CHEMICAL THERMODYNAMICS

INTRODUCTION

Thermodynamics means "heat" and dynamics "motion" and so thermodynamic means "motion of heat" ie., flow of heat. Thus thermodynamics deals with the relationship between heat and work. Actually, it deals with the interconversion of one kind of energy such as heat energy, electrical energy, chemical energy, mechanical energy etc., into another energy

TERMINOLOGY OF THERMODYNAMICS

SYSTEM, BOUNDARY, SURROUNDINGS

1. **System**

A thermodynamic system is defined as the part of the universe, which is selected for theoretical and experimental investigation. A system usually has a definite amount of a specific substance.

2. **Surroundings**

The remaining part of the universe is called surrounding, which is separated from the system by a definite boundary

3. **Boundary**

The region or interface separating the system from the surrounding is called the boundary.

Types of System

1. **Isolated System**

A system which cannot exchange both energy and matter with its surroundings is called an isolated system. It has no mechanical or thermal contact with surroundings.

2. **Closed System**

A System which can exchange energy but not matter with its surroundings it called a closed system.

3. **Open System**

A system which can exchange energy as well as matter with its surroundings is called a open system.

4. **Homogeneous System**

When a System is completely uniform throughout, it is called a homogeneous system

5. **Heterogeneous System**

When a system is not uniform throughout, which consists of two or more phases, it is called a heterogeneous system.

Properties of a System

The properties of a system can be divided into three classes

1. Intensive properties

The properties which do not depend on the amount of substance but depend only on nature of the substance present in the system are called intensive properties.

Examples: Temperature, pressure, concentration and density.

2. Extensive properties

The properties which depend on the amount of substance present in the system is called extensive properties.

Examples: Mass, volume, internal energy (E), enthalpy (H),entropy (S), Free Energy (G).

3. Macroscopic properties

The properties associated with a macroscopic system (ie., consisting of large number of particles) are called macroscopic properties.

Examples: Density, viscosity, pressure, volume, temperature etc.,

Table 2.1 Some Intensive and Extensive Properties

No	Intensive Properties	Extensive Properties
1	Temperature	Mass
2	Density	Internal energy(E)
3	Pressure	Enthalpy
4	Concentration	Entropy
5	Viscosity	Free Energy (G)
6	Boiling point	Number of moles
7	Freezing point	

Process and their Types

A system may change from one state to another by an operation. The operation by which this change of state occurs is called a process.

Different types of process are as follows

Isothermal Processes

Those processes in which the temperature remains fixed are termed isothermal process. This is achieved by placing the system in a thermostat.

i.e. dT = 0

Adiabatic processes

Those processes in which no heat can flow into or out of the system are called adiabatic processes. This is achieved by carrying the process in an insulated container

i.e. dq = 0

Isobaric Processes

Those processes which take place at constant pressure are called isobaric processes. *ie., dp = 0*

Isochoric Processes

Those processes in which the volume remains constant are known as isochoric process. *i.e., dv = 0*

Cyclic Processes

When initial and final status of a system in a process is the same, the process is called a cyclic process. In this process, a system undergoes various processes and returns back to its initial state. *ie., dE = 0, dH = 0.*

Irreversible Process

If the driving force and the opposing force differ by a large amount, the process is called irreversible process.

Reversible Process

If the driving force and opposing force differ by an infinitesimally small amount, the process is called reversible process.

Internal Energy (E) (or) (U)

Internal energy is defined as the total amount of energy associated with the given substance. Thus,

$$E = E_V + E_r + E_t + E_e + E_n$$

The absolute value of internal energy (E) of a substance cannot be determined accurately, because it is not possible to determine the exact values of the various constituent energies *(ie., E_V, E_r, E_t, E_e, E_n)* But, the change in internal energy (ΔE) can be easily measured with the help of first law of thermodynamics.

Enthalpy (H)

It is "the heat content of the system" (or) "the sum of internal energy and pressure-volume energy (work done) of a system, under a particular set of conditions".

$$i.e., \quad H = E + PV$$

Unit: K.Jmol^{-1}

Zeroth Law of Thermodynamics

It deals with thermal equilibrium among the systems which are in physical contact.

First Law of Thermodynamics

This law is simply the law of conservation of energy. It can be stated in different ways as follows.

Energy can neither be created nor destroyed, but it can be converted from one form to another form.

$$E_2 = E1 + q\text{-}w$$

$$E_2\text{-} E_1 = q\text{-}w$$

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

i.e., Change in internal energy = Heat supplied to the system –Worked done by the system.

The above equation provides relationship between change in internal energy (ΔE) of the system, heat supplied to the system (q), and work (w) done by the system. This is the **Mathematical Statement** of the first law of thermodynamics.

Need for the second law of thermodynamics

1. The second law predicts the feasibility of a process and also it explains why it is not possible to convert heat into an equivalent amount of work.
2. The second law is able to predict the direction of energy transformed and also the direction of spontaneous process.

THE SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics has been formulated to explain the spontaneity (feasibility) of physical and chemical process. This law introduces two new thermodynamic functions entropy and free energy to explain the spontaneity (feasibility) of the processes. The second law of thermodynamics can be understood by discussing the meaning of the terms spontaneity, entropy and free energy.

Statements of second law of thermodynamics

The second law of thermodynamics states that work can always be converted into heat, but heat cannot be completely converted into work, only a fraction of heat can be converted into work and the rest remains unavailable and unconverted.

The second law of thermodynamics has been stated in number of ways, all the statements have the same meaning.

Clausius Statement

It is impossible to construct a machine which can transfer heat from a cold body to a hot body, unless some external work is done on the machine.

Kelvin Statement

It is impossible to take heat from a hot body and convert it completely into work by a cyclic process without transferring a part of heat to a cold body.

Interms of Entropy

A spontaneous process in always accompanied by an increase in entropy of the universe. (ie., system and surroundings)

ENTROPY

Definition

Entropy is a measure of degree of disorder or randomness in a molecular system. It is also considered as a measure of unavailable form of energy.

Thus, when a system goes from a more orderly state, randomness increases, and hence entropy of the system increases.

For example

   i.   When a solid changes to liquid, there is an increase in entropy
  ii.   When solidification occurs, entropy decreases.
 iii.   When a gas is liquefied, entropy decreases,
  iv.   When ice is melted, entropy increases

Mathematical Expression for Entropy

The change in entropy (ΔS) of a system is equal to the ratio of heat change (q) to the temperature (T) of the reversible cyclic process.

$$\Delta S = \frac{q_{rev}}{T}$$

Units of entropy: Cal/deg (or) JK^{-1}

Significance of Entropy

1. **Entropy and Unavailable Energy**

When heat is supplied to the system, some portion of this heat is used to do some work. This portion of heat is called available energy. The remaining portion of heat is called unavailable energy. Thus the second law of thermodynamics states that the entropy is a measure of unavailable energy. Hence entropy is defined as unavailable energy per unit temperature.

$$Entropy = \frac{Unavailable - energy}{Temperature}$$

2. **Entropy and randomness (disorder)**

Entropy is a measure of randomness in a system. Increase in entropy means change from an ordered state to disordered state.

Example: All natural processes are spontaneous process, accompanied by increase in free energy.

3. **Entropy and probability**

An irreversible (spontaneous) process tends to proceed from less probable state to more probable state. Since in a spontaneous process entropy increases, entropy may be defined as **a function of probability of the thermodynamic state.**

Entropy change in a reversible (non-spontaneous) process

Consider an isothermal and reversible expansion of an ideal gas. If the system absorbs q amount of heat from the surrounding at temperature T, the increase in entropy of the system is given by

$$\Delta S_{system} = \frac{q}{T}$$

But the entropy of the surroundings decreases, because the surroundings loose the same amount of heat q .i.e,

$$\Delta S_{surroundings} = \frac{-q}{T}$$

Hence, the net change in the entropy is given by

$$\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings}$$

ie
$$\Delta S_{Total} = \frac{q}{T} + \left[\frac{-q}{T}\right]$$

$$\boxed{\Delta S_{Total} = 0}$$

i.e., In a reversible isothermal process, there is no net change in entropy.

ENTROPY CHANGE IN AN IRREVERSIBLE (SPONTANEOUS) PROCESS

Consider a system maintained at a higher temperature T_1 and its surrounding maintained at a lower temperature T_2. If q amount of heat passes irreversibly from the system to surroundings. Then,

Decrease in entropy of the system, $\Delta S_{system} = -q/T_1$

Increase in entropy of the surroundings, $\Delta S_{sorroundings} = +q/T_2$

Hence, net change in the entropy is given by

$$\Delta S_{Total} = \Delta S_{System} + \Delta S_{Sorroundings}$$

$$\Delta S_{Total} = \frac{q}{T_2} + \left[\frac{-q}{T_1}\right]$$

$$= q\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$= q\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

Since $T_1 > T_2$, $T_1 - T_2$ is positive. Hence

ΔS_{Total} = Positive

$$\boxed{\Delta S_{Total} > 0}$$

i.e., In an irreversible process, the entropy of the system increases.

Since all spontaneous process is natural and irreversible process, the entropy of the system always increases.

Entropy Change in an Isothermal Expansion of an Ideal Gas

According to first law of thermodynamics

$$dE = q - PdV$$

$$dE = q - w \qquad\qquad \text{………(1)}$$

[PdV=W]

In a reversible isothermal expansion, there is no change of internal energy (dE=0)

Equation (1) becomes,

$$q_{rev} - w = 0$$

$$q_{rev} = w \qquad\qquad \text{………(2)}$$

The work done in the expansion of n moles of a gas from volume V_1 to V_2 at constant temperature T is given by

$$w = nRT \ln\frac{V_2}{V_1} \qquad\qquad \text{……… (3)}$$

When equation (3) is introduced in equation (2), we get

$$q_{rev} = nRT \ln \frac{V_2}{V_1} \qquad\qquad \therefore \Delta S = \frac{Q_{rev}}{T}$$

$$T\Delta S = nRT \ln \frac{V_2}{V_1}$$

(or)

$$\Delta S = \frac{1}{T} nRT \ln \frac{V_2}{V_1}$$

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

$$\Delta S = 2.303 nR \log \frac{V_2}{V_1}$$

(or)

(or),   **$P_1V_1 = RT$;**

$$V_1 = \frac{RT}{P_1}$$

$P_2V_2 = RT$;

$$V_2 = \frac{RT}{P_2}$$

$$\Delta S = 2.303 nR \log \frac{P_1}{P_2}$$

Entropy Change in Physical Transformations

Entropy change takes, when the system undergoes physical transformation such as vapourization, fusion.

Let ΔH be the quantity of heat absorbed in calories at constant temperature and pressure. Then the entropy change is given by

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

But the enthalpy change, $\Delta H = L \times M$

The above equation becomes

$$\Delta S = \frac{L \times M}{T}$$

Where,

L = Latent heat in calories

M = Molecular weight in grams

T = Temperature in kelvin

Latent heat of vapourisation of water = 540 Cals/gm (100° C)

Latent heat of fusion of ice at 0° C = 80 Cals/gm

Problems Based on Entropy Change

The following note must be kept in our mind during the calculation of ΔS

Note: (1) for mole of substance, latent heat must be multiplied by mol.wt. of the substance ie.,

$$\Delta H = L \times M$$

Unit: Cals (or) J/K/Mole

(2) For some gram of substance, latent heat alone must be used (no molecular weight) i.e.,

$$\Delta S = L$$

Unit: Cals (or) J/K/gm.

CLAUSIUS INEQUALITY (OR) CLAUSIUS THEOREM

Clausius theorem is a mathematical explanation of the II law of thermodynamics called clausius inequality. It states that, the cyclic integral of $\dfrac{\partial Q}{T}$ is always less than (or) equal to zero`

(or)

The amount of heat transferred to the system divided by its temperature is equal to or less than zero is known as clausius inequality.

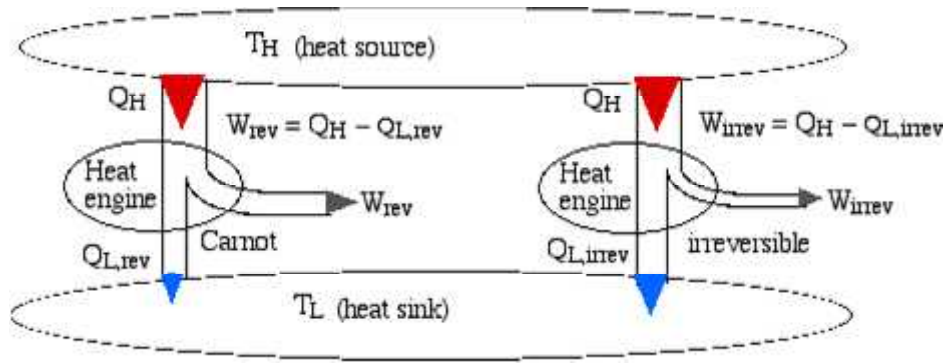$$\oint \frac{\delta Q}{T} \leq 0$$

Where,

δQ = Differential heat transfer at the system boundary during a cycle.

T = Absolute temperature at the boundary.

$\oint$ = Integration over the entire cycle.

Thus, the clausius inequality is valid for all cycles, reversible (or) irreversible process.

Proof of clausius inequality

Reversible and irreversible Heat Engine.

Consider two heat engines, one a reversible heat (carnot) engine and the other an irreversible heat engine. For the purpose of developing the clausius inequality we assume that both the engines absorb the same amount of heat Q_H from the heat source having a temperature of T_H. Both the engines reject the heat to a sink at a temperature T_L. Applying the first law of thermodynamics to both the engines

$$W_{rev} = Q_H - Q_{L.rev}$$

$$W_{irrev} = Q_H - Q_{L.irrev}$$

Since the reversible engine (carnot) is more efficient than the reversible engine, it must reject less heat ($Q_{L.rev}$) to the thermal sink (T_L) than that of rejected by the irreversible engine ($Q_{L.irrev}$). So the reversible heat engine for the same heat input Q_H.

$$W_{rev} = Q_H - Q_{L.rev} > W_{irrev} = Q_H - Q_{L.irrev}$$

For reversible heat engine (carnot)

Consider first the reversible heat engine. The reversible heat transfer can only occur isothermally (at constant T), so the cyclic integral of the heat transfer divided by the temperature C an be written as

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} = \frac{Q_{L.rev}}{T_L}$$

$$\therefore \frac{Q_{L.rev}}{T_L} = \frac{Q_H}{T_H}$$

$$\oint \frac{\partial Q}{T} = 0$$

For irreversible heat engine

The above diagram shows that the two heat engines (reversible and irreversible) have the same value of heat transfer from the thermal source Q_H. But heat rejection Q_L is more in irreversible engine than the reversible one

$$Q_{L.irrev} > Q_{L.rev}$$

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} = \frac{Q_{L.rev}}{T_L} < 0$$

Thus, for any reversible (or) irreversible heat engine we obtain the clausius inequality.

$$\oint \frac{\delta Q}{T} \leq 0 \quad \textbf{SPONTANEOUS PROCESS}$$

Definition

A process which proceeds on its own without any outside assistance is termed as a spontaneous (or) natural process.

Spontaneity

It is defined as ***"the tendency of a process to occur naturally is called the spontaneity".***

CRITERIA OF SPONTENEITY

Some important criteria of spontaneous physical and chemical changes are given below.

1. **A Spontaneous Change is One-way or Unidirectional.**
   For reverse change to occur, work must be done.
2. **For a spontaneous change to occur, time is no factor.**
   A spontaneous reaction may take place rapidly or very slowly.
3. **Once a system is in equilibrium state, it does not undergo any further spontaneous change in state, if left undisturbed.**
   To take the system away from equilibrium some external work must be done on the system.
4. **If the system is not equilibrium state (Unstable) a spontaneous change is inevitable.**
   The change will continue till the system attains the state of equilibrium.
5. **A spontaneous change is accompanied by decrease of internal energy (ΔE) or enthalpy (ΔH).**
   It implies that only such reactions are exothermic reactions. But the melting of ice and evaporation of rain water are endothermic process, which processed spontaneous.

Example of Spontaneous Processes

 1. Water Flows Downhill Spontaneously

We cannot reverse the direction of flow without some external aid.

2. Heat Flows Spontaneously

When two reservoirs, one hot and cold, are connected, heat flows spontaneously from the hot reservoir to the cold one, but not from cold to hot. For the reverse process, i.e. for the

transfer of heat from a cold reservoir to a hot a reservoir, as in a refrigerator, energy has to be supplied from outside the system.

3. Electricity Flows Spontaneously

Electricity flows spontaneously from a point of higher potential to a point of lower potential. The direction of flow of current can be reversed only by applying an external field in the opposite direction.

6. **A Gas Expands Spontaneously**

A gas expands spontaneously from a region of high pressure to a region of high pressure to a region of low pressure or in vacuum.

From the above examples it is concluded that, all natural processes proceed spontaneously (i.e., without external aid) and are thermodynamically irreversible in character.

Criteria for the Spontaneous Process (or) Gibbs Free Energy and Spontaneity

According to the second law of thermodynamics a process is said to be spontaneous only when ΔS_{total} is positive. i.e., entropy of the universe (system + surroundings) increases. The criteria of spontaneity involves the entropy of surroundings, which is difficult to measure. So, we need a criteria, which does not involve the entropy of surroundings. The change in Gibbs free energy provides such a criteria.

We know that, the total entropy change (ΔS_{total}) is given by

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} \qquad \ldots\ldots\ldots (1)$$

If a reaction is carried out at constant T and P

The amount of heat transferred by the system to surroundings is given by $\Delta S_{system} = (-q_p)_{system}$

The amount of heat taken by the surroundings is equal to $\Delta S_{surroundings} = (-q_p)_{system}$

$$(-q_p)_{surroundings} = (-q_p)_{system} = -\Delta H_{system}$$

Since the surroundings is a large area the temperature of the surroundings remain constant, so we have

$$\Delta Ssurroundings = \frac{(-q_p)_{system}}{T} = \frac{-\Delta H_{system}}{T} \qquad \ldots\ldots\ldots (2)$$

On substituting equation 2 in 1 we get

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

Multiply the equation by T

$$T\Delta S_{Total} = T\Delta S_{system} - \Delta H_{system} \qquad \ldots\ldots\ldots (3)$$

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

$$\left[\because \Delta G = \Delta H - T\Delta S\right] \qquad \ldots\ldots\ldots (4)$$

Equation (4) is introduced in equation (3)

$$T\Delta S_{Total} = \Delta H_{system} - \Delta G - \Delta H_{system}$$

$$-T\Delta S_{total} = \Delta G \qquad \text{(or)} \qquad T\Delta S_{total} = -\Delta G \qquad \ldots\ldots\ldots (5)$$

The equation (5) is the criterion for spontaneity interms of free energy of the system. Thus

When ΔG = -ve ($\Delta G < 0$), the process is spontaneous.

When ΔG = 0, the process is in equilibrium.

When ΔG = +ve ($\Delta G > 0$), the process in non-spontaneous.

Conditions of Spontaneity Enthalpy, Entropy and Free energy changes and the Nature of Reaction

ΔH	ΔS	ΔG=ΔH-T ΔS	conclusion
- (exothermic)	+	-	Spontaneous change
- (exothermic)	-	-(at low T)	Spontaneous change
		+(at high T)	Non-Spontaneous
+ (endothermic)	+	+(at low T)	Non-Spontaneous
		-(at high T)	Spontaneous
+ (endothermic)	-	+	Forbidden in the forward direction

Thus the sign of ΔG provides a criterion for spontaneity under conditions of constant temperature and pressure.

If ΔG is negative	The reaction is natural process and can proceed spontaneously
If ΔG is positive	The reaction is unnatural process and cannot proceed spontaneously

FREE ENERGIES (OR) NEW THERMODUNAMIC FUNCTIONS

Need for new thermodynamic function

As suggested by the second law of thermodynamics, $\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings}$ can be used to predict spontaneity of a process. For a Spontaneous process ΔS_{total} is always positive or greater than zero.

i.e., $\Delta S_{total} > 0$

In order to find out the spontaneity of a process, we have to see the change in entropy of the system as well as surroundings. It is very difficult to find out the change in entropy of the surroundings every time. So the following two new thermodynamic functions are introduced, which can be determined more conveniently

1. Helmholtz free energy (A) (or) Helmholtz work function

2. Gibbs free energy (G) (or) Free Energy

Helmholtz free energy (A) (or) Helmholtz work function

It is also known that a part of internal energy of a system can be used at constant temperature to do some useful work. This part of internal energy (E), which is isothermally available, is called "work function" (A) of the system. It is mathematically defined as

$$A = E - TS$$

Significance of the Work Function (A)

The work function is given by

$$A = E - TS \qquad \qquad \dots\dots\dots (1)$$

For a small change in a reversible system at constant temperature,

$$\Delta A = \Delta E - T\Delta S$$

But, the entropy change (ΔS) is given as

$$\Delta S = \frac{q_{rev}}{T}$$

(or) $\qquad \qquad T\Delta S = q_{rev}$

Substituting equation (3) in (2), we get

$$\Delta A = \Delta E - q_{rev}$$

But, according to first law of thermodynamics

$$\Delta E = q - w$$

(or) $\qquad \qquad \Delta E - q = w$

Comparing equation (4) and (5)

$$\Delta A = -w$$

(or) $\qquad \qquad \Delta A = -w_{max}$

(or) $\qquad -\Delta A = w_{max}$

Where,

$\qquad w_{max}$ = maximum work.

Thus, the decrease of work function ($-\Delta A$) of a process at constant temperature gives a maximum work obtained from the system.

Gibbs free energy (G) (or) Thermodynamic Potential

We know that a part of the total energy of a system is converted into work and the is unavailable. The part of the energy which is converted into useful work is called available energy. The isothermally available energy present in a system is called free energy (G). It is mathematically defined as

Available energy (G) = Total energy (H) – Unavailable energy (TS)

$\qquad G = H - TS$

Significance of Gibbs Free Energy (G)

Free energy (or) Gibbs free energy (G) is the total available energy present in a reversible system at constant temperature and pressure as useful work. It is given by

$$G = H - TS \qquad\qquad \dots\dots\dots (1)$$

For a small change in a reversible system at constant temperature

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

But we know that the enthalpy change ΔH is given as

$$\Delta H = \Delta E + P\Delta V \qquad\qquad \dots\dots\dots (3)$$

Substituting equation (3) in (2) we get

$$\Delta G = \Delta E + P\Delta V - T\Delta S \qquad\qquad \dots\dots\dots (4)$$

But, $\qquad \Delta A = \Delta E - T\Delta S$ (or) $\Delta E = \Delta A + T\Delta S$

Hence equation (4) may be written as

$$\Delta G = \Delta A + P\Delta V$$

Since $\Delta A = - w_{max}$

$$\therefore \Delta G = - w_{max} + P\Delta V$$

$$-\Delta G = w_{max} - P\Delta V$$

Where,

$p\Delta v$ = work done by expansion (mechanical work)

w_{max} = maximum work that is obtained from the system

(or) w_{max} -PΔV = network or useful work

Hence, $-\Delta G = w_{useful}$

Thus, the decrease of free energy ($-\Delta G$) of a process at constant temperature and pressure is equal to the useful work obtainable from the system.

Standard Free Energy Change (G°)

It is defined as, "The free energy change for a process at 25°C in which the reactants are converted into products in their standard states." Thus

$$\Delta G^\circ = \sum \Delta G^\circ_{(products)} - \sum \Delta G^\circ_{(reacants)}$$

The value of ΔG° can be calculated for a reaction from the standard free energies of formation ($\Delta G^\circ f$)

$$\Delta G^\circ f = \sum \Delta G^\circ_{f(products)} - \sum \Delta G^\circ_{f(reacants)}$$

=[Sum of standard free energies of formation of products] –[Sum of standard free energies of formation of reactants]

GIBBS'S HELMHOLTZ EQUUATION (OR) RELATION BETWEEN ΔG and ΔH

Consider the following relations,

$$G = H - TS \text{ (Gibbs free energy)}$$

$$H = E + PV \text{ (enthalpy)}$$

$$\therefore \quad G = E + PV - TS$$

For INFINISTESIMAL CHANGE,

$$dG = dE + P\,dV + V\,dP - T\,dS - S\,dT \qquad \ldots\ldots\ldots\ldots (1)$$

But according to first and second law of thermodynamics,

$$dE = dq - Pdv \text{ (first law)}$$

$$dq = T\,dS(\text{ second law})$$

$$\therefore \quad dE = T\,ds - P\,dV \qquad \ldots\ldots\ldots\ldots (2)$$

Substituting equation (2) in(1) we get,

$$dG = Tds - P\,dV + PdV + V\,dP - T\,dS - S\,dT$$

$$\therefore \qquad dG = VdP - S\,dT \qquad\qquad\qquad \dots\dots\dots (3)$$

At constant pressure dP =0, equation (3) becomes

$$dG = -SdT \qquad\qquad\qquad\qquad \dots\dots\dots (4)$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad\qquad\qquad\qquad \dots\dots\dots (5)$$

Substituting equation (5) in G = H-TS, We get

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_p$$

(or)

$$G - T\left(\frac{\partial G}{\partial T}\right)_p = H \qquad\qquad \dots\dots\dots (6)$$

This is one form of the Gibb's – Helmholtz equation,

For any two states of the system the equation (4) may be written as

$$dG_1 = -S_1 dT \text{ (initial state)}$$

$$dG_2 = -S_2 dT \text{ (final state)}$$

To get the change

$$dG_2 - dG_1 = -S_2 dT - (-S_1 dT)$$

$$d(G_2 - G_1) = -(S_2 - S_1)dT$$
$$d(\Delta G) = -\Delta S\,dT \qquad\qquad \dots\dots\dots (7)$$

At constant pressure the equation (7) becomes

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = -\Delta S \qquad\qquad \dots\dots\dots (8)$$

But according to definition of free energy

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

(or)

$$- \Delta S = \frac{\Delta G - \Delta H}{T} \qquad \text{.......... (9)}$$

Substituting equation (9) in (8) we get

$$\frac{\Delta G - \Delta H}{T} = \left[\frac{\partial(\Delta G)}{\partial T} \right]_p$$

(or)

$$\Delta G - \Delta H = T \left[\frac{\partial(\Delta G)}{\partial T} \right]_p$$

$$\therefore \qquad \Delta G = \Delta H + T \left[\frac{\partial(\Delta G)}{\partial T} \right]_p \qquad \text{.......... (10)}$$

Similarly

$$\Delta A = \Delta E + T \left[\frac{\partial(\Delta G)}{\partial T} \right]_p$$

This is another form of Gibbs – Helmholtz equation.

Significance of Gibbs – Helmholtz equation

1. Gibb's – Helmholtz equation relates the free energy change (ΔG) to the enthalpy change (ΔH) and the rate of change of free energy with temperature at constant pressure.

2. It helps in understanding the nature of the chemical reaction. Ie., ΔG is negative, the reaction occurs spontaneously, if ΔG of reactants and products are equal, the reaction is in equilibrium.

$$\text{i.e., } \Delta G = 0$$

Application of Gibb's – Helmholtz Equation

1. Calculation of Enthalpy Change (ΔH) for the cell Reaction (Galvanic Cell)

If a cell yields nF Coulombs of electricity in a reversible manner, it must be equal to the decrease in the free energy, then

$$- \Delta G = nFE^{\circ} \qquad \text{.......... (1)}$$

Where,

       n = No. of electrons involved in the process

       F = Faraday = 96,500 Coulombs,

       E° = Energy in Volts

Hence, Gibb's – Helmholtz equation is written as

$$-nFE^{\circ} = \Delta H + T\left[\frac{\partial(-nFE^{\circ})}{\partial T}\right]_{p}$$

(or)

$$-nFE^{\circ} = \Delta H - nFT\left[\frac{\partial E^{\circ}}{\partial T}\right]_{p}$$

(or)

$$\Delta H = -nFE^{\circ} + nFT\left(\frac{\partial E^{\circ}}{\partial T}\right)_{p} \qquad \ldots\ldots\ldots (2)$$

$$\Delta H = -nF\left[E^{\circ} - T\left(\frac{\partial E^{\circ}}{\partial T}\right)_{p}\right] \qquad \ldots\ldots\ldots (3)$$

2. Calculation of Emf of the cell

The equation (2) is divided by nF and it becomes

$$\frac{\Delta H}{nF} = -E^{\circ} + T\left(\frac{\partial E^{\circ}}{\partial T}\right)_{p}$$

$$E^{\circ} = \left[\frac{-\Delta H}{nF}\right] + T\left(\frac{\partial E^{\circ}}{\partial T}\right)_{p} \qquad \ldots\ldots\ldots (4)$$

3. Calculation of Entropy Change (ΔS)

ΔH and ΔS are related by the equation

$$\Delta G = \Delta H - T\Delta S \qquad \ldots\ldots\ldots (5)$$

We know that ΔG = - nFE°

ΔH can be calculated from the equation (3). Hence ΔS can be calculated easily from the equation (5).

4. Gibbs- Helmholtz equation is applicable for a process occurring at constant pressure. It is used to calculate ΔH from the values of free energy change at two different temperature.

5. For a reaction at constant volume the equation can be modified as

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

THERMODYNAMIC RELATIONS (OR) MAXWELL RELATIONS

The various expressions connecting internal energy (E), enthalpy (H), Helmholtz free energy (A), and Gibbs free energy (G), with relevant parameters such as pressure, temperature, volume and entropy may be given as

   i. $dE = TdS - PdV$

   ii. $dH = T\,dS + VdP$

  iii. $dA = -\,SdT - PdV$

  iv. $dG = -\,SdT + VdP$

From these expressions the Maxwell relations are obtained as follows

1. The combined form of first and second law is

$$dE = TdS - PdV \qquad\qquad \text{............ (1)}$$

If V is constant, so that $dV = 0$, then equation (1) yields

$$\left(\frac{\partial E}{\partial S}\right)_V = T \qquad\qquad \text{............ (2)}$$

If S is constant, so that $dS = 0$, then equation (1) yields

$$\left(\frac{\partial E}{\partial V}\right)_S = -P \qquad\qquad \text{............ (3)}$$

Differentiating equation (2) w.r.to V at constant S yields

$$\frac{\partial^2 E}{\partial S \partial V} = \left(\frac{\partial T}{\partial V}\right)_S$$

.... (4)

Differentiating equation (3) w.r.to S at constant V yields

$$\frac{\partial^2 E}{\partial V \partial S} = -\left(\frac{\partial P}{\partial S}\right)_V$$

.... (5)

It follows from equation (4) and (5) that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

.... (6)

Equation (6) is a Maxwell relation.

2. Enthalpy is defined by

$$H = E + PV$$

$$dH = dE + PdV + VdP$$

But, $\quad dE + P\,dE = TdS$

$$dH = T\,dS + V\,dP$$

.... (7)

If *P* is constant, so that *dP = 0*, then equation (7) yields

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

.... (8)

If *S* is constant, so that *dS = 0*, then equation (7) yields

$$\left(\frac{\partial H}{\partial P}\right)_S = V$$

.... (9)

Differentiating equation (8) w.r.to *P* at constant *S* yields

$$\frac{\partial^2 H}{\partial S \partial P} = \left(\frac{\partial T}{\partial P}\right)_S$$

.... (10)

Differentiating equation (9) w.r.to *S* at constant *P* yields

$$\frac{\partial^2 H}{\partial P \partial S} = \left(\frac{\partial V}{\partial S}\right)_P$$

.... (11)

It follows from equation (10) and (11) that

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

.... (12)

Equation (12) is also a Maxwell relation.

3. Helmholtz free energy (work function A) is given by

$$A = E - TS$$

$$dA = dE - T\,dS - S\,dT$$

But the combined first and second law of thermodynamics is

$$T\,dS = dE + P\,dV$$

$$dE = TdS - P\,dV$$

$$\therefore dA = -S\,dT - P\,dV$$

.... (13)

If V is constant, so that $dV = 0$, then equation (13) yields

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

.... (14)

If T is constant, so that $dT = 0$, then equation (13) yields

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

.... (15)

Differentiating equation (14) w.r.to V, at constant T yields

$$\frac{\partial^2 A}{\partial T \partial V} = -\left(\frac{\partial S}{\partial V}\right)_T$$

.... (16)

Differentiating equation (15) w.r.to T, at constant V yields

$$\frac{\partial^2 A}{\partial V \partial T} = -\left(\frac{\partial P}{\partial T}\right)_V$$

.... (17)

It follows from equation (10) and (11) that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

.... (18)

Equation (18) is also a Maxwell relation.

4. Gibbs free energy G is defined as

$$G = H - TS$$

$$dG = dH - T\,ds - SdT$$

But
$$H = E = +PV$$

$$dH = dE + P\,dV + V\,dP$$

$$\left[\because Tds = dE + PdV\right]$$

$$\dots\dots\dots (19)$$

Thus, dG=-SdT+VdP

If P is constant, so that $dP = 0$, then equation (19) yields

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\dots\dots\dots (20)$$

If T is constant, so that $dT = 0$, then equation (19) yields

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\dots\dots\dots (21)$$

Differentiating equation (20) w.r.to P, at constant T yields

$$\frac{\partial^2 G}{\partial T\partial P} = -\left(\frac{\partial S}{\partial P}\right)_T$$

$$\dots\dots\dots (22)$$

Differentiating equation (21) w.r.to T, at constant V yields

$$\frac{\partial^2 G}{\partial P\partial T} = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\dots\dots\dots (23)$$

It follows from equation (22) and (23) that

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

(or)

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\dots\dots\dots (24)$$

Equation (24) is also a Maxwell relation.

Thus equations (6), (12), (18), (24) are known as Maxwell relations.

Significance of Maxwell Relations

Maxwell relation is very important and helpful in many ways.

i. Using these relations tedious experimental work can be reduced into simple paper and pencil exercise.

ii. Maxwell relations are also very useful to deduce many other thermodynamic relations viz., Clapeyran equation, thermodynamic equation of state, etc.

CLAUSIUS – CLAPEYRON EQUATION

Consider a system consisting of only 1 mole of a substance existing in two phases A and B. The free energies of the substance in two phases A and B be G_A and G_B. Let the temperature and pressure of the system be T and P respectively. The system is in equilibrium, So there is no change in free energy i.e.,

$$G_A = G_B \qquad \text{.......... (1)}$$

If the temperature of the system be raised to $T + dT$, the pressure becomes $P + dP$ and the free energies become $G_A + dG_A$ and $G_B + dG_B$ respectively. Then the equation (1) becomes

$$G_A + dG_A = G_B + dG_B \qquad \text{...........(2)}$$

We Know that

$$G = H - TS \text{ (Gibbs free enery)}$$

$$H = E + PV \text{ (Enthalpy)}$$

$$G = E + PV - TS \qquad \text{........... (3)}$$

$$dG = dE + PdV + VdP - TdS - SdT \qquad \text{........... (4)}$$

But, $dE = dq - dw$ [I law of thermodynamics]

$$dq = dE + dw$$

$$dq = dE + PdV \qquad \text{............ (5)}$$
$$[dW = PdV]$$

We know that for reversible equation,

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

$$dq = Tds \qquad \text{............ (6)}$$

Substituting equation 6 in equation 5

$$TdS = dE + PdV$$

$$\therefore dE = TdS - PdV \qquad \ldots\ldots\ldots\text{.}(7)$$

Substituting equation (7) in (4)

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

$$dG = VdP - SdT \qquad \ldots\ldots\ldots\text{.}(8)$$

Here, the work done is due to volume change only, so equation 8 may be applied to phase A as well as B

$$dG_A = V_A dP - S_A dT \qquad \ldots\ldots\ldots(9)$$

$$dG_B = V_B dP - S_B dT \qquad \ldots\ldots\ldots(10)$$

Where,

V_A and V_B are the molar volumes of phase A & B respectively.

S_A and S_B are their molar entropies.

Since $G_A = G_B$, hence from equation (2)

$$dG_A = dG_B \qquad \ldots\ldots\ldots\text{.}(11)$$

Substituting equation (9) and (10) in equation (11)

$$V_{A.} dP - S_A dT = V_B dP - S_B dT \qquad \ldots\ldots\ldots\text{..}(12)$$

$$S_B dT - S_A dT = V_B dP - V_{A.} dP \qquad \ldots\ldots\ldots\text{..}(13)$$

$$dT(S_B - S_A) = dP(V_B - V_A) \qquad \ldots\ldots\ldots\text{..}(14)$$

$$\frac{(S_B - S_A)}{(V_B - V_A)} = \frac{dP}{dT} \qquad \ldots\ldots\ldots\text{..}(15)$$

S_B-S_A represents the change in entropy when 1 mole of the substance passes from the initial phase A to the final phase B. It may be denoted as ΔS

Hence equation (15) becomes

$$\frac{\Delta S}{(V_B - V_A)} = \frac{dP}{dT} \qquad \ldots\ldots\ldots\text{.. }(16)$$

We know that entropy change (ΔS) at constant T is

$$\Delta S = \frac{q}{T} \qquad \ldots\ldots\ldots\text{.. }(17)$$

Substituting equation (17) in (16)

$$\frac{dP}{dT} = \frac{q}{T(V_B - V_A)}$$ .... (18)

This is the clausius-clapeyron equation.

Applications of clausius – clapeyron equation

1. **Calculation of latent heat of vapourization**

   If the vapour pressure of a liquid at two temperatures T1 and T2 be P1 and P2 respectively. The molar heat of vapourisation ΔHv can be calculated.

2. **Calculation of boiling point (or) freezing point**

   If the freezing point or the boiling point of a liquid at one pressure is known, it is possible to calculate it at another pressure by using Clasius – Clapeyron equation

3. **Calculation of Vapour pressure at another temperature**

   If latent heat of vpourization is known, it is possible to calculate the vapour pressure of a liquid at given temperature is known.

4. **Calculation of a molar elevation constant**

   Molar elevation constant of a solvent can be calculated.

VAN'T HOFF ISOTHERM

Van't Hoff isotherm gives a quantitative relationship between the free energy change and equilibrium constant. It can be derived as follows.

Consider a general reaction

$$aA + bB \leftrightarrow cC + dD$$

We know that

$$G = H - TS \qquad\qquad \therefore H = E + PV$$

(or) $$G = E + PV - TS$$

(or) $$dG = dE + PdV + VdP - TdS - SdT$$ .... (1)

But according to first and second law of thermodynamics

$$dE = dq - PdV \qquad \textit{(I law)}$$

$$dq = TdS \qquad \textit{(II law)}$$

$$\therefore dE = TdS - PdV \qquad \dots\dots\dots (2)$$

Substituting equation (2) in (1) it becomes

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

$$\therefore dG = VdP - SdT \qquad \dots\dots\dots. (3)$$

At constant temperature, $dT = 0$, equation (3) becomes

$$(dG)_T = V.dP$$

$\because$ Free energy change for 1 mole of any gas at a constant temperature is given by

$$dG = V.dP$$

$$dG = RT.\frac{dP}{P} \qquad \dots\dots\dots. (4)$$

$$[\because PV = RT; \quad V = \frac{RT}{P}]$$

On integrating the equation (4) becomes

$$\int dG = RT \int \frac{dP}{P}$$

$$G = G^\circ + RT \ln P \qquad \dots\dots\dots.. (5)$$

Where, G° = integration constant (standard free energy)

Let the free energies of A,B,C and D at their respective pressure P_A, P_B, P_C, and P_D are G_A, G_B, G_C and G_D respectively. Then the free energy change for the above reaction is given by

$$\Delta G = \sum G_{product} - \sum G_{reactant}$$

$$= [cG_C + dG_D] - [aG_A - bG_B] \qquad \dots\dots\dots. (6)$$

Substituting the value of G_A, G_B, G_C and G_D from equation (5) in (6), we get

$$\Delta G = [cG^o{}_C + cRT \ln P_C + dG^o{}_D + dRT \ln P_D] - [aG^o{}_A + aRT \ln P_A + bG^o{}_B + bRT \ln P_B]$$

$$= [cG^o{}_C + dG^o{}_D - aG^o{}_A - bG^o{}_B] + RT \ln \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

(or)

$$\Delta G = \Delta G^o + RT \ln \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

.... (7)

We know that, at equilibrium, $\Delta G=0$,

$$\therefore = \Delta G^\circ + RT \ln \left[\frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \right]_{eq}$$

$$\Delta G^o + RT \ln K_{eq} = 0$$

.... (8)

$$\left[\because \left[\frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \right]_{eq} = K_{eq} \right]$$

This equation (8) may be written as

$$\Delta G^o = -RT \ln K_{eq}$$

.... (9)

From equation (9) and (8), the equation (7) becomes

$$\Delta G^o = -RT \ln K_{eq} + RT \ln \left[\frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \right]_{eq}$$

(or)

$$-\Delta G^o = RT \ln K_{eq} - RT \ln \left[\frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \right]_{eq}$$

.... (10)

This expression is called Van't Hoff isotherm.

VAN'T HOFF EQUATION (OR) VAN'T HOFF ISOCHORE (OR) VARIATION OF EQUILIBRIUM CONSTANT WITH TEMPRATURE

The effect of temperature on equilibrium constant is quantitatively given by Van't Hoff equation. It can be derived by combining the Van't Hoff isotherm with Gibbs – Helmholtz equation as given below.

According to the Van't Hoff isotherm, the standard free energy change (ΔG°) is related to the equilibrium constant (K) by the following equation.

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

.... (1)

Differentiate equation (1) w.r.to temperature at constant pressure, we get

$$\left(\frac{\partial\left(\Delta G^{\circ}\right)}{\partial T}\right)_{p} = -R\ln Kp - RT\frac{d\left(\ln Kp\right)}{dT} \qquad \cdots\cdots\cdots (2)$$

When the equation (2)is multiplied by T, we get

$$T\left\{\frac{\partial\left(\Delta G^{\circ}\right)}{\partial T}\right\}_{p} = RT\ln Kp - RT^{2}\frac{d\left(\ln Kp\right)}{dT} \qquad \cdots\cdots\cdots (3)$$

ΔG° is substituted for $-RT\ ln\ Kp,$ we have

$$T\left\{\frac{\partial\left(\Delta G^{\circ}\right)}{\partial T}\right\}_{p} = \Delta G^{\circ} - RT^{2}\frac{d\left(\ln Kp\right)}{dT} \qquad \cdots\cdots\cdots (4)$$

Gibb's-Helmholtz's equation for substance in their standard states may be written as

$$\Delta G^{\circ} = \Delta H^{\circ} + T\left\{\frac{\partial\left(\Delta G^{\circ}\right)}{\partial T}\right\}_{p} \qquad \cdots\cdots\cdots (5)$$

Equation (5) is introduced in equation (4)

$$T\left\{\frac{\partial\left(\Delta G^{\circ}\right)}{\partial T}\right\}_{p} = \Delta H^{\circ} + T\left\{\frac{\partial\left(\Delta G^{\circ}\right)}{\partial T}\right\}_{p} - RT^{2}\frac{d\left(\ln Kp\right)}{dT} \qquad \cdots\cdots\cdots (6)$$

$$T\left\{\frac{\partial\left(\Delta G^{\circ}\right)}{\partial T}\right\}_{p} - T\left\{\frac{\partial\left(\Delta G^{\circ}\right)}{\partial T}\right\}_{p} - \Delta H^{\circ} = -RT^{2}\frac{d\left(\ln Kp\right)}{dT}$$

$$-\Delta H^{\circ} = -RT^{2}\frac{d\left(\ln Kp\right)}{dT}$$

(or)

$$\Delta H^{\circ} = RT^{2}\frac{d\left(\ln Kp\right)}{dT}$$

(or)

$$\frac{d\left(\ln Kp\right)}{dT} = \frac{\Delta H^{\circ}}{RT^{2}} \qquad \cdots\cdots\cdots (7)$$

The equation (7) is known as Van't Hoff's equation.

Since enthalpy change (ΔH) does not very appreciably with change in partial pressure of the reactants or products, the Van't Hoff's equation may be written as

$$\frac{d(\ln Kp)}{dT} = \frac{\Delta H}{RT^2} \qquad \ldots\ldots (8)$$

The equation (8) is integrated between T_1 and T_2 at which the equilibrium constants are K_P^1 and K_P^2 K2p respectively and ΔH is constant

$$\int_{k_p^1}^{k_p^2} d(\ln Kp) = \frac{\Delta H}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \qquad \ldots\ldots (9)$$

(or)

$$\ln K_p^2 - \ln K_p^1 = \frac{-\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$= \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \ldots\ldots (10)$$

$$= \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

(or)

$$\ln K_p^2 - \ln K_p^1 = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_2 T_1}\right] \qquad \ldots\ldots (11)$$

The Equilibrium constant K_P^2 at temperature T_2 can be calculated, if the equilibrium constant K_P^1 at temperature T_1 is known, provided the heat of the reaction (ΔH) is known.