

The free energy of formation $\Delta_f G^\circ$ has the same standard state as $\Delta_f H^\circ$

Since free energy is composed of both enthalpy and entropy the Gibbs free energy is a relative and not an absolute quantity. Recall that

Enthalpy is relative (reference state in which most stable form of elemental compounds form has 0 enthalpy of formation)

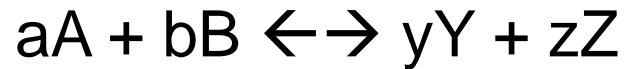
Entropy is absolute ($T = 0$ K has 0 for perfect crystal)

The free energy of formation is zero for elemental compounds in their most stable form at 298 K.

For example, H_2 , O_2 , N_2 , S_8 , C(graphite), Hg liquid etc. all have $\Delta_f G^\circ = 0$.

General derivation for ΔG and ΔG° based on chemical potential

Let's consider an idealized reaction:



At constant T and P we will write the total Gibbs energy as

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

In the general case we can write

$$dG = \sum_{I=1}^N \mu_I dn_I$$

$$dn = \frac{dn_i}{\nu_i}$$

products are created
(positive)

$$dn = - \frac{dn_i}{\nu_i}$$

reactants are consumed
(negative)

Using a generalized progress variable, dn

The overall reaction becomes

$$dG = y\mu_Y dn + z\mu_Z dn - a\mu_A dn - b\mu_B dn$$

Which reflects the relative change in the stoichiometric amount of each species.

We now define $\Delta_{rxn}G$:

$$\Delta_{rxn}G = \left(\frac{\partial G_m}{\partial n} \right)_{T,P}$$

We can write the Gibbs energy as:

$$\Delta G = y\mu_Y + z\mu_Z - a\mu_A - b\mu_B$$

Application of the chemical potential

We apply the chemical potential

$$\mu_I(T) = \mu_I^{\circ}(T) + RT \ln\left(\frac{P}{1 \text{ bar}}\right)$$

which can be expressed in terms of each species, A, B, Y and Z. For example,

$$\mu_A = \mu_A^{\circ} + RT \ln P_A \quad \mu_B = \mu_B^{\circ} + RT \ln P_B$$

Substitute

$$\Delta G = y(\mu_Y^{\circ} + RT \ln P_Y) + z(\mu_Z^{\circ} + RT \ln P_Z) \\ - a(\mu_A^{\circ} + RT \ln P_A) - b(\mu_B^{\circ} + RT \ln P_B)$$

Rearrange

$$\Delta G = y\mu_Y^{\circ} + z\mu_Z^{\circ} - a\mu_A^{\circ} - b\mu_B^{\circ} \\ + RT \ln P_Y^y + RT \ln P_Z^z - RT \ln P_A^a - RT \ln P_B^b$$

to obtain

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

Definition of ΔG^0 and Q

We can make the identifications

$$\Delta G^0 = y\mu_Y^0 + z\mu_Z^0 - a\mu_A^0 - b\mu_B^0 \quad Q = \frac{P_Y^y P_Z^z}{P_A^a P_B^b}$$

Initially,

$$\Delta G \neq 0$$

The free energy will tend to decrease as the reaction proceeds. Eventually, the free energy will stop changing and become constant. Then the condition

$$\Delta G = 0$$

will be met. Therefore,

$$0 = \Delta G^0 + RT \ln K \quad \Delta G^0 = -RT \ln K$$

$$K = \exp \left\{ -\frac{\Delta G^0}{RT} \right\}$$

Conversion to concentration

We can express the reaction quotient in terms of pressure for Gases or concentration (usually molarity) for liquids. To convert the reaction quotient from pressure,

$$Q = \frac{P_Y^y P_Z^z}{P_A^a P_B^b}$$

to molarity we use the ideal gas law

$$P = \frac{nRT}{V} = \left(\frac{n}{V}\right) RT = cRT$$

where c is the molarity $c = n/V$. Therefore,

$$Q = \frac{c_Y^y c_Z^z}{c_A^a c_B^b} RT^{y+z-a-b}$$

Obviously, the same considerations apply to K , the equilibrium constant.

Must the system be at equilibrium?

The significance of the reaction quotient is that it represents the actual ratio of products and reactants at a given time. the system may not be at equilibrium simply because the mixing of reactants has not had time to reach equilibrium.

However, it is also possible that coupled process lead to a steady state, which is not at equilibrium. This is the situation in a living cell, for example. It may also be the case in a chemical reactor used in industry. Clever use of flow and coupled chemical reactions can drive processes that normally would not be favorable.