CHEMICAL EQUILIBRIUM

- Most of the chemical reactions when carried out in closed vessels do not go to completion.
- Under these conditions, a reaction starts by itself or by initiation, continues for some time at diminishing rates and ultimately ***appears to stop***.
- The reactants may still be present but they do not appear to change into products any more.
- Thus, in a given time as much of the products are formed as react back to give the reactants.
- The reaction in such condition is said to be in a state of equilibrium

- The attainment of equilibrium can be recognized by noting constancy of observable properties such as pressure, concentration, density or colour.

Law of Mass Action

- Gives the relationship between the quantities of the reacting substances and the products formed.
- The rate at which a substance reacts is proportional to its active mass and the rate of a reaction is directly proportional to the product of the active masses of the reaction substances.

- Consider a general reversible chemical reaction

$$aA + bB \rightleftharpoons mM + nM$$

- Assuming that active masses are equivalent to molar concentrations,

$$r_f \propto [A]^a[B]^b = k_f[A]^a[B]^b$$

$$r_r \propto [M]^m[N]^n = k_r[M]^m[N]^n$$

- k_f and k_r are proportionality constants.
- At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction, that is

$$k_f[A]^a[B]^b = k_r[M]^m[N]^n$$

$$\frac{k_f}{k_r} = k_{eq} = \frac{[M]^m[N]^n}{[A]^a[B]^b}$$

- k_{eq} is called the equilibrium constant
- The equilibrium concentrations can be written in terms of activities (a_i), partial pressures (p_i), molar concentrations (c_i), or mole fraction (x_i) of the species involved in the reaction.

EQUILIBRIUM EXPRESSION FROM THERMODYNAMIC PRINCIPLES

- Consider once again the general reversible chemical reaction

$$aA + bB \rightleftharpoons mM + nM$$

- Where the reactants and products are assumed to be gases
- The chemical potential (i.e. Gibbs free energy) of the reactants consisting of $\boldsymbol{a}$ moles of A and $\boldsymbol{b}$ moles of B is given by the expression

$$G_{reactants} = a\mu_A + b\mu_B$$

- Where μ_A and μ_B are the chemical potentials of A and B
- Similar, for the products we have

$$G_{product} = m\mu_M + n\mu_n$$

- In each case, pressure and temperature are constant
- The free energy of the reaction is equal to the difference between the free energy of the products and that of the reactants, that is,

$$\Delta G_{rxn} = G_{product} - G_{reactant}$$

$$= (m\mu_M + n\mu_n)\ - (a\mu_A + b\mu_B)$$

- At equilibrium, the free energy change $\Delta G = 0$ so that,

$$(m\mu_M + n\mu_n) - (a\mu_A + b\mu_B) = 0$$

- The chemical potential of the *i*th species in the gaseous is,

$$\mu_i = \mu_i^o + RT \ln p_i$$

- Where p_i is the partial pressure of the *i*th component and μ_i^o is its standard chemical potential (i.e., when the partial pressure of the *i*th component is unity)

- Therefore,

$$[m(\mu_M^o + RT\ln p_M) + n(\mu_N^o + RT\ln p_N)] -$$

$$[a(\mu_A^o + RT\ln p_A) + b(\mu_B^o + RT\ln p_B)] = 0$$

or

$$RTln\left(\frac{p_M^m p_N^n}{p_A^a p_B^b}\right) = -[(m\mu_M^o + n\mu_N^o) - (a\mu_A^o - b\mu_B^o)]$$

$$= -\left(G_{products}^o - G_{reactants}^o\right)$$

$$= -\Delta G_{rxn}^o$$

- or

$$\frac{(p_M^m p_N^n)}{\left(p_A^a p_B^b\right)} = e^{\left(\frac{-\Delta G^o}{RT}\right)}$$

- Since ΔG^o depends only on temperature and R is the gas constant, hence the right hand side of the equation at constant temperature. Thus,

$$\frac{p_M^m p_N^n}{p_A^a p_B^b} = \text{constant} = K_p$$

- This equation is the **law of chemical equilibrium**

- If the chemical potentials of various species are expressed in terms of mole fractions (x_i), then

$$\mu_i = \mu_i^o + RT \ln x_i$$

- So that

$$\frac{x_M^m x_N^n}{x_A^a x_B^b} = K_x$$

- If the chemical potentials of various species are expressed in terms of mole fractions (c_i), then

$$\frac{[M]^m [N]^n}{[A]^a [B]^b} = K_c$$

- If the reactants and products are not ideal gases, then the **thermodynamic equilibrium constant**, K_{th}, is defined as

$$K \equiv K_{th} = \frac{a_M^m a_N^n}{a_A^a a_B^b}$$

- Where a_is are the activities.
- For non-ideal, i.e., real gases

$$K \equiv K_f = \frac{f_M^m f_N^n}{f_A^a f_B^b}$$

Where f_is are the fugacities.

- For a mixture of real gases,

$$\gamma_i = \frac{f_i}{P_i}$$

Or

$$f_i = \frac{\gamma_i}{P_i}$$

- Where γ_is are the activity coefficients.
- Hence,

$$K_f = \frac{f_M^m f_N^n}{f_A^a f_B^b} = \frac{\gamma_M^m \gamma_N^n}{\gamma_A^a \gamma_B^b} x \frac{P_M^m P_N^n}{P_A^a P_B^b} = K_\gamma K_f$$

Van’t Hoff reaction isotherm

- Since

$$\frac{p_M^m p_N^n}{p_A^a p_B^b} = K_p \quad and \quad \frac{p_M^m p_N^n}{p_A^a p_B^b} = e^{\left(\frac{-\Delta G^o}{RT}\right)}$$

- It follows that

$$\Delta G^o = -RTlnK_p$$

- This equation is known as the **van’t Hoff reaction isotherm**
- It is very important in that it permits the calculation of ΔG^o of the reaction from the known value of the equilibrium constant K_p and vice-verse

Distinction between ΔG^o and ΔG

- $\boldsymbol{\Delta G^o}$ is the difference in the free energy of products and reactants when all of them are in their standard state
- This does not refer to the actual reaction at equilibrium
- $\Delta \boldsymbol{G}$, however, refers to the difference in the free energy of products and reactants at the actual measured concentrations (or partial pressures) of the components
- When $\Delta \boldsymbol{G}$ = 0, the reaction is at equilibrium and the concentrations (or partial pressures) of the components are those which appear in the equilibrium constant expression

Relations between K_p, K_c and K_x

(a) $K_p \ and \ K_x$

- In an ideal gas mixture, each component obeys Dalton's law of partial pressures

$$P_i = x_i P_T$$

- For the general reaction

$$aA + bB \rightleftharpoons mM + nM$$

$P_A = x_A P_T, P_B = x_B P_T, P_M = x_M P_T, P_N = x_N P_T$

And

$$K_p = \frac{P_M^m P_N^n}{P_A^a P_B^b} = \left(\frac{x_M^m x_N^n}{x_A^a x_B^b}\right) P_T{}^{(m+n)-(a+b)} = K_x (P_T)^{\Delta n}$$

(b) $\boldsymbol{K_p \text{ and } K_c}$

- In an ideal gas mixture,

$$P_i V = n_i RT$$

- So that

$$P_i = \left(\frac{n_i}{V}\right) RT = c_i RT$$

$$P_A = c_A RT, P_B = c_B RT, P_M = c_M RT, P_N = c_N RT$$

- And

$$K_P = \frac{P_M^m P_N^n}{P_A^a P_B^b} = \left(\frac{c_M^m c_N^n}{c_A^a c_B^b}\right) RT^{(m+n)-(a+b)} = K_c (RT)^{\Delta n}$$

- Hence

$$K_P = K_x (P_T)^{\Delta n} = K_c \; (RT)^{\Delta n}$$

DE DONDER'S TREATMENT OF CHEMICAL EQUILIBRIUM

- For simplicity, we shall discuss gas-phase reactions first.
- Consider the general gas phase reaction described by the balanced equation

$$\nu_A A(g) + \nu_B B\ (g) \rightleftharpoons \nu_Y Y\ (g) + \nu_Z Z\ (g)$$

- We define a quantity ξ, called the extent of reaction, such that the number of moles of the reactants and products are given by;

$$n_A = n_{A,o} - \nu_A \xi$$
$$n_B = n_{B,o} - \nu_B \xi$$

$$n_Y = n_{Y,o} + \nu_Y \xi$$
$$n_Z = n_{Z,o} + \nu_Z \xi$$

or

$$n_i = n_{i,o} + \nu_i \xi$$

$n_{i,o} = \text{initial number of moles}$
$\nu_i = stochiometric\ coefficent, negative$
$\quad for\ reactants, positive\ for\ products$
$\xi = extent\ of\ the\ reaction$

$$dn_i = \nu_i d\xi$$

- Now let's consider a system containing reactants and products at constant *T and P.*
- The Gibbs energy for this multi component system is a function of *T, P,* n_A, n_B, n_Y, and n_Z
- *which we can express mathematically as:*

$$G = G(T, P, n_A, n_B, n_Y, n_Z)$$

- The total derivative of *G is given by:*

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

$$+ \left(\frac{\partial G}{\partial n_A}\right)_{TP,n_{j\nLeftrightarrow A}} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{TP,n_{j\nLeftrightarrow B}} dn_B$$

$$+ \left(\frac{\partial G}{\partial n_Y}\right)_{TP,n_{j\nLeftrightarrow Y}} dn_Y + \left(\frac{\partial G}{\partial n_Z}\right)_{TP,n_{j\nLeftrightarrow Z}} dn_Z$$

- where the subscript n_j *in the first two partial derivatives stands for* n_A, n_B, n_Y, and n_Z

- But;

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

- Therefore;

$$dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z$$

- Where,

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{TP, n_B, n_Y, n_Z} = chemical\, potential$$

- The fundamental of thermodynamics is given by

$$dG = -SdT + VdP + \sum \mu_i dn_i$$

- At constant temperature and pressure

$$(dG)_{T,P} = \sum \mu_i dn_i$$

- But

$$dn_i = \nu_i d\xi$$

- Hence,

$$(dG)_{T,P} = \sum_{i=1}^{N} \mu_i \, \nu_i d\xi$$

- Or

$$\left(\frac{dG}{d\xi}\right)_{T,P} = \sum_{i=1}^{N} \mu_i \nu_i$$

- Denoting the right side by ΔG_{rxn}, so that

$$\left(\frac{dG}{d\xi}\right)_{T,P} = \sum_{i=1}^{N} \mu_i \nu_i = \Delta G_{rxn}$$

$$\left(\frac{dG}{d\xi}\right)_{T,P} = \nu_Y \mu_Y + \nu_Z \mu_Z - \nu_A \mu_A - \nu_B \mu_B = \Delta G_{rxn}$$

- ΔG_{rxn} is defined as the change in Gibbs energy when the extent of reaction changes by one mole.

- A spontaneous process at constant T and P corresponds to $dG < 0$. If the forward reaction is spontaneous, $d\xi > 0$ and

$$\left(\frac{dG}{d\xi}\right)_{T,P} < 0 \quad \text{(forward rxn spontaneous)}$$

- If the reverse reaction is spontaneous, $d\xi < 0$ and

$$\left(\frac{dG}{d\xi}\right)_{T,P} > 0 \quad \text{(reverse rxn spontaneous)}$$

- If the equilibrium state has been attained, there is no tendency for the reaction to proceed, and $dG = 0$, so that

$$\left(\frac{dG}{d\xi}\right)_{T,P} = \sum_i \mu_i \, \nu_i = 0 \ \ \text{(equilibrium)}$$

- The situation is as represented in the Figure , with a smooth minimum in G at the equilibrium value of ξ.
- A system in any non-equilibrium state will spontaneously react to approach the equilibrium state at the minimum in the curve representing G as a function of ξ, beginning from either side of the minimum.

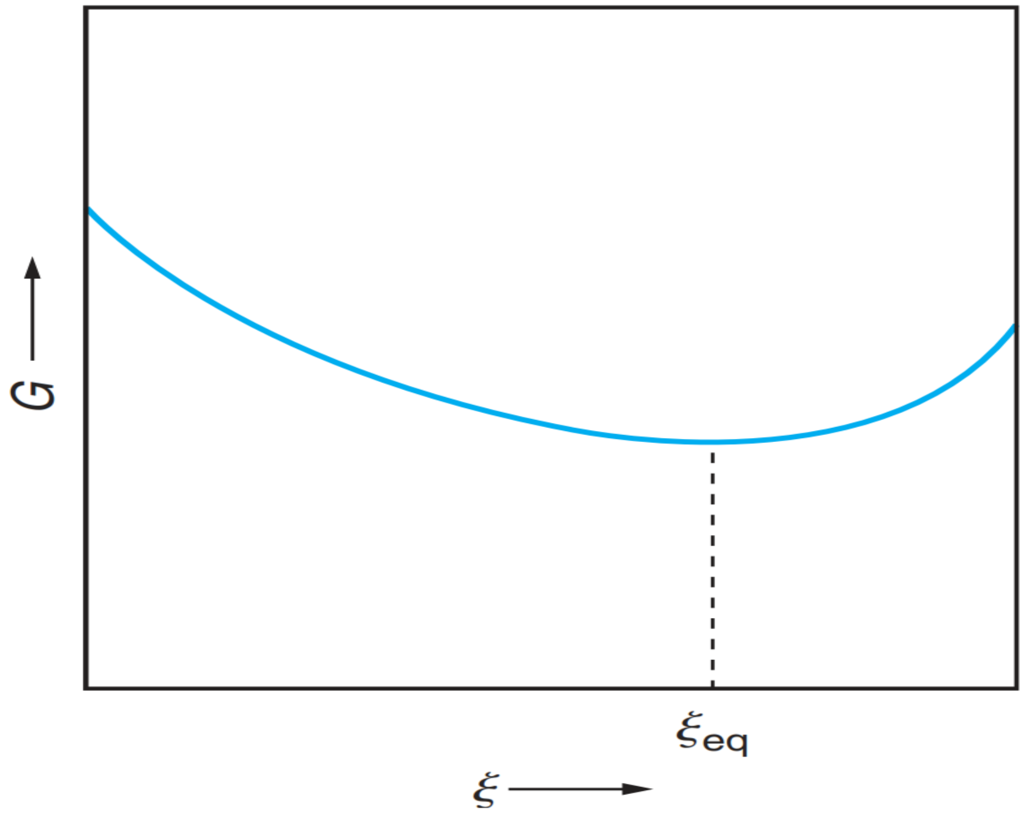


Figure 7.1 The Gibbs Energy of a Reacting System as a Function of the Progress Variable.

- The chemical potential of a general substance i in terms of its activity a_i

$$\mu_i = \mu_i^o + RT ln\, a_i$$

- Where μ_i^o is the chemical potential of substance i in whatever standard state applies.
- The rate of change of the Gibbs energy per mole of reaction is now expressed in terms of activities:

$$\left(\frac{dG}{d\xi}\right)_{T,P} = \sum_{i=1}^{N} \nu_i \mu_i^o + RT \sum_{i=1}^{N} \nu_i ln\, a_i$$

- If it is possible to maintain all of the reactants and products in their standard states, all activities are equal to unity.
- The second sum in the right-hand side of Eq. vanishes and the change in G for 1 mole of reaction is

$$\Delta G^{o} = \int_{o}^{1} \left\{ \left(\frac{dG}{d\xi}\right)_{T,P} \Bigg|_{standard\,state} \right\} d\xi$$

$$= \int_{o}^{1} \sum_{i=1}^{N} \nu_i \mu_i^{o}\, d\xi = \sum_{i=1}^{N} \nu_i \mu_i^{o} \int_{o}^{1} d\xi$$

- so that for 1 mole of reaction

$$\Delta G^{o} = \sum_{i=1}^{N} \nu_i \mu_i^{o}$$

- It follows that so that for 1 mole of reaction

$$\left(\frac{dG}{d\xi}\right)_{T,P} = \Delta G_{rxn} = \sum_{i=1}^{N} \nu_i \mu_i^{o} + RT \sum_{i=1}^{N} \nu_i ln\, a_i$$

- Becomes

$$\Delta G_{rxn} = \Delta G^{o} + RT \sum_{i=1}^{N} \nu_i ln\, a_i$$

- Or

$$\Delta G_{rxn} = \Delta G^{o} + RTlnQ$$

- Where

$$Q = \frac{(a_Y)^{\nu_Y}(a_Z)^{\nu_Z}}{(a_A)^{\nu_A}(a_B)^{\nu_B}} = \prod_{i=1}^{N} a_i^{\nu_Y}$$

$$\Delta G_{rxn} = \Delta G_{rxn}^{o} + RTln\prod_{i=1}^{N} a_i^{\nu_Y}$$

- As we can see from this equation, is the change in Gibbs energy for the reaction when the activities of reactants and products are all unity.
- In other words, ΔG^{o} is the change in Gibbs energy when separate reactants in their standard states their standard states. ΔG_{rxn} is the change in the Gibbs energy in a specified reaction when separated reactants at specified activities are converted to separated products at specified activities.

- The product in the last term is much like an equilibrium constant, except that the activities of reactants and products can have any values we want.
- This product of activities is called the and is represented by Q:

$$Q = \prod_{i=1}^{N} a_i^{\nu_Y}$$

- So that

$$\Delta G_{rxn} = \Delta G^o + RTlnQ$$

- This equation gives the change in Gibbs energy for a specified chemical reaction when the reactants and products have activities a_i, so it can be used to test for spontaneity in the forward direction ($\Delta \mathrm{G}_\mathrm{r} < 0$) or backward direction ($\Delta \mathrm{G}_\mathrm{r} > 0$).
- Dividing the Gibbs energy (*dG = dH - TdS*) by dξ

$$\Delta G_{rxn} = \left(\frac{dG}{d\xi}\right)_{T,P} = \left(\frac{dG}{d\xi}\right)_{T,P} + T\left(\frac{dG}{d\xi}\right)_{T,P}$$

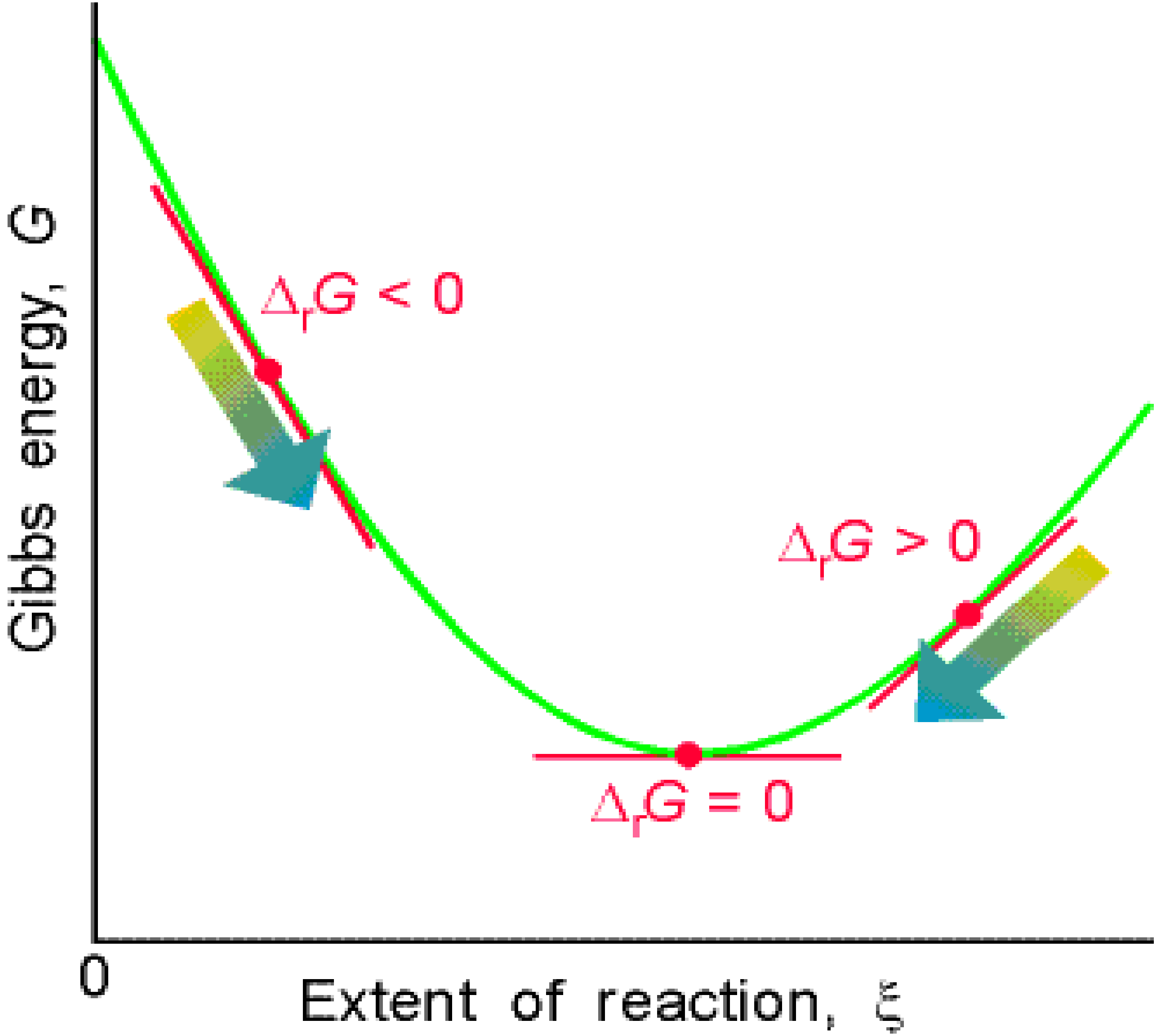
$$\Delta G_{rxn} = \ \Delta H_r - T\Delta S_r$$

Gibbs energy of the reaction

- The fundamental of thermodynamics is

$$\Delta G_{rxn} = \Delta G^{o}_{rxn} + RTln\frac{(a_Y)^{\nu_Y}(a_Z)^{\nu_Z}}{(a_A)^{\nu_A}(a_B)^{\nu_B}}$$

- The reaction quotient now expressed in terms of activities, a_A
- Activity expressions are to be defined as we look at
  a) Chemical equilibrium
  b) Electrochemical equilibrium
  c) Acid-Base equilibrium


Gibbs energy, G
$\Delta_r G < 0$
$\Delta_r G > 0$
$\Delta_r G = 0$
0
Extent of reaction, ξ

EQUILIBRIUM CONDITION

- At equilibrium, $\Delta G_r = 0$
- So that the equation

$$\Delta G_{rxn} = \Delta G^{o}_{rxn} + RTln\frac{(a_Y)^{\nu_Y}(a_Z)^{\nu_Z}}{(a_A)^{\nu_A}(a_B)^{\nu_B}}$$

- Becomes

$$\Delta G^{o}_{rxn} = -RTln\frac{(a_Y)^{\nu_Y}(a_Z)^{\nu_Z}}{(a_A)^{\nu_A}(a_B)^{\nu_B}}$$

- Or

$$\Delta G^{o}_{rxn} = -RTlnK_{eq}$$

$$K_{eq} = \text{equilibrium constant}$$

Thermodynamic stability and Kinetic stability of a chemical reaction

Thermodynamic	Kinetic	Comment
$\Delta G < 0$	unstable	Reaction favourable
$\Delta G = 0$	stable	Reaction can proceed if kinetic factor (e.g. T, P, catalyst) are changed
$\Delta G > 0$	stable	Reaction not favourable