : The thermodynamic properties which depends upon the quantity of matter contained in the system are called extensive properties. Eg. No. of moles, area, volume mass ,internal energy, enthalpy, entropy, free energy etc.

b.Intensive Properties : The thermodynamic properties which depend only upon the quality but not upon the quantity of matter contained in the system are called intensive properties. Eg. Temperature, pressure , density , viscosity, surface tension , refractive index , boiling point , freezing point etc.

Thermodynamic Process

The operation by which system can be changed from one state to another is called thermodynamic process. The various types of thermodynamic process are discussed below.

a. Isothermal Process: The process which is carried out at constant temperature condition is called isothermal process. During isothermal process, $\Delta T=0$ or $\partial T=0$.

b. Adiabatic Process : The process in which heat can neither enter nor leave the system is called adiabatic process. During adiabatic process , $\Delta q = 0$ or $\partial q=0$ or q=0.

c. Isobaric Process : The process which is carried out at constant pressure condition is called isobaric process. During isobaric process , $\Delta P=0$ or $\partial P=0$.

d. Isochoric Process : The process which is carried out at constant volume condition is called isochoric process. During isochoric process , $\Delta V=0$ or $\partial V=0$.

e. Cyclic Process: The process in which system comes to its initial stage after a series of different stages is called cyclic process. During cyclic process, $\Delta E= 0$ & $\Delta H=0$.

f. Reversible Process: If the process occurs very slowly such that during every step driving force is only infinitesimally greater than opposing force and which can be reversed back is called reversible process. It is ideal process and has only theoretical importance.

g. Irreversible Process: The process which occurs rapidly or in a single step and which cannot be reversed is called irreversible process. All natural process are irreversible. It is a real process and has practical importance.

Question: Write the differences between reversible and irreversible process.

Exchange of energy between System and surrounding

Energy exchanges between system and surrounding in two forms.

i. As heat: If the system and surrounding differs in temperature, then energy exchanges between them in the form of heat. Suppose the system is at higher temperature than surrounding. In this case, energy exchanges from system to surrounding in the form of heat till both are at thermal equilibrium which is denoted by -q. If surrounding is at higher temperature than system, then energy exchanges from surrounding to the system in the form of heat till both are at thermal equilibrium which is denoted by +q.

ii. As work : If the system and surrounding are at different pressures, then energy is exchanged between them in the form of work.

Suppose , a gas is kept in a cylinder fitted with frictionless piston. If the pressure of gaseous system is greater than that of surrounding, the gas expands and the piston moves in upward direction. In this case, work is done by the system against surrounding which is denoted by +w. If the pressure of surrounding is greater than that of gaseous system, then gas contracts and piston moves in downward direction. In this case, work is done on system by surrounding which is denoted by -w. In both cases of expansion and contraction of gas, mechanical work or Pressure- Volume work or PV work can be calculated as follows.   i.e. W = PΔV

where, P is opposing pressure and ΔV is change in volume.

Internal Energy (Intrinsic Energy) [E]

A chemical compound contains various forms of energy in it due to its chemical nature. These energies are kinetic energy, potential energy, chemical bond energy, nuclear energy, electrical energy, rotational energy, vibrational energy translational energy etc. The sum of all these molecular energies in the chemical compound which arises due to chemical nature is called internal energy. It is denoted by E.

A definite amount of compound under the given set of conditions contains definite amount of internal energy. When the chemical reaction occurs, the internal energy of product differs from that of reactant. This difference in internal energy between reactant and product is denoted by ΔE and can be written as follows.

i.e. $\Delta E = E_p – E_r$ where E_p is the internal energy of product & E_r is the internal energy of reactant.

If $\Delta E = +ve$, the reaction is endothermic & if $\Delta E = -ve$, the reaction is exothermic.

Absolute value of internal energy (E) cannot be determined however , the change in internal energy (ΔE) can be determined experimentally.

First Law of Thermodynamics

It is based upon law of conservation of energy. It states that,
" *The total energy in the universe always remains constant.*"
OR, " *Energy can neither be created nor destroyed.*"
It means that if energy in one form disappears, exactly
equivalent amount of energy will reappear in another form.
Thus, the energy always remains conserved in the universe.
.   Suppose, 'q' amount of heat is absorbed by the system.
This absorbed heat can be used for two purposes. A part of the
heat is used to increase the internal energy of the system and
the remaining heat is used to do the work by the system against
surrounding.   i.e. q = ΔE + W
where, q is the heat absorbed by system, ΔE is the increase in
internal energy of system & W is work done by the system.

This equation can also be written as, $\Delta E = q - W$

If W is mechanical work then, $W = P\Delta V$

So above equation becomes, $\Delta E = q - P\Delta V$

Sign Convention(conventional)

i. If ΔE= +ve, there is increase in internal energy of the system.

ii. If ΔE= -ve, there is decrease in internal energy of the system.

iii. If q=+ve, heat is absorbed by the system.

iv. If q= -ve, heat is released from the system.

v. If W=+ve, work is done by the system.

vi. If W=-ve, work is done on the system.

ΔE at constant volume

At constant volume (isochoric process), $\Delta V = 0$

So, first law of thermodynamics can be written as, $q = \Delta E + P\Delta V$

At constant volume condition, $\Delta V = 0$ & $q = q_v$

So, above equation becomes, $q_v = \Delta E$

i.e. *Heat absorbed by the system at constant volume becomes equal to the increase in internal energy of the system.*

ΔE at adiabatic Process

At adiabatic condition, the heat can neither enter nor leave the system. i.e. q =0

From first law of thermodynamics, we have   q = ΔE + W

During adiabatic process, q=0

So, above equation becomes,   ΔE= -W or, -ΔE= W

i.e. *Increase in   internal energy of the system during adiabatic process becomes equal to the work done on the system and vice versa.*

Enthalpy (Heat Content) [H]

In addition to the internal energy, substance consist of additional energy due to environmental conditions like pressure, volume etc.To deal this additional energy, enthalpy is introduced. *It can be defined as the total heat content of the substance at constant pressure. It can also be defined as the sum of internal energy and product of pressure and volume.*

i.e. $H = E + PV$

It is state function and extensive property. It is significant at constant pressure condition. Since most of the reactions occur at constant pressure, enthalpy is superior than internal energy. Absolute value of enthalpy cannot be determined however, the change in enthalpy (ΔH) can be determined experimentally.

i.e. $\Delta H = H_p - H_r$ where, H_p is the enthalpy of product & H_r is the enthalpy of reactant.

If $H_p > H_r$, then ΔH = +ve   i.e. endothermic process.

If $H_p < H_r$, then ΔH = -ve   i.e. exothermic process.

ΔH at constant Pressure

From First Law of Thermodynamics, we have,

q= ΔE + W

or, q = ΔE + PΔV

If the process occurs at constant pressure condition ,then above equation becomes,

q_p = Ep-Er + P(Vp-Vr)

.   =Ep-Er + PVp- PVr

.   = Ep + PVp – (Er + PVr)

.   =Hp – Hr   [H= E+ PV]

So, q_p = ΔH

i.e. *Heat absorbed by the system at constant pressure becomes equal to the increase in enthalpy of the system.*

Relation between ΔH & ΔE

The enthalpy change for a reaction becomes,

ΔH = Hp - Hr

From the definition of enthalpy, we have,   H=E+PV
If the process occurs at constant pressure and temperature then above equation becomes,

.   ΔH = (Ep+ PVp)- (Er + PVr)

.   = Ep+ PVp-Er-PVr

.   = Ep-Er + PVp-PVr

.   = ΔE+ P(Vp-Vr)
or,   ΔH= ΔE + PΔV ………………(i)
From ideal gas equation, we have,   PV=nRT
If the process occurs at constant pressure and temperature then
above equation becomes,   PΔV = ΔnRT…………..(ii)
From equation (i) & (ii), we get**,   ΔH = ΔE + ΔnRT**
where, Δn= change in no. of moles of gaseous reactant and product. .
=*no. of moles of* gaseous product *- no. of moles of* gaseous reactant

Heat of Reaction or Enthalpy of Reaction(ΔH)

It is the heat change when the no. of moles of reactant as indicated by balanced chemical equation are completely reacted to form the product.

$25^{\circ}C$ temperature and 1 atm pressure is taken as standard condition. Heat of reaction during standard condition is called standard heat of reaction (ΔH°).

Laws of Thermochemistry

Laplace and Lavoisier's Law of Thermochemistry

It is based upon law of conservation of energy. It states that, 'The heat change (enthalpy change) of a chemical reaction is exactly equal and opposite when the reaction is reversed.'

e.g $C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -94$ Kcal

$CO_2(g) \longrightarrow C(s) + O_2(g) \quad \Delta H = +94$ Kcal
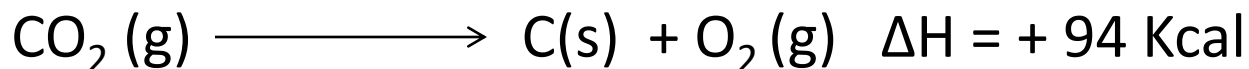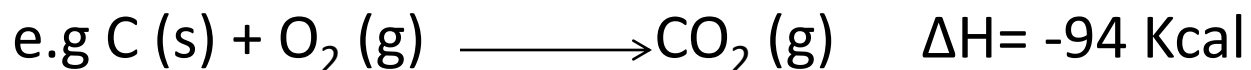
Hess's Law of constant heat summation [V. imp.]
It was given by G.H. Hess in 1840 after a series of experiments made on heat of reaction. It states that, *" The amount of heat liberated or absorbed during a chemical reaction will always be the same regardless of whether the reaction takes place in a single step or in a series of steps."*

Let us consider that A can be converted into Z directly.

i.e. $A \longrightarrow Z + Q_1$ (direct conversion)

Again let us consider that the same change can be performed in several steps.

i.e. $A \longrightarrow B + q_1$

. $B \longrightarrow C + q_2$ (indirect conversion)

. $C \longrightarrow Z + q_3$

If $Q_2 = q_1 + q_2 + q_3$, then according to Hess's Law, $Q_1 = Q_2$

Illustration

Hess's law can be illustrated by taking an example of conversion of carbon to carbon dioxide. Carbon can be converted into carbon dioxide directly or indirectly which can be represented as follows. i.e. $C + O_2 \xrightarrow{\text{path-1}} CO_2$ ...

..

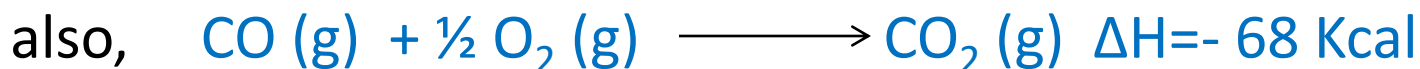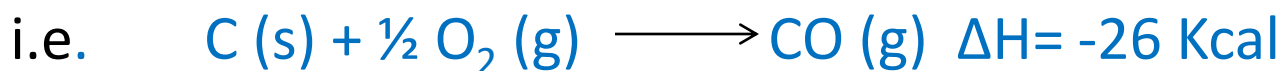. . $\frac{1}{2} O_2 \searrow CO \nearrow \frac{1}{2} O_2$.
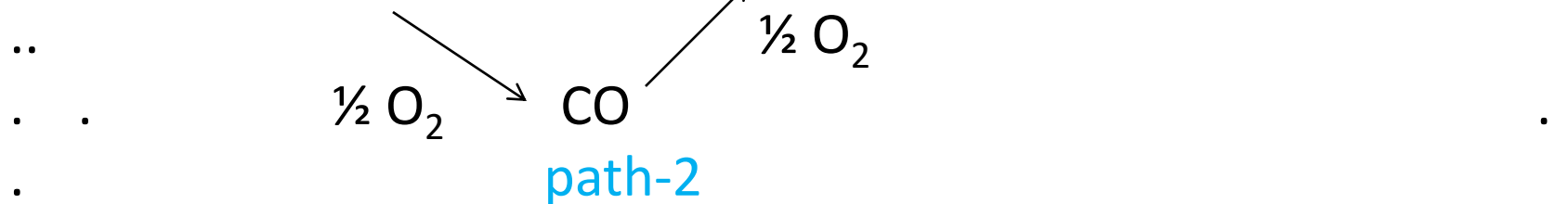
. path-2

i. In path-1, carbon is converted into carbondioxide directly. When carbon is burnt in excess of air, carbondioxide is formed with the liberation of 94 Kcal energy.

i.e. $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -94$ Kcal
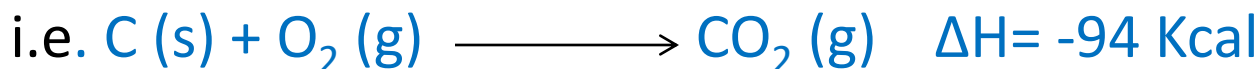
ii. In path-2, carbon is converted into carbondioxide indirectly. When carbon is burnt in limited supply of air, carbonmonoxide is formed with the liberation of 26 Kcal energy. Thus formed CO is again burnt in air to form CO_2 with the liberation of 68 Kcal energy.

i.e. $C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$ $\Delta H = -26$ Kcal

also, $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -68$ Kcal

During indirect conversion, a total of [26+ 68]=94Kcal of energy is liberated which is equal to that during direct conversion. Thus, this data illustrates Hess's law.

Applications of Hess's Law

The various applications of Hess's law are as follows.

i. It is used to calculate the heat of reaction in which it is not possible to determine experimentally.

ii. It is used to calculate the heat of reaction for very slow and very fast reaction.

iii. It is used to calculate the heat of reaction for hypothetical reaction.
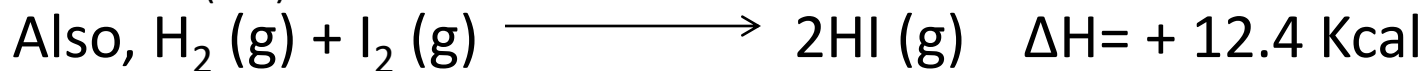
Different forms of Heat of reaction

Depending upon the nature of reaction, heat of reaction are given different names which are discussed below.

i.Heat of Formation or Enthalpy of Formation (ΔH_f)

It is the heat change when 1 mole of product is formed from its constituent elements. If the constituent elements consists of allotropes, then it must be the most stable allotrope.

e.g. $H_2(g) + Cl_2(g) \longrightarrow 2HCl\ (g)$ $\Delta H = -44 Kcal$

So, $\Delta H_{f\ (HCl)} = -44/2 = -22 Kcal$
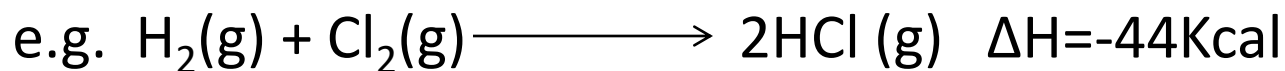
Also, $H_2\ (g) + I_2\ (g) \longrightarrow 2HI\ (g)$ $\Delta H = +12.4\ Kcal$

So, $\Delta H_{f\ (HI)} = +12.4/2 = +6.2\ Kcal$

Heat of formation may be both positive or negative. It helps to predict the thermodynamic stability of the compound. Any compound with higher negative value of heat of formation is more stable.

E.g. HCl is more stable than HI.

Heat of formation for the most stable allotrope of an element at standard condition is taken as zero .

E.g. Graphite, Rhombic Sulphur, O_2 etc.

ii. Heat of Combustion or Enthalpy of Combustion (ΔHc)

It is the heat change when 1 mole of the substance is burnt in air to form completely oxidized product. If the substance consists of allotropes, then it must be most stable allotrope.

E.g. $C (s) + O_2 (g) \longrightarrow CO_2(g)$ $\Delta H= -94$ Kcal
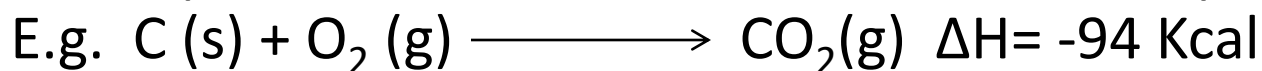
Combustion reaction is always exothermic. Heat of combustion helps to predict the efficiency or calorific value of fuel & food. Any fuel with higher negative value of heat of combustion is a better fuel.
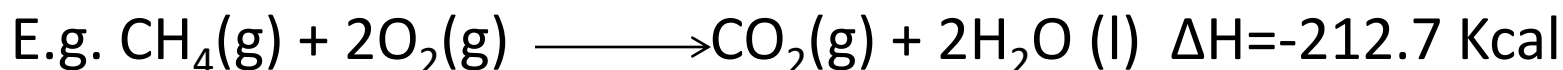
E.g. $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O (l)$ $\Delta H=-212.7$ Kcal
i.e. Methane is better fuel than carbon.

iii. Heat of Neutralization or Enthalpy of Neutralization (ΔH_N) *

It is the heat change when one gram equivalent of an acid is neutralized by base or vice versa in their dilute or aqueous solution.

E.g. $HCl(aq) + NaOH (aq) \longrightarrow NaCl (aq) + H_2O (l)$ $\Delta H=-13.7$ Kcal

Heat of neutralization is always exothermic (-ve).

Heat of neutralization for strong acid and strong base is always a constant value of -13.7 Kcal. It is because, the strong electrolyte is almost completely ionized in its dilute or aqueous solution and neutralization reaction involves the combination of H+ ion from acid with OH- ion from base to form water molecule.

i.e. $H^+ (aq) + OH^- (aq) \longrightarrow H_2O (l)$ $\Delta H = -13.7$ Kcal
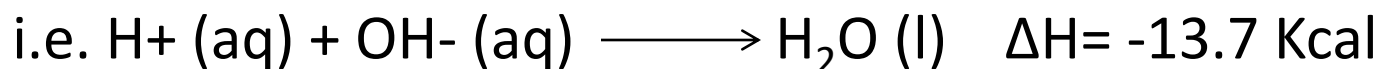
However, if at least one weak electrolyte is taken then heat of neutralization is always lesser than -13.7 Kcal. It is because, the weak electrolyte is only partially ionized in its dilute or aqueous solution and it absorbs some heat to increase its degree of dissociation (α). This absorbed heat is called heat of dissociation.
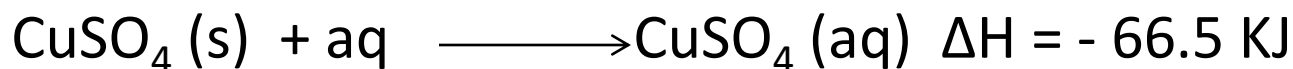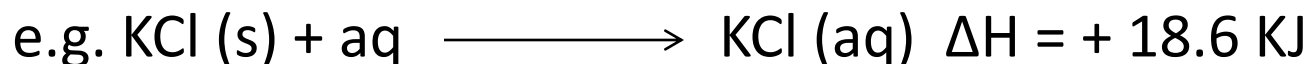
E.g. $CH_3COOH (aq) + NaOH (aq) \longrightarrow CH_3COONa(aq) + H_2O (l)$.

. $\Delta H = -13.2$ Kcal
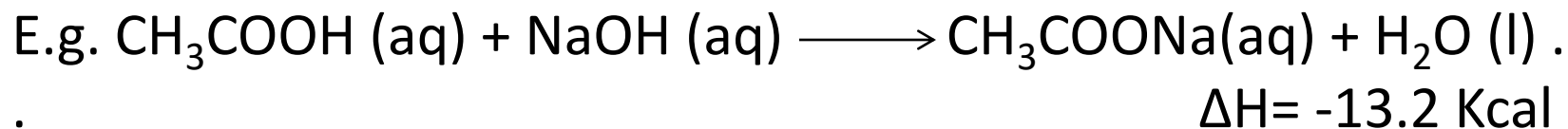
So, Heat of dissociation of $CH_3COOH = +0.5$ Kcal

iv. Enthalpy of solution (Heat of solution)

It is defined as the heat change when 1 mole of the substance is dissolved in large volume of solvent such that further addition of the solvent does not produce any more heat change.

Water is usually used as solvent and the symbol aq (aqueous) is used to represent it at large dilution.

e.g. $KCl (s) + aq \longrightarrow KCl (aq)$ $\Delta H = + 18.6 \ KJ$

$CuSO_4 (s) + aq \longrightarrow CuSO_4 (aq)$ $\Delta H = - 66.5 \ KJ$

Bond Energy or Bond Enthalpy or Bond dissociation Energy

During chemical reaction, existing bond in reactant must be broken down whereas new bond in product must be formed. To break the bond, energy must be absorbed (ΔH=+ve) whereas formation of new bond releases energy (ΔH=-ve). If the magnitude of absorbed energy is greater than that of released energy, the reaction becomes endothermic and vice-versa.

The energy required to break a particular type of bond is called bond energy. *It can be defined as the energy required to break the bond in one mole of gaseous covalent compound to form the products in gaseous state.*

E.g. H_2(g) $\longrightarrow$ 2H (g) ΔH=+104 Kcal [Bond energy of H_2]

The enthalpy change for a reaction can be calculated as follows:

i.e. ΔH= Hp - Hr

.   = Heat of formation of product – Heat of formation of reactant

.   = Bond energy of reactant – Bond energy of product

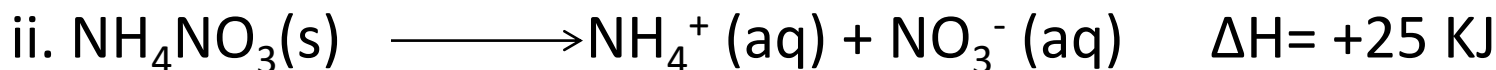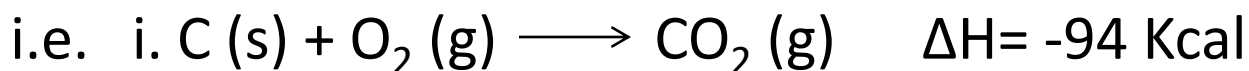# Spontaneous Process (Feasible Process)

The process which occurs on its own ,without the aid of any external agency is called spontaneous process. All natural process are spontaneous.

E.g.   i. Rusting of iron   ii. Melting of ice

iii. Dissolution of ammonium nitrate in water etc.

The term 'spontaneous' does not mean that the process is fast but it means that the process is possible at the given set of conditions.

Decrease in energy & Spontaneity of process

Let us consider the following two examples:

i.e.   i. $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -94$ Kcal

ii. $NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq)$ $\Delta H = +25$ KJ

The first reaction is an example of spontaneous exothermic reaction which occurs with decrease in energy. The second reaction is an example of spontaneous endothermic reaction which occurs with increase in energy. Hence from above two examples, it is clear that the process occurs spontaneously either with increase or decrease in energy. Hence, *energy or enthalpy is not the sole criteria for the spontaneity of process.*

Limitations of First law of Thermodynamics
(Necessity of Second law of Thermodynamics)

i. It puts no restriction over the direction of flow of heat.

ii. It does not deal about the spontaneity of process.

To overcome these limitations of first law, second law of thermodynamics is needed.

Entropy (S)

All spontaneous process are characterized by increase in randomness or disorder of the system. To deal this phenomena, entropy is introduced.

Entropy can be defined as the measure of randomness or disorder of the system. Greater the randomness, higher will be the entropy and hence more spontaneous will be the process and vice-versa.

It is state function and extensive property and is significant at constant temperature condition. Absolute value of entropy can be determined using Third law of Thermodynamics. Entropy change (ΔS) can also be determined experimentally.

i.e. $\Delta S = S_{product} - S_{reactant}$.

. $= S_{final\ state} - S_{initial\ state}$

Among three states of matter, $S_{solid} < S_{liquid} \ll S_{gas}$

Second Law of Thermodynamics

All spontaneous process are characterized by increase in randomness or disorder of the system. This is the basis for second law of thermodynamics.

It states that, *" In all spontaneous process, there is always an increase in entropy of universe."*

Mathematically, $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$

The spontaneity of process in terms of entropy can be written as follows.

i. If ΔS = +ve, the process is spontaneous.

ii. If ΔS = -ve, the process is non- spontaneous.

iii. If ΔS = 0, the process is in equilibrium.

Entropy change and its calculation

To predict the spontaneity of process in terms of entropy, the entropy change of universe must be determined. The entropy change of universe can be determined by knowing the entropy change of system and surrounding as follows.

i.e. $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$

Entropy change of System

The entropy change of system can be determined by knowing the entropy of reactant and product as follows.

i.e. $\Delta S = S_{product} - S_{reactant}$

Let us consider the following reaction.

i.e. $aA + bB \longrightarrow cC + dD$ The entropy change of system for this reaction can be calculated as follows.

i.e. $\Delta S = S_{product} - S_{reactant}$

$= [c \times S(C) + d \times S(D)] - [a \times S(A) + b \times S(B)]$

$= \sum S(product) - \sum S(reactant)$

Entropy change during Phase Transformation

A process occurs reversibly or irreversibly. If a process occurs reversibly at T kelvin and the heat absorbed or released during this process is known then, entropy change during this phase transformation can be calculated as follows.

i.e. $\Delta S = q_{rev} / T = \Delta H / T$

where, q_{rev} (ΔH) = heat absorbed or released during phase transformation

T= temperature of phase transformation in kelvin scale

The unit for entropy change is JK^{-1} or cal K^{-1} or $Jmol^{-1}K^{-1}$ or cal $mol^{-1}K^{-1}$ etc.

This formula can be modified for various phase transformations as follows.

i. Entropy of fusion (ΔS_{fus}):

$\Delta S_{fus} = \Delta H_{fus} / T_m$

where, ΔH_{fus}= latent heat of fusion per mole

T_m = melting point in kelvin scale

ii. Entropy of vaporization (ΔS_{vap})

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

where, ΔH_{vap}= latent heat of vaporization per mole

T_b = boiling point in kelvin scale

iii. Entropy of Sublimation (ΔS_{sub}):

$\Delta S_{sub} = \Delta H_{sub} / T_s$

where, ΔH_{sub}= latent heat of sublimation per mole

T_s = Sublimation temperature in kelvin scale

Entropy change of Surrounding

If heat is liberated from the system, it is absorbed by surrounding and vice-versa. Hence, the total combination of system and surrounding can be considered as reversible. So, entropy change of surrounding can be calculated as follows:

i.e. Entropy change of surrounding

=   Heat absorbed or released from surrounding

. .   Temperature of Surrounding in Kelvin scale

or, $\Delta S_{surr} = \Delta H_{surr} / T_{surr}$

This formula can be modified in terms of system as follows.

i.e. $\Delta S_{surr} = - \Delta H_{sys} / T_{sys}$

Gibb's Free Energy (Free Energy) [G]

While predicting the spontaneity of process in terms of entropy, the entropy change of both system and surrounding must be known. The entropy change of system can be determined easily whereas it is difficult to determine the entropy change of surrounding. So, to predict the spontaneity of process easily, Gibb's free energy is introduced. *It can be defined as the energy that can be converted into useful work at constant temperature and pressure. It can also be defined as the difference between enthalpy and product of temperature in kelvin and entropy.*

i.e. $G = H - TS$

It is denoted by G and it is state function & extensive property. It is significant at constant temperature and pressure.

When reaction occurs, reactant changes into product. The free energy of reactant differs from that of product. This change in free energy is denoted by ΔG and it can be written as follows.

i.e. $\Delta G = \Delta H - T\Delta S - S\Delta T$

If the reaction occurs at constant temperature and pressure, then above equation becomes,

. $\Delta G = \Delta H - T\Delta S$ …………(i)   [Since, $\Delta T = 0$]

This equation (i) is called Gibb's – Helmholtz equation and is very useful to predict the spontaneity of process.

The spontaneity of process in terms of free energy change can be written as follows.

i. If ΔG = -ve, the process is spontaneous.

ii. If ΔG = +ve, the process is non- spontaneous.

iii. If ΔG = 0, the process is in equilibrium.

From second law of thermodynamics, we have,

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$

But, $\Delta S_{surr} = - \Delta H_{sys} / T_{sys}$

So, above equation becomes, $\Delta S_{univ} = \Delta S_{sys} - \Delta H_{sys} / T_{sys}$

or, $T\Delta S_{univ} = T\Delta S - \Delta H$

or, $- T\Delta S_{univ} = \Delta H - T\Delta S$ ……….(ii)

From equation (i) & (ii) $(\Delta G)_{T,P} = - T\Delta S_{univ}$

Free energy is superior than entropy because it is related to system only whereas entropy is related to both system and surrounding.

The interplay of ΔH, ΔS & ΔG for the spontaneity of process are tabulated below.

.   ΔG = ΔH - TΔS

ΔH	ΔS	ΔG	Type of Process
_	+	_	Spontaneous at all temperature
+	_	+	Non spontaneous at all temperature
_	_	(-)	Spontaneous at lower temperature
_	_	(+)	Non spontaneous at higher temperature
+	+	(-)	Spontaneous at higher temperature
+	+	(+)	Non spontaneous at lower temperature
0	0	0	Equilibrium

Free Energy Change (ΔG)

It is the change in free energy when reactant is converted into product. It is denoted by ΔG and can be calculated as follows.

. 　　　　i.e. 　$\Delta G = \Delta H - T\Delta S$

. 　　Also, 　　$\Delta G = \Delta G_{f(product)} - \Delta G_{f\,(reactant)}$

. 　　　　= Free energy of formation 　- Free energy of formation

. 　　　　　of product 　　　　　　　　　　　of reactant

$25^{o}C$ temperature, 1 atm pressure and unit concentration of reactant is taken as standard condition. Free energy change during standard condition is called standard free energy change (ΔG^{o}). . 　　　　i.e. 　$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$

. 　　Also, 　　$\Delta G^{o} = \Delta G^{o}_{f(product)} - \Delta G^{o}_{f\,(reactant)}$

. 　= Std. Free energy of formation 　- Std. Free energy of formation

. 　　　　　of product 　　　　　　　　　　　of reactant

Free energy of formation can be defined as the free energy change when 1 mole of product is formed from its constituent elements. Free energy of formation for the most stable allotrope of an element at standard condition is taken as zero.
E.g. Graphite, Rhombic sulphur, O_2 etc.

Relation between ΔG⁰ & Equilibrium constant (K)

During non standard condition, ΔG and ΔG⁰ are related to each other as follows.

.   i.e. $\Delta G = \Delta G^0 + RT \ln Q$

where, Q= reaction quotient

If the reaction comes to an equilibrium then, ΔG=0 & Q=K

So above equation becomes,

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

.   or, $\Delta G^0 = - RT \ln K$

.   or, $\Delta G^0 = - 2.303 \, RT \log K$

Relation between Free Energy & Useful work

From First law of Thermodynamics, we have,

. $\qquad q = \Delta E + w$

The work done by system consists of two parts

. $\qquad$ i.e. $w = w_{exp} + w_{useful}$

So, above equation becomes

. $\qquad q = \Delta E + w_{exp} + w_{useful}$

If the process occurs at constant pressure condition then the work of expansion becomes,

. $\qquad w_{exp} = P\Delta V$

So, above equation becomes

. $\qquad q = \Delta E + P\Delta V + w_{useful}$

. $\qquad$ or, $q = \Delta H + w_{useful}$ ....(i)

If the process occurs reversibly at constant temperature 'T' kelvin then entropy change can be calculated as follows.

.   i.e. $\Delta S = q/T$

.   or, $q = T\Delta S$ …………..(ii)

Substituting the value of 'q' in equation (i) , we get

. $T\Delta S = \Delta H + w_{useful}$

or, $-w_{useful} = \Delta H - T\Delta S$ ………..(iii)

From Gibb's – Helmholtz equation, we have

. $\Delta G = \Delta H - T\Delta S$ ………………(iv)

From equation (iii) & (iv), we get

. $\Delta G = - w_{useful}$

or, $-(\Delta G)_{T,P} = w_{useful}$

i.e. Decrease in free energy at constant temperature and pressure becomes equal to the useful work done by the system.