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Application of Equilibrium Criteria to Chemical Reactions

it is shown that the total Gibbs energy of a closed system at constant *T* and *P* must decrease during an irreversible process and that the condition for equilibrium is reached when G^t attains its minimum value. At this equilibrium state,

$$(dG^t)_{T,P} = 0$$

Thus if a mixture of chemical species is not in chemical equilibrium, any reaction that occurs at constant *T* and *P* must lead to a decrease in the total Gibbs energy of the system.

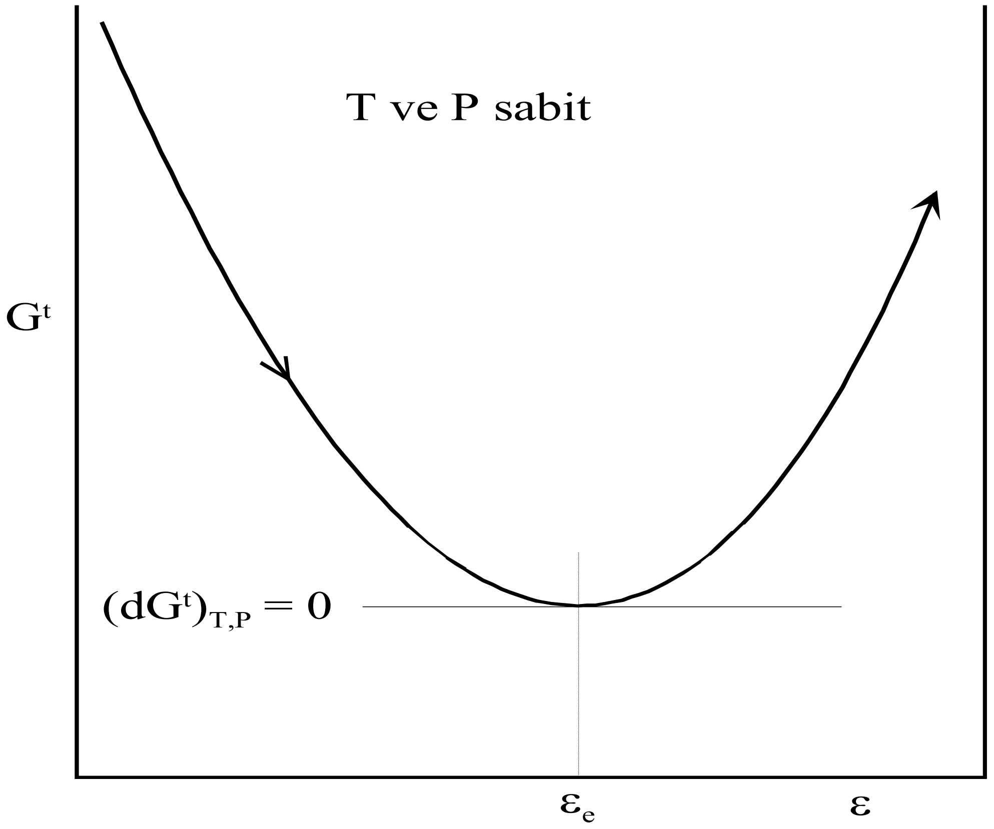

Figure : The total Gibbs energy in relation to the reaction coordinate.

Figure indicates the two distinctive features of the equilibrium state for given *T* and *P*: (1) The total Gibbs energy G^t is a minimum; (2) its differential is zero.

Each of these may serve as a criterion of equilibrium. Thus, we may write an expression for G^t as a function of ε and seek the value of ε which minimizes G^t, or we may differentiate the expression, equate it to zero, and solve for ε.

The Standard Gibbs Energy Change and the Equilibrium Constant

Equation , the fundamental property relation for single-phase systems, provides an expression for the total differential of the Gibbs energy:

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i$$

If changes in the mole numbers n_i occur as the result of a single chemical reaction in a closed system, then by Eq. each dn_i may be replaced by the product $\nu_i d\varepsilon$.. Equation , then becomes

$$d(nG) = (nV)dP - (nS)dT + \sum_i \nu_i \mu_i d\varepsilon$$

Since nG is a state function, the right-hand side of this equation is an exact differential expression; it follows that

$$\sum_i \nu_i \mu_i = \left[\frac{\partial(nG)}{\partial\varepsilon}\right]_{T,P} = \left[\frac{\partial(G^t)}{\partial\varepsilon}\right]_{T,P}$$

The difference between these two equations is then

$$\mu_i - G_i^o = RT \ln \frac{\hat{f}_i}{f_i^o}$$

The ratio $\hat{f}_i / f_i^o$ is called the *activity* $\hat{a}_i$ of species *i* in solution. Thus by definition,

$$\hat{a}_i \equiv \frac{\hat{f}_i}{f_i^o}$$

and the preceding equation becomes

$$\mu_i = G_i^o + RT \ln \hat{a}_i$$

Combining the equations to eliminate μ_i gives for the equilibrium state of a chemical reaction

$$\sum_i \nu_i (G_i^o + RT \ln \hat{a}_i) = 0$$

or

$$\sum_i \nu_i G_i^o + RT \sum_i \ln(\hat{a}_i)^{\nu_i} = 0$$

or

$$\ln \prod_i (\hat{a}_i)^{\nu_i} = \frac{-\sum_i \nu_i G_i^o}{RT}$$

where $\prod_i$ signifies the product over all species *i*. In exponential form, Eq. becomes

$$\boxed{\prod_i (\hat{a}_i)^{\nu_i} = \exp \frac{-\sum_i \nu_i G_i^o}{RT} \equiv K}$$

Included in this equation is the definition of *K*. Since G_i^o is a property of pure species *i* in its standard state at fixed pressure, it depends only on temperature. Equation shows that *K* is also a function of temperature only. In spite of its dependence on temperature, *K* is called the equilibrium *constant* for the reaction. Equation may now be written

$$\boxed{-RT\ln K = \sum_i \nu_i G_i^o \equiv \Delta G^o}$$

The final term ΔG^o is the conventional way of representing the quantity $\sum_i \nu_i G_i^o$. It is called the *standard Gibbs energy change of reaction.*

The standard states are arbitrary, but must always be at the equilibrium temperature *T*. The standard states selected need not be the same for all species taking part in a reaction.

However, for a *particular* species the standard state represented by G_i^o must be the same state as for the fugacity f_i^o upon which the activity $\hat{a}_i$ is based.

The function $\sum_i \nu_i G_i^o \equiv \Delta G^o$ in Eq. is the difference between the Gibbs energies of the products and reactants (weighted by their stoichiometric coefficients) when each is in its standard state as a pure substance at the system temperature and at a fixed pressure.