

Chemical Equilibrium (7) (1)

Criteria of thermodynamic equilibrium

If the free energy change ΔG of a chemical reaction is negative, the reaction can take place spontaneously, ~~if~~ i.e. the reaction is feasible. If the free energy change is zero, the reaction is in a state of equilibrium and if the free energy change is positive, the reaction would not proceed.

We have from thermodynamics

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

There are two factors which contribute to the value of ΔG . The energy factor ΔH and the entropy factor, $T\Delta S$. Neither ΔH nor $T\Delta S$ alone can determine the spontaneity of a reaction. Depending upon the relative magnitude of ΔH and ΔS and their sign following situation ~~may arise~~ may arise.

(i) If $\Delta H = -ve$ $\Delta S = +ve$.
i.e. both the ^{factors} ~~conditions~~ are favourable towards spontaneity.

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

$$\Delta G = -ve \text{ only (large } -ve \text{ value)}$$

The reaction is spontaneous (highly feasible) at all temperatures.

(ii) If $\Delta H = +ve$ $\Delta S = +ve$,
i.e. only ^{entropy} ~~energy~~ factor is favourable.

For negative value of ΔG , $T\Delta S$ must be greater than ΔH ($T\Delta S > \Delta H$). The process may be spontaneous at high temp^r, and non spontaneous ($\Delta G = +ve$) at low temperature.

(iii) If $\Delta H = -ve$, $\Delta S = -ve$.

i.e. only energy factor is favourable.

(2)

The reaction will be spontaneous (feasible) when $\Delta H > T\Delta S$

In this case temp^r plays a major role.

When temperature is low, $T\Delta S$, is less ΔG may have negative value.

(iv) If $\Delta H = +ve$, $\Delta S = -ve$,

That is, both the factors are not favourable, ΔG will be positive at all temperatures and the reaction will ~~be~~ not be feasible at all.

If neither factor predominates, i.e. both the opposing factors are exactly equal (ΔH is numerically equal to $T\Delta S$), then ΔG will be zero. Under these circumstances, the reaction will be in a state of equilibrium, i.e. no net reaction would occur in any direction.

Chemical Equilibrium

Fugacity, activity & activity co. efficient.
Fugacity :- The concept of fugacity was given by G.B Lewis as a substitute for the pressure in real gases.

We know that.

$$dG = v dP - S dT \rightarrow (1)$$

For isothermal process, when T is constant-

$$dG = \int_{P_1}^{P_2} v dP$$
$$G(P_2) = G(P_1) + \int_{P_1}^{P_2} v dP$$

$P_1 = \text{Initial pressure}$
 $P_2 = \text{Final pressure}$

For molar quantities

$$G_m(P_2) = G_m(P_1) + \int_{P_1}^{P_2} v_m dP$$
$$G_m(P_2) = G_m(P_1) + RT \ln \frac{P_2}{P_1} \rightarrow (1) \left[\begin{array}{l} PV = RT \\ V = \frac{RT}{P} \end{array} \right]$$

$$\left(\frac{\Delta G_m}{T} \right) = RT \ln \frac{P_2}{P_1}$$

If $P_1 = P^0$ (standard pressure 1 bar), the free energy G of a perfect gas at pressure P is related to standard free energy G^0 by

$$G_m(P) = G_m^0 + RT \ln \frac{P}{P_0} \rightarrow (2)$$

This equation is not valid for real gases, because real gases do not obey the relation $PV = nRT$

~~$G_m = G^0 + RT \ln f$~~ In order to make this equation (equⁿ) to real gases, Lewis introduced a new function 'f', called fugacity,

$$G_m(P) = G_m^0 + RT \ln f \quad [P_0 = 1 \text{ bar}]$$

For n moles

$$G_{\text{gas}} = G_m^0 + nRT \ln f \rightarrow (3)$$

G^0 is the free energy of n moles of real gas when fugacity is 1.

(2)

Fugacity has the dimension of pressure.

$$f \propto P$$
$$f = \phi P \quad \phi = \frac{f}{P}$$

ϕ = fugacity coefficient, it depends on temp^r, press^r
and For ideal gas $\phi = 1$. For real gases it is always less than 1. Fugacity is not a physical property of substance it is a calculated property which is intrinsically related to the chemical potential as.

$$\mu_i = \mu_i^0 + RT \ln f_i$$

It is the relation for the chemical potential of i th component of a real gas.

μ_i^0 is the standard chemical potential of i th component and f_i is the fugacity of that component.

Fugacity at low pressure:- At low pressure, and high temp^r, the real gas approaches to ideal gas. The ratio f/p , approaches unity ($\phi = 1$). The fugacity function therefore may be defined as

$$\lim_{P \rightarrow 0} f/p = 1$$

Thus, at low pressures, fugacity is equal to pressure. The two terms ~~diff~~ ^{differ} materially only at high pressures.

Fugacity of a liquid component in a liquid mixture:-

The equation $\mu_i = \mu_i^0 + RT \ln f_i \rightarrow (5)$

is valid not only for the fugacity of a gas in a gaseous mixture but also for the fugacity of a pure liquid in a liquid mixture.

(3)

We know that, in case of phase equilibria, the chemical potential of any given component, is the same in all phases. Thus, if there are three phases a, b and c, containing ~~three components~~, a component i , then at equilibrium

$$(\mu_i)_a = (\mu_i)_b = (\mu_i)_c.$$

Let, for example a liquid 'i' is in equilibrium with its vapour. The chemical potential of the liquid $(\mu_i)_l$ is equal to the chemical potential of its vapour $(\mu_i)_g$ i.e.

$$(\mu_i)_l = (\mu_i)_g \rightarrow (6)$$

Now according to eqnⁿ (5), the chemical potential for the vapour can be written as,

$$(\mu_i)_g = (\mu_i^\circ)_g + RT \ln f_i$$

where $(\mu_i^\circ)_g$ is the chemical potential of the vapour when fugacity is equal to 1.

~~The~~ Now, from eqnⁿ (6)

$$(\mu_i)_l = (\mu_i^\circ)_l + RT \ln f_i$$

where $(\mu_i^\circ)_l$ is the chemical potential of the liquid when ^{the} ~~fugacity~~ is equal to 1.

Thus the fugacity of a pure liquid would be ^{the} same as that of its vapour, in equilibrium with it at a given temperature.

Activity and activity co-efficient :-

Activity term is used to replace concentration term in non ideal solution.

The chemical potential of a real or ideal solute is given by

$$\mu_i = \mu_i^\circ + RT \ln \left(\frac{P_i}{P_i^\circ} \right) \rightarrow (1)$$

where μ_i° is the chemical potential of pure 'i' and μ_i is the chemical potential of 'i' present in solution.

(6)

For an ideal solution, the solvent obeys Raoult's law, at all concentration and we write

$$\mu_i = \mu_i^0 + RT \ln x_i \rightarrow (2) \quad \left[\begin{array}{l} \text{Raoult's law} \\ P_i = x_i P_i^0 \end{array} \right]$$

For a non-ideal solution, i.e. the solution which does not obey Raoult's law, it can be written as,

$$\mu_i = \mu_i^0 + RT \ln a_i \rightarrow (3)$$

The quantity a_i is the activity of "i", a kind of effective pressure.

Since the eqnⁿ (1) is true for both real and ideal ~~gas~~ solution [Here only pressure is used instead of fugacity], we can compare it with eqnⁿ (3)

$$a_i = P_i / P_i^0$$

Now, we have for real solⁿ $\mu_i = \mu_i^0 + RT \ln a_i$

$$\text{For ideal solⁿ } \mu_i^{\text{ideal}} = \mu_i^0 + RT \ln x_i \rightarrow (4)$$

$$\text{eqn (5)} - \text{eqn (4)} \quad \text{eqn (4)} - \text{eqn (5)}$$

$$\begin{aligned} \mu_i - \mu_i^{\text{ideal}} &= RT \ln a_i - RT \ln x_i \\ &= RT \ln (a_i / x_i) \end{aligned}$$

The ratio a_i / x_i is thus a measure of the departure from ideal behaviour. ~~It~~ It is defined as the activity coefficient γ_i , $\gamma_i = a_i / x_i$.

$$\text{So that } a_i = \gamma_i x_i$$

$$\begin{aligned} \mu &= \mu_i^0 + RT \ln a_i \\ &= \mu_i^0 + RT \ln \gamma_i x_i \\ &= \mu_i^0 + RT \ln x_i + RT \ln \gamma_i \end{aligned}$$

In an ideal solution $\gamma = 1$,

a_i and γ_i both are dimensionless and have non negative value.

⑦

Thermodynamic derivation between Gibbs free energy of reaction and reaction Quotient.

Let us consider a general reversible reaction



Where the reactants and products are assumed to be ideal gases.

~~We know that chemical potentials of gases are given by~~

We know that Gibbs free energy of reactants consisting a moles of A and b moles of B is given by the expression.

$$G_{\text{reactant}} = a\mu_A + b\mu_B \quad \rightarrow \textcircled{1}$$

Where μ_A and μ_B are the chemical potentials of the species A and B, respectively. Similarly for the products, we have.

$$G_{\text{product}} = m\mu_M + n\mu_N \quad \rightarrow \textcircled{2}$$

In each case, pressure and temperature are constant.

The free energy of reaction

$$\begin{aligned} (\Delta G)_{\text{reaction}} &= G_{\text{product}} - G_{\text{reactant}} \\ &= (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B) \quad \rightarrow \textcircled{3} \end{aligned}$$

The chemical potential of any species (let for i th species) is given by

$$\mu_i = \mu_i^\circ + RT \ln p_i \quad (\text{For gaseous state}) \quad \rightarrow \textcircled{4}$$

Where p_i is the partial pressure of the i th component and μ_i° is its standard chemical potential (when partial pressure of i th component is unity.)

Substituting this value in eqnⁿ $\textcircled{3}$

(8)

$$\begin{aligned}
 (\Delta G)_{\text{reaction}} &= \left[m(\mu_M^\circ + RT \ln P_M) + n(\mu_N^\circ + RT \ln P_N) \right] \\
 &\quad - \left[a(\mu_A^\circ + RT \ln P_A) + b(\mu_B^\circ + RT \ln P_B) \right] \\
 &= \left[(m\mu_M^\circ + n\mu_N^\circ) - (a\mu_A^\circ + b\mu_B^\circ) \right] + RT \ln \left(\frac{P_M^m P_N^n}{P_A^a P_B^b} \right)
 \end{aligned}$$

→ (5)

$$(\Delta G)_{\text{reaction}} = (\Delta G^\circ)_{\text{reaction}} + RT \ln \left(\frac{P_M^m P_N^n}{P_A^a P_B^b} \right) \rightarrow (6)$$

The factor $\frac{P_M^m P_N^n}{P_A^a P_B^b}$ is called pressure coefficient, reaction coefficient or reaction quotient, and is represented as Q_p .

$$(\Delta G)_{\text{reaction}} = \Delta G^\circ + RT \ln Q_p \rightarrow (7)$$

Now, suppose at some given temperature T and total pressure P , the reaction is allowed to take place and when equilibrium is established and the partial pressure of each component remains unaltered with time, then free energy change $\Delta G = 0$.

Putting $(\Delta G)_{\text{reaction}}$ in eqn (6) equal to zero.

$$0 = \Delta G^\circ + RT \ln \left(\frac{P_M^m P_N^n}{P_A^a P_B^b} \right)_{\text{equil}^m}$$

$$\Delta G^\circ = -RT \ln \left(\frac{P_M^m P_N^n}{P_A^a P_B^b} \right)_{\text{equil}^m} \rightarrow (8)$$

Where the subscript equilibrium points the ^{values of} partial pressure of various constituents at equilibrium which are definite.