

13.5: $\Delta_r G$ is the rate at which the Gibbs Free Energy Changes with The Extent of Reaction

For the reaction $a A + b B \rightleftharpoons c C + d D$, let us call the consumption of a moles of A one “unit of reaction.” $\Delta_r G$ corresponds to the actual Gibbs free energy change for one unit of reaction only in the limiting case where the reaction occurs in an arbitrarily large system. For a closed system of specified initial composition, n_A^o , n_B^o , n_C^o , and n_D^o , whose composition at any time is specified by n_A , n_B , n_C , and n_D , the extent of reaction, ξ , is

$$\xi = - \left(\frac{n_A - n_A^o}{a} \right) = - \left(\frac{n_B - n_B^o}{b} \right) = \frac{n_C - n_C^o}{c} = \frac{n_D - n_D^o}{d}$$

At constant pressure and temperature, every possible state of this system is represented by a point on a plot of $\Delta_r G$ versus ξ . Every such state is also represented by a point on a plot of G_{system} versus ξ .

From the general result that $(dG_{system})_{PT} = 0$ if and only if the system is at equilibrium, it follows that $\Delta_r G(\xi_{eq}) = 0$ if and only if ξ_{eq} specifies the equilibrium state. (We can arrive at the same conclusion by considering the heat exchanged for one unit of reaction in an infinitely large system at equilibrium. This process is reversible, and it occurs at constant pressure and temperature, so we have $\Delta_r H = q_P^{rev}$, $\Delta_r S = q_P^{rev}/T$, and $\Delta_r G = q_P^{rev} + T(q_P^{rev}/T) = 0$.)

Below, we show that

$$\Delta_r G(\xi) = \left(\frac{\partial G_{system}}{\partial \xi} \right)_{PT}$$

for any value of ξ . (In Section 15.9, we use essentially the same argument to show that this conclusion is valid for any reaction among any substances.) Given this result, we see that the equilibrium composition corresponds to the extent of reaction, ξ_{eq} , for which the Gibbs free energy change for one unit of the reaction is zero

$$\Delta_r G(\xi_{eq}) = 0$$

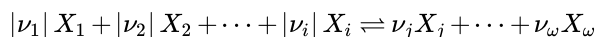
and

$$\left(\frac{\partial G_{system}}{\partial \xi} \right)_{PT} = 0$$

So that the Gibbs free energy of the system is a minimum.

In the next section, we show that the condition $\Delta_r G(\xi_{eq}) = 0$ makes it easy to calculate the equilibrium extent of reaction, ξ_{eq} . Given the stoichiometry and initial composition, the equation for $\Delta_r G(\xi_{eq})$ specifies the equilibrium composition and the partial pressures P_A , P_B , P_C , and P_D . This is the usual application of these results. Setting $\Delta_r G = 0$ enables us to answer the question: If we initiate reaction at a given composition, what will be the equilibrium composition of the system? Usually this is what we want to know. The amount by which the Gibbs free energy changes as the reaction goes to equilibrium is seldom of interest.

To show that $\Delta_r G = (\partial G / \partial \xi)_{PT}$ for any reaction, it is helpful to introduce modified stoichiometric coefficients, ν_j , defined such that $\nu_j > 0$ if the j -th species is a product and $\nu_j < 0$ if the j -th species is a reactant. That is, for the reaction $a A + b B \rightleftharpoons c C + d D$, we define $\nu_A = -a$, $\nu_B = -b$, $\nu_C = c$, and $\nu_D = d$. Associating successive integers with the reactants and products, we represent the j -th chemical species as X_j and an arbitrary reaction as



Let the initial number of moles of ideal gas X_j be n_j^o ; then $n_j = n_j^o + \nu_j \xi$. (For species that are present but do not participate in the reaction, we have $\nu_j = 0$.)

We have shown that the Gibbs free energy of a mixture of ideal gases is equal to the sum of the Gibbs free energies of the components. In calculating $\Delta_r G$, we assume that this is as true for a mixture undergoing a spontaneous reaction as it is for a mixture at equilibrium. In doing so, we assume that the reacting system is homogeneous and that its temperature and pressure are well defined. In short, we assume that the Gibbs free energy of the system is the same continuous function of temperature, pressure, and composition, $G = G(T, P, n_1, n_2, \dots)$, whether the system is at equilibrium or undergoing a spontaneous reaction. For the

equilibrium system, we have $(\partial G/\partial T)_{P,n_j} = -S$ and $(\partial G/\partial P)_{T,n_j} = V$. When we assume that these functions are the same for a spontaneously changing system as they are for a reversible system, it follows that

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_j} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_j} dP + \sum_j \left(\frac{\partial G}{\partial n_j}\right)_{P,T,n_{i \neq j}} dn_j = -SdT + VdP + \sum_j \left(\frac{\partial G}{\partial n_j}\right)_{P,T,n_{i \neq j}} dn_j$$

whether the system is at equilibrium or undergoing spontaneous change. At constant temperature and pressure, when pressure-volume work is the only work, the thermodynamic criteria for change, $dG_{TP} \leq 0$ become

$$\sum_j \left(\frac{\partial G}{\partial n_j}\right)_{P,T,n_{i \neq j}} dn_j \leq 0$$

When a reaction occurs in the system, the composition is a continuous function of the extent of reaction. We have $G = G(T, P, n_1^o + \nu_1 \xi, n_2^o + \nu_2 \xi, \dots)$. At constant temperature and pressure, the dependence of the Gibbs free energy on the extent of reaction is

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T,n_m} = \sum_j \left(\frac{\partial G}{\partial (n_j^o + \nu_j \xi)}\right)_{P,T,n_{m \neq j}} \left(\frac{\partial (n_j^o + \nu_j \xi)}{\partial \xi}\right)_{P,T,n_{m \neq j}}$$

Since

$$\left(\frac{\partial G}{\partial (n_j^o + \nu_j \xi)}\right)_{P,T,n_{m \neq j}} = \left(\frac{\partial G}{\partial n_j}\right)_{P,T,n_{m \neq j}} = \bar{G}_j$$

and

$$\left(\frac{\partial (n_j^o + \nu_j \xi)}{\partial \xi}\right)_{P,T,n_{m \neq j}} = \nu_j$$

it follows that

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T,n_m} = \sum_j \nu_j \bar{G}_j = \Delta_r G$$

Moreover, we have

$$(dG)_{PT} = \left(\frac{\partial G}{\partial \xi}\right)_{P,T,n_m} d\xi$$

The criteria for change, $(dG)_{PT} \leq 0$, become

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T,n_m} d\xi \leq 0$$

From our definition of ξ , we have $d\xi > 0$ for a process that proceeds spontaneously from left to right, so the criteria become

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T,n_m} \leq 0$$

or, equivalently,

$$\sum_j \nu_j \bar{G}_j = \Delta_r G \leq 0$$

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