

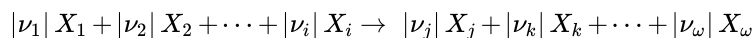
15.8: The Rate of Gibbs Free Energy Change with Extent of Reaction

In [Section 13.5](#), we demonstrate that the Gibbs free energy change for a reaction among ideal gases is the same thing as the rate at which the Gibbs free energy of the system changes with the extent of reaction. That is, for an ideal-gas reaction at constant temperature and pressure, we find $\Delta_r G = (\partial G / \partial \xi)_{TP}$. We can now show that this conclusion is valid for any reaction.

With the introduction of the activity function, we have developed a very general expression for the Gibbs free energy of any substance in any system. For substance A at a fixed temperature, we have

$$\bar{G}_A = \mu_A = \tilde{\mu}_A^o + RT \ln \tilde{a}_A$$

For a reaction that we describe with generalized substances and stoichiometric coefficients as



we can write the Gibbs free energy change in several equivalent ways:

$$\begin{aligned} \Delta_r G &= \sum_{j=1}^{\omega} \nu_j \bar{G}_j \\ &= \Delta_r \mu \\ &= \sum_{j=1}^{\omega} \nu_j \mu_j \leq 0 \end{aligned}$$

The Gibbs free energy of the system is a function of temperature, pressure, and composition,

$$G = G(P, T, n_1, n_2, \dots, n_\omega)$$

To introduce the dependence of the Gibbs free energy of the system on the extent of reaction, we use the stoichiometric relationships $n_j = n_j^o + \nu_j \xi$. (n_j is the number of moles of the j^{th} reacting species; n_j^o is the number of moles of the j^{th} reacting species when $\xi = 0$. If the k^{th} substance does not participate in the reaction, $\nu_k = 0$.) Then,

$$G = G(P, T, n_1^o + \nu_1 \xi, n_2^o + \nu_2 \xi, \dots, n_\omega^o + \nu_\omega \xi)$$

At constant temperature, pressure, and composition, the dependence of the Gibbs free energy on the extent of reaction is

$$\begin{aligned} \left(\frac{\partial G}{\partial \xi} \right)_{PTn_m} &= \sum_{j=1}^{\omega} \left(\frac{\partial G}{\partial (n_j^o + \nu_j \xi)} \right)_{PTn_m, j} \left(\frac{\partial (n_j^o + \nu_j \xi)}{\partial \xi} \right)_{PTn_m} \\ &= \sum_{j=1}^{\omega} \nu_j \mu_j \end{aligned}$$

It follows that

$$\left(\frac{\partial G}{\partial \xi} \right)_{PTn_m} = \Delta_r G \leq 0$$

expresses the thermodynamic criteria for change when the process is a chemical reaction.

If a reacting system is not at equilibrium, the extent of reaction is time-dependent. We see that the Gibbs free energy of a reacting system depends on time according to

$$\frac{dG}{dt} = \left(\frac{\partial G}{\partial \xi} \right)_{PTn_m} \left(\frac{d\xi}{dt} \right) = \Delta_r \mu \left(\frac{d\xi}{dt} \right)$$

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