11.9: Effects of Temperature and Pressure on Equilibrium Position

The advancement ξ of a chemical reaction in a closed system describes the changes in the amounts of the reactants and products from specified initial values of these amounts. We have seen that if the system is maintained at constant temperature and pressure, ξ changes spontaneously in the direction that decreases the Gibbs energy. The change continues until the system reaches a state of reaction equilibrium at the minimum of G. The value of the advancement in this equilibrium state will be denoted ξ_{eq}, as shown in Fig. 11.15. The value of ξ_{eq} depends in general on the values of T and p. Thus when we change the temperature or pressure of a closed system that is at equilibrium, ξ_{eq} usually changes also and the reaction spontaneously *shifts* to a new equilibrium position.

To investigate this effect, we write the total differential of G with T, p, and ξ as independent variables

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \Delta_{\mathrm{r}}G\,\mathrm{d}\xi \tag{11.9.1}$$

and obtain the reciprocity relations

$$\left(\frac{\partial \Delta_{\mathrm{r}}G}{\partial T}\right)_{p,\xi} = -\left(\frac{\partial S}{\partial \xi}\right)_{T,p} \qquad \left(\frac{\partial \Delta_{\mathrm{r}}G}{\partial p}\right)_{T,\xi} = \left(\frac{\partial V}{\partial \xi}\right)_{T,p} \tag{11.9.2}$$

We recognize the partial derivative on the right side of each of these relations as a molar differential reaction quantity:

$$\left(\frac{\partial \Delta_{\mathrm{r}}G}{\partial T}\right)_{p,\xi} = -\Delta_{\mathrm{r}}S \qquad \left(\frac{\partial \Delta_{\mathrm{r}}G}{\partial p}\right)_{T,\xi} = \Delta_{\mathrm{r}}V \tag{11.9.3}$$

We use these expressions for two of the coefficients in an expression for the total differential of $\Delta_{\mathrm{r}}G$:

$$\mathrm{d}\Delta_{\mathrm{r}}G = -\Delta_{\mathrm{r}}S\,\mathrm{d}T + \Delta_{\mathrm{r}}V\,\mathrm{d}p + \left(\frac{\partial \Delta_{\mathrm{r}}G}{\partial \xi}\right)_{T,p}\mathrm{d}\xi \tag{11.9.4}$$
$$\text{(closed system)}$$

Since $\Delta_{\mathrm{r}}G$ is the partial derivative of G with respect to ξ at constant T and p, the coefficient $(\partial \Delta_{\mathrm{r}}G/\partial \xi)_{T,p}$ is the partial *second* derivative of G with respect to ξ:

$$\left(\frac{\partial \Delta_{\mathrm{r}}G}{\partial \xi}\right)_{T,p} = \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p} \tag{11.9.5}$$

We know that at a fixed T and p, a plot of G versus ξ has a slope at each point equal to $\Delta_{\mathrm{r}}G$ and a minimum at the position of reaction equilibrium where ξ is ξ_{eq}. At the minimum of the plotted curve, the slope $\Delta_{\mathrm{r}}G$ is zero and the second derivative is positive (see Fig. 11.15). By setting $\Delta_{\mathrm{r}}G$ equal to zero in the general relation $\Delta_{\mathrm{r}}G = \Delta_{\mathrm{r}}H - T\Delta_{\mathrm{r}}S$, we obtain the equation $\Delta_{\mathrm{r}}S = \Delta_{\mathrm{r}}H/T$ which is valid only at reaction equilibrium where ξ equals ξ_{eq}. Making this substitution in Eq. 11.9.4, and setting $\mathrm{d}\Delta_{\mathrm{r}}G$ equal to zero and $\mathrm{d}\xi$ equal to $\mathrm{d}\xi_{\mathrm{eq}}$, we obtain

$$0 = -\frac{\Delta_{\mathrm{r}}H}{T}\,\mathrm{d}T + \Delta_{\mathrm{r}}V\,\mathrm{d}p + \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p}\mathrm{d}\xi_{\mathrm{eq}} \tag{11.9.6}$$
$$\text{(closed system)}$$

which shows how infinitesimal changes in T, p, and ξ_{eq} are related.

Now we are ready to see how ξ_{eq} is affected by changes in T or p. Solving Eq. 11.9.6 for $\mathrm{d}\xi_{\mathrm{eq}}$ gives

$$\mathrm{d}\xi_{\mathrm{eq}} = \frac{\dfrac{\Delta_{\mathrm{r}}H}{T}\,\mathrm{d}T - \Delta_{\mathrm{r}}V\,\mathrm{d}p}{\left(\dfrac{\partial^2 G}{\partial \xi^2}\right)_{T,p}} \tag{11.9.7}$$
$$\text{(closed system)}$$

The right side of Eq. 11.9.7 is the expression for the total differential of ξ in a closed system at reaction equilibrium, with T and p as the independent variables. Thus, at constant pressure the equilibrium shifts with temperature according to

$$\left(\frac{\partial \xi_{\mathrm{eq}}}{\partial T}\right)_p = \frac{\Delta_{\mathrm{r}}H}{T\left(\dfrac{\partial^2 G}{\partial \xi^2}\right)_{T,p}} \tag{11.9.8}$$
$$\text{(closed system)}$$

and at constant temperature the equilibrium shifts with pressure according to

$$\left(\frac{\partial \xi_{\text{eq}}}{\partial p}\right)_T = -\frac{\Delta_{\text{r}} V}{\left(\dfrac{\partial^2 G}{\partial \xi^2}\right)_{T,p}}$$

<div align="right">(11.9.9)
(closed system)</div>

Because the partial second derivative $(\partial^2 G/\partial \xi^2)_{T,p}$ is positive, Eqs. 11.9.8 and 11.9.9 show that $(\partial \xi_{\text{eq}}/\partial T)_p$ and $\Delta_{\text{r}} H$ have the same sign, whereas $(\partial \xi_{\text{eq}}/\partial p)_T$ and $\Delta_{\text{r}} V$ have opposite signs.

These statements express the application to temperature and pressure changes of what is known as *Le Chatelier's principle*: When a change is made to a closed system at equilibrium, the equilibrium shifts in the direction that tends to oppose the change. Here are two examples.

1. It is easy to misuse or to be misled by Le Chatelier's principle. Consider the solution process $B^*(s) \rightarrow B(sln)$ for which $(\partial \xi_{\text{eq}}/\partial T)_p$, the rate of change of solubility with T, has the same sign as the molar differential enthalpy of solution $\Delta_{\text{sol}} H$ at saturation. The sign of $\Delta_{\text{sol}} H$ at saturation may be different from the sign of the molar *integral* enthalpy of solution, $\Delta H_{\text{m}}(sol)$. This is the situation for the dissolution of sodium acetate shown in Fig. 11.9. The equilibrium position (saturation) with one kilogram of water is at $\xi_{\text{sol}} \approx 15$ mol, indicated in the figure by an open circle. At this position, $\Delta_{\text{sol}} H$ is positive and $\Delta H_{\text{m}}(sol)$ is negative. So, despite the fact that the dissolution of 15 moles of sodium acetate in one kilogram of water to form a saturated solution is an exothermic process, the solubility of sodium acetate actually *increases* with increasing temperature, contrary to what one might predict from Le Chatelier's principle (L. K. Brice, *J. Chem. Educ.*, **60**, 387–389, 1983).

   Another kind of change for which Le Chatelier's principle gives an incorrect prediction is the addition of an inert gas to a gas mixture of constant volume. Adding the inert gas at constant V increases the pressure, but has little effect on the equilibrium position of a gas-phase reaction regardless of the value of $\Delta_{\text{r}} V$. This is because the inert gas affects the activities of the reactants and products only slightly, and not at all if the gas mixture is ideal, so there is little or no effect on the value of Q_{rxn}. (Note that the dependence of ξ_{eq} on p expressed by Eq. 11.9.9 does not apply to an open system.)