

A quantitative approach to Le Chatelier's principle

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Here we will try and give a quantitative description of yet another phenomenon which you have used extensively in a qualitative manner: the principle of Le Chatelier.

It is fairly easy to show how a change in temperature or pressure affects the equilibrium value of the extent of a reaction. We need to only determine the sign of $(\partial\xi_e/\partial T)_p$ and $(\partial\xi_e/\partial p)_T$, where ξ_e is the equilibrium extent of the reaction. We begin by writing the identity

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \Delta_r G.$$

Because $(\partial G/\partial \xi)_{T,p}$ is itself a function of T, p , and ξ , we may write the total differential expression,

$$d\left(\frac{\partial G}{\partial \xi}\right) = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial \xi}\right) dT + \frac{\partial}{\partial p}\left(\frac{\partial G}{\partial \xi}\right) dp + \frac{\partial}{\partial \xi}\left(\frac{\partial G}{\partial \xi}\right) d\xi$$

We will denote $\frac{\partial}{\partial \xi}\left(\frac{\partial G}{\partial \xi}\right)$ by G'' . Using the first equation the total differential becomes

$$d\left(\frac{\partial G}{\partial \xi}\right) = \left(\frac{\partial \Delta_r G}{\partial T}\right) dT + \left(\frac{\partial \Delta_r G}{\partial p}\right) dp + G'' d\xi.$$

The temperature, $\left(\frac{\partial G}{\partial T}\right)_p$, and pressure coefficient, $\left(\frac{\partial G}{\partial p}\right)_T$ are known to be $-\Delta S$ and ΔV respectively, which is made use of now. This results in

$$d\left(\frac{\partial G}{\partial \xi}\right) = -\Delta_r S dT + \Delta_r V dp + G'' d\xi.$$

We insist that variations in temperature, pressure, and advancement of reaction all occur while keeping the reaction in equilibrium, resulting in the left hand side of the above expression being zero, because that is after all the condition for equilibrium. Moreover, at equilibrium $\Delta_r G = 0$ implying that $\Delta_r S = \Delta_r H/T$, so the equation becomes

$$0 = -\left(\frac{\Delta_r H}{T}\right) (dT)_{\text{eq}} + \Delta_r V (dp)_{\text{eq}} + G''_{\text{eq}} (d\xi_{\text{eq}}).$$

At equilibrium, the variation of G with ξ is at a minimum which implies that G''_{eq} is positive.

At constant pressure, $dp = 0$, and hence we obtain

$$\left(\frac{\partial \xi}{\partial T}\right)_p = \frac{\Delta_r H}{T G''_{\text{eq}}}.$$

And similarly for a pressure variation at constant temperature, we have

$$\left(\frac{\partial \xi}{\partial p}\right)_T = -\frac{\Delta_r V}{G''_{\text{eq}}}.$$

These two equations are quantitative statements of the principle of Le Chatelier: they describe the dependence of the extent of the reaction at equilibrium on temperature and pressure. For example, the sign of $\left(\frac{\partial \xi}{\partial T}\right)_p$ depends on the sign of $\Delta_r H$ because, as already remarked, G'' is positive at equilibrium. If the reaction is endothermic, $\Delta_r H$ is positive, then an increase in temperature increases the extent of the reaction. Similarly, the sign of $\left(\frac{\partial \xi}{\partial p}\right)_T$ depends on $\Delta_r V$. If ΔV is $-$, the product volume is less than the reactant volume and an increase in pressure shifts the equilibrium to the right because $\left(\frac{\partial \xi}{\partial p}\right)_T$ is positive.

The principle of Le Chatelier may thus be stated as follows: If the external constraints under which an equilibrium is established are changed, the equilibrium will shift in such a way to moderate the effect of the change.

If, for example, the volume of a nonreactive system is decreased by a specified amount, the pressure rises correspondingly. In a reactive system, the equilibrium shifts to the low volume side, so the pressure increment is less than in the nonreactive case. The response of the system is moderated by the shift in equilibrium position.

Similarly, if we extract a fixed quantity of heat from a nonreactive system, the temperature decreases by a definite amount. In a reactive system, withdrawing the same amount of heat will not produce as large a decrease in temperature because the equilibrium shifts to the low enthalpy side. This implies that the apparent heat capacity of a reactive system is larger than that of a nonreactive one.