

UNIT - II

General conditions of equilibrium and spontaneity:

Reversible change should take place under equilibrium conditions. Since present equilibrium in a change cannot be realised, reversible changes are ideal.

The condition for a reversible change is taken as the condition for equilibrium.

$$ds = \frac{q_{rev}}{T}$$

$Tds = q_{rev}$ This is the conditions for eqn. in a state.

In a irreversible change, there is no eqn. It takes place spontaneously.

Therefore, the condition for an irreversible change is taken as the condition for spontaneity.

$$ds > \frac{q_{irr}}{T}; \quad Tds > q_{irr}$$

The above two conditions for equilibrium and spontaneity are stated as

$$Tds \geq q$$

According to first law $q = dE + W$
 $Tds \geq dE + W - dE - W + Tds \geq 0$; $-dE - PdV + Tds \geq dE$ is the work done other than work of expansion. These are the conditions for equilibrium and spontaneity in a system in terms of entropy.

Definition of A and G: (2)

1. The Helmholtz free energy + [A] maximum work function definition:

$$A = E - TS$$

Helmholtz free energy (also called work function). 'A' is defined as a thermodynamic property, a decrease in which (i.e.) ΔA give the maximum work that can be obtained from a system during a given change (i.e.) $-\Delta A = W_{rev}$

2. The Gibbs free energy + [G] Net work function definition:

$$G = H - TS$$

Gibbs free energy (also called energy function) 'G' is defined as a thermodynamic property, a decrease in which (i.e.) $-\Delta G$ gives the network that can be obtained from a system during a change.

i.e. $\Delta G = H - P\Delta V$

3. Difference between Helmholtz free energy & Gibbs free energy

	Helmholtz free Energy	Gibbs free energy
1. Definition	$A = E - TS$	$G = H - TS$
2. Indicates	maximum work content of the system	useful work that could be obtained (Net work)
3. Value	$-\Delta A = W_{rev}$	$-\Delta G = W_{rev} - P\Delta V$

Physical significance of dA :- (3)

Consider the general conditions for equilibrium and spontaneity

$$-dE - PdV - du + Tds \geq 0$$

At constant volume $PdV = 0$

$$\therefore -(dt - Tds) - du \geq 0$$

At constant temperature $dA = dE - Tds$

$$\text{so } -dA - du \geq 0$$

No work other than work of expansion takes place in the chemical reaction and ordinary physical changes. For these

changes $du = 0$ and $\therefore -dA \geq 0 ; dA \leq 0$

condition for equilibrium : $dA = 0$

condition for spontaneity : $dA < 0$

Physical significance of dG :

Consider the general condition for equilibrium and spontaneity

$$-dE - PdV - du + Tds \geq 0$$

$$-(dE + PdV) - du + Tds \geq 0$$

$$-dH - du + Tds \geq 0$$

At constant temperature $dH - Tds = dG$:

$-dG - du \geq 0$. No work other than work of expansion takes place in chemical reaction and ordinary physical changes.

for these change $-dG \geq 0 ; dG \leq 0$

condition for equilibrium at constant

T and P ; $dG = 0$

condition for spontaneity at constant

T and p ; $dG < 0$

Temperature and pressure depends of G_1 :- (4)

The following fundamental equation relates Gibbs free energy change with change in T and P

$$dG_1 = -SdT + vdp$$

At constant pressure $dp = 0$

$$\left[\frac{dG_1}{dT} \right]_P = -S$$

At constant temperature $dT = 0$

$$\left[\frac{dG_1}{dp} \right]_T = v$$

At constant pressure ΔG_1 is inversely related to temperature. But at constant temperature ΔG_1 is directly related to pressure.

$$\text{Further } dG_1 = -SdT + vdp$$

At constant temperature $dT = 0$; $\therefore dG_1 = vdp$

But for an ideal gas $Pv = nRT$ and $v = \frac{nRT}{P}$

$$\text{So } dG_1 = nRT \frac{dp}{P}$$

$$\text{Integrating } \int_{G_1}^{G_2} dG_1 = nRT \int_{P_1}^{P_2} \frac{dp}{P}$$

$$G_2 - G_1 = nRT \ln \frac{P_2}{P_1}$$

$$\text{or } \boxed{\Delta G_1 = 2.303 nRT \log \frac{P_2}{P_1}}$$

$$\Delta G_1 = 2.303 nRT \log \frac{V_1}{V_2}$$

Gibbs-Helmholtz equation:- (5)

This can be derived from second law of thermodynamics by making use of the free energy equations.

Let G_1 represent free energy of a system in its initial state at temperature T . Suppose, temperature rises to $T+dT$ where dT is infinitesimally small. Let the free energy at the new temperature be $G_1 + dG_1$.

Now suppose that when the system in its final state, its free energy is given by G_2 at the temperature T , and by $G_2 + dG_2$ at the temperature $T+dT$. If the pressure remains constant all along the equation $dG = -SdT$ is applicable

$$dG_1 = -S_1 dT \quad \text{--- (1)}$$

$$dG_2 = -S_2 dT \quad \text{--- (2)}$$

Where S_1 & S_2 are the entropies of the system in the initial and final state of the system, respectively.

~~Subtract~~ Sub. eqn. (1) from eqn (2), we have

$$d(G_2 - G_1) = -(S_2 - S_1)dT$$

$$d\Delta G = -\Delta S dT$$

As the pressure is constant, therefore

$$\left(\frac{d(\Delta G)}{dT} \right)_P = -\Delta S \quad \text{--- (3)}$$

Also, since from the eqn. $\Delta G = \Delta H - T\Delta S$

$$\therefore -\Delta S = \frac{\Delta G - \Delta H}{T} \quad (6)$$

~~hence~~ hence eqn (3) becomes,

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

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

This equation is known as Gibbs-Helmholtz equation.

Concept of Chemical Potential:-

Gibbs free energy 'G' is an extensive property. must be a function not only of temperature and pressure but of the no. of moles of the various components present in the system as well.

Let T and p be the temperature and pressure, respectively of a system and let $n_1, n_2, n_3, \dots, n_j$ be the respective no. of moles of the constituents 1, 2, 3, \dots, j .

Gibbs free energy 'G' as a function of T, P, n_1, n_2, \dots, n_j is

$$G = f(T, P, n_1, n_2, n_3, \dots, n_j)$$

where $n_1 + n_2 + n_3 + \dots + n_j = \text{Total no. of moles} = N (\text{Say})$

Then for a small change on temperature, pressure and the no. of moles of the components, the change in free energy dG , will be given by the expression:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, N} dT + \left(\frac{\partial G}{\partial P}\right)_{T, N} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2, \dots, n_j} dn_1 +$$

$$\left(\frac{\partial G}{\partial n_2}\right)_{T, P, n_1, n_3, \dots, n_j} dn_2 + \left(\frac{\partial G}{\partial n_j}\right)_{T, P, n_1, n_2, \dots, n_j} dn_j \quad \textcircled{7}$$

$$\left(\frac{\partial G}{\partial n_j}\right)_{T, P, n_1, n_2, \dots}$$

The quantity $\left(\frac{\partial G}{\partial n_j}\right)_{T, P, n_1, \dots, n_j}$ is called Partial molar free energy (\overline{G}_i) (or) chemical potential (μ_i) of the concerned compound i . Thus.

$$\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_1, \dots, n_j} = \overline{G}_i = \mu_i \quad \text{Chemical}$$

potential. This term chemical potential was first introduced by Gibbs.

Chemical potential in mixture of ideal Gases :-

In an ideal gas $pV = nRT$ — ①

Consider now a gaseous system consisting of a no. of ideal gases. Let n_1, n_2, \dots be the no. of moles of each constituent present in the mixture.

Then in the ideal gas equation ①, n , the total no. of moles, may be replaced by $(n_1 + n_2 + \dots)$. Hence,

$$V = \frac{nRT}{P} = (n_1 + n_2 + \dots) \frac{RT}{P} \quad \text{--- ②}$$

Differentiating equation ② with respect to n_i , at constant temperature and pressure, we have

$$\left(\frac{dv}{dn_i}\right)_{T,P,n_1,n_2} = \bar{v}_i = \frac{RT}{P} \quad \text{--- (3)}$$

Substituting eqn. (3) in eqn of the variation of chemical potential (μ_i) of any constituent 'i' with pressure (i.e.)

$$\left(\frac{d\mu_i}{dP}\right)_{T,N} = \bar{v}_i \quad \text{--- (4)}$$

$$\left(\frac{d\mu_i}{dP}\right)_{T,N} = \frac{RT}{P} \quad \text{--- (5)}$$

For a constant composition of the gas and at a constant temperature, eqn (5) may also be expressed in the form

$$d\mu_i = \frac{RT}{P} dP = RT d \ln P \quad \text{--- (6)}$$

Let P_i be the partial pressure of the constituent 'i' present in the mixture. Since each constituent behaves as an ideal gas, therefore,

$$P_i V = n_i RT \quad \text{--- (7)}$$

It follows from eqn. (6) and (7), that

$$P_i = \frac{n_i}{n} P \quad \text{--- (8)}$$

Since n_i and n are constant, therefore on taking logarithms and then differentiating we get

$$d \ln P_i = d \ln P \quad \text{--- (9)}$$

On integrating eqn. (9), we get

$$\mu_i = \mu_i(p) + RT \ln p_i \quad \text{--- (9) --- (11)}$$

where $\mu_i(p)$ is the integration constant, the value of which depends upon the nature of the gas and also on the temperature

It is evident from equation (11), the chemical potential of any constituent of a mixture of ideal gases is determined by its partial pressure in the mixture

$$\mu_i = \mu_i(c) + RT \ln c_i$$

where $\mu_i(c)$ is a constant depending upon the nature of the gas and the temperature.

$\mu_i(c)$ represents chemical potential of the constituent 'i' when the concentration of the constituent in the mixture is unity at a constant temperature.

$$(x_i = \frac{n_i}{n} \text{ (mole fraction)})$$

$$\mu_i = \mu_i(x) + RT \ln x_i$$

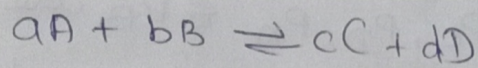
where the quantity $\mu_i(x)$ is also a constant which depends both on the temperature and the total pressure.

$\mu_i(x)$ represents the chemical potential of the constituent 'i' when its mole fraction at a constant temperature and pressure

is unity.

Van't Hoff's Reaction Isotherm: - (10)

Consider a mixture of four ideal gases A, B, C and D. Suppose the following reaction takes place



The chemical potential of various gases are

$$\mu_A = \mu_A^\circ + RT \ln P_A ; \mu_B = \mu_B^\circ + RT \ln P_B$$

$$\mu_C = \mu_C^\circ + RT \ln P_C ; \mu_D = \mu_D^\circ + RT \ln P_D$$

The free energy change of reaction

$$\Delta G = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B)$$

$$\therefore \Delta G = (c\mu_C^\circ + cRT \ln P_C + d\mu_D^\circ + dRT \ln P_D) -$$

$$a\mu_A^\circ + aRT \ln P_A + b\mu_B^\circ + bRT \ln P_B$$

$$\Delta G = (c\mu_C^\circ + d\mu_D^\circ - a\mu_A^\circ + b\mu_B^\circ) + RT \ln \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{P_C^c P_D^d}{P_A^a P_B^b} \quad \text{--- (1)}$$

ΔG° is the free energy change of the reaction at one atm. It is called standard free energy change of reaction.

$P_A \ \& \ P_B \Rightarrow$ Partial pressure of A & B before starting the reaction.

$P_C \ \& \ P_D \Rightarrow$ Partial pressure of C & D after completing of reaction

If the reaction is at equilibrium $\Delta G = 0$

$$\therefore 0 = \Delta G_i^\circ + RT \ln \frac{P_C^c P_D^d}{P_A^a P_B^b} \quad (\text{or}) \quad (1)$$

$$\Delta G_i^\circ = -RT \ln \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

In this equation P_C, P_D, P_A & P_B are partial pressures measured when there is equilibrium. $\frac{P_C^c \cdot P_D^d}{P_A^a P_B^b}$ is known as equilibrium constant. It is denoted as K_p

$$\therefore \Delta G_i^\circ = -RT \ln K_p \quad \text{--- (2)}$$

Since ΔG_i° is standard free energy change, K_p depends on temperature only. It should not change with pressure.

Applying (2) in (1), we have,

$$\Delta G_i = -RT \ln K_p + RT \ln \frac{P_C^c P_D^d}{P_A^a P_B^b} \quad \text{--- (3)}$$

(or)

$$\Delta G_i = -RT \ln K_p + RT \ln Q_p \quad \text{--- (4)}$$

Equation (3) & (4) are different forms of Van't Hoff's reaction isotherm.

Van't Hoff's equation (or) Van't Hoff's isochore :-

The temperature dependence of equilibrium constant is explained by Van't Hoff's isochore

Derivation :

consider van't Hoff isotherm for a chemical equilibrium

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

Rearranging, $\ln K_p = -\frac{1}{R} \cdot \frac{\Delta G^\circ}{T}$

Differentiating with temperature

$$\frac{d \ln K_p}{dT} = -\frac{1}{R} \frac{d \Delta G^\circ / T}{dT} \quad \text{--- (1)}$$

According to Gibbs-Helmholtz eqn.

$$\frac{d \Delta G^\circ / T}{dT} = -\frac{\Delta H^\circ}{T} \quad \text{Substituting in eqn. (1)}$$

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$$

This equation is known as van't Hoff's isochore. ΔH° is standard enthalpy change for the chemical reaction.

If ΔH° is constant, van't Hoff isochore can be integrated

$$d \ln K_p = \frac{\Delta H^\circ}{R} \cdot \frac{dT}{T^2}$$

Integrating between limits,

$$\int_{\ln K_{p1}}^{\ln K_{p2}} d \ln K_p = \frac{\Delta H^\circ}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\ln \frac{K_{p2}}{K_{p1}} = \frac{\Delta H^\circ}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{K_{p2}}{K_{p1}} = \frac{\Delta H^\circ}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

This is the integrated form of van't Hoff's equation or van't Hoff's isochore.

Third law of Thermodynamics:-

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Statement :-

The entropy of a pure, perfectly crystalline substance is zero at the absolute zero of temperature.

Explanation :-

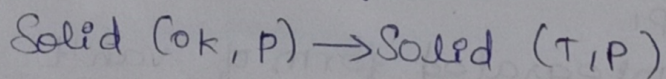
In a perfect crystal at absolute zero temperature, each atom must be at a crystal lattice point and it must have the lowest energy. This means that in such a state there will be perfect order. In other words, there will be no disorder or randomness. So its entropy will be zero.

Application :-

It is used to evaluate entropy from heat capacity data.

Application of Absolute Entropies from heat capacity data :-

From third law of thermodynamics one can evaluate the entropy of a substance at any temperature. The entropy so obtained is known as third law entropy. The method of evaluation of third law entropy is illustrated below. Consider the change.



The change in entropy for the above constant pressure change.

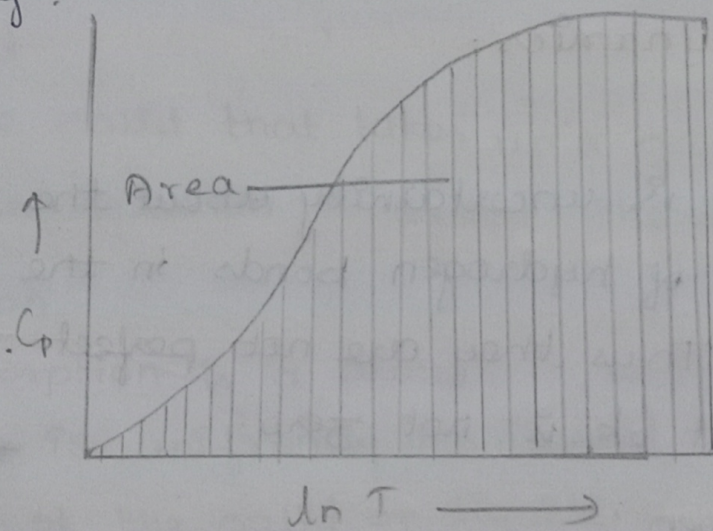
$$\Delta S = S_T - S_0$$

but $\Delta S = \int_0^T \frac{C_p}{T} dT$; $\therefore S_T = S_0 + \int_0^T \frac{C_p}{T} dT$

From third law S_0 , entropy ~~pressure~~ at 0K , is zero.

$$\therefore S_T = \int_0^T \frac{C_p}{T} dT = \int_0^T C_p d \ln T.$$

The value of $\int_0^T C_p d \ln T$ can be calculated graphically. A graph of C_p versus $\ln T$ is plotted and extrapolated to the absolute zero of temperature as shown in figure. The area under the graph gives the value of S_T , the absolute entropy at temperature T . This S_T is some times called third law entropy.



Exceptions to third law :-

The following few cases are found to be exception to third law:

1. CO, NO, N₂O :-

In each of these cases the entropy value obtained by statistical method

is found to be higher than the values based on the third law of thermodynamics (5)

Reason:-

These gases have two arrangements of molecules in their crystal lattices as follows :-

CO and OC ; NO and ~~NO~~ ON ; NNO and ONN,

This means that they do not have a definite structure. So they are not perfect crystals. So their entropy at 0K is not zero.

2. Water :-

Here also the entropy value obtained by statistical method is higher than the value based on the third law of thermodynamics.

Reason:-

There is uncertainty about the position of hydrogen bonds in the crystal. Thus they are not perfect. So its entropy at 0K is not zero.

3. Hydrogen :-

Here also the entropy values obtained by statistical method is higher than the value based on third law of thermodynamics.

Reason:

Solid hydrogen contains ortho and para forms. ⁽¹⁶⁾ So there is still some randomness of distribution. So its entropy is not zero.