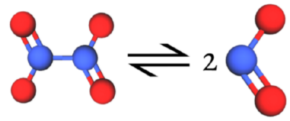
13.11: The Effect of a Change in Temperature

In a chemical equilibrium there is almost always a difference in energy, and hence in enthalpy, between the reactants and the products. The thermochemical equation for dissociation of N_2O_4 for example, is

$$\mathrm{N_2O_4}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$$



$$\Delta H_m = 54.8 \text{ kJ mol}^{-1}$$

Because of this enthalpy difference, any shift in the equilibrium toward further dissociation will result in the absorption of heat energy and a momentary decrease in temperature. Conversely, a shift in the reverse direction will cause a small rise in temperature. If we increase the temperature of a mixture of N_2O_4 and NO_2, the mixture should respond in such a way as to oppose the rise in temperature.

This can happen if some N_2O_4 in the mixture dissociates, since the resulting absorption of energy will produce a cooling effect. We would therefore expect that by raising the temperature of the equilibrium mixture, we would shift the equilibrium in favor of dissociation. Indeed we see in the result of Example 3 from Calculating the Extent of a Reaction that raising the temperature from 200 to 600 K changes an equilibrium mixture which is almost pure N_2O_4 into an equilibrium mixture which is almost pure NO_2.

In the general case, if we raise the temperature of any mixture of species which are in chemical equilibrium with each other, Le Chatelier's principle tells us that we will shift the equilibrium in the direction of those species with the higher energy. Thus, if the reaction is *endothermic*, as in the dissociation just discussed, raising the temperature will swing the equilibrium toward the *products*, and the value of the equilibrium constant K_c will increase with temperature.

Conversely, if the reaction is *exothermic*, a rise in temperature will favor the *reactants*, and K_c will get smaller as the temperature increases. We can also turn the argument around. If we find a reaction for which K_c increases with temperature, we know immediately that the reaction must be endothermic. Conversely, if K_c decreases as temperature increases, the reaction must be exothermic.