

## 21.1: Temperature Dependence of Equilibrium Constants - the van't Hoff Equation

The value of  $K_p$  is independent of pressure, although the composition of a system at equilibrium may be very much dependent on pressure. Temperature dependence is another matter. Because the value of  $\Delta G_{rxn}^o$  is dependent on temperature, the value of  $K_p$  is as well. The form of the temperature dependence can be taken from the definition of the Gibbs function. At constant temperature and pressure

$$\frac{\Delta G_{T_2}^o}{T_2} - \frac{\Delta G_{T_1}^o}{T_1} = \Delta H^o \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Substituting

$$\Delta G^o = -RT \ln K$$

For the two values of  $\Delta G^o$  and using the appropriate temperatures, yields

$$\frac{-RT_2 \ln K_2}{T_2} - \frac{-RT_1 \ln K_1}{T_1} = \Delta H^o \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

And simplifying the expression so that only terms involving  $K$  are on the left and all other terms are on the right results in the **van 't Hoff equation**, which describes the temperature dependence of the equilibrium constant.

$$\ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H^o}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (21.1.1)$$

Because of the assumptions made in the derivation of the Gibbs-Helmholtz equation, this relationship only holds if  $\Delta H^o$  is independent of temperature over the range being considered. This expression also suggests that a plot of  $\ln(K)$  as a function of  $1/T$  should produce a straight line with a slope equal to  $-\Delta H^o/R$ . Such a plot is known as a **van 't Hoff plot**, and can be used to determine the reaction enthalpy.

### ✓ Example 21.1.1

A certain reaction has a value of  $K_p = 0.0260$  at  $25^\circ\text{C}$  and  $\Delta H_{rxn}^o = 32.4 \text{ kJ/mol}$ . Calculate the value of  $K_p$  at  $37^\circ\text{C}$ .

#### Solution

This is a job for the van 't Hoff equation!

- $T_1 = 298 \text{ K}$
- $T_2 = 310 \text{ K}$
- $\Delta H_{rxn}^o = 32.4 \text{ kJ/mol}$
- $K_1 = 0.0260$
- $K_2 = ?$

So Equation 21.1.1 becomes

$$\ln \left( \frac{K_2}{0.0260} \right) = -\frac{32400 \text{ J/mol}}{8.314 \text{ K/(mol K)}} \left( \frac{1}{310 \text{ K}} - \frac{1}{298 \text{ K}} \right)$$

$$K_2 = 0.0431$$

Note: the value of  $K_2$  **increased** with **increasing** temperature, which is what is expected for an **endothermic** reaction. An increase in temperature should result in an increase of product formation in the equilibrium mixture. But unlike a change in pressure, a change in temperature actually leads to a change in the value of the equilibrium constant!

### ✓ Example 21.1.2

Given the following average bond enthalpies for P–Cl and Cl–Cl bonds, predict whether or not an increase in temperature will lead to a larger or smaller degree of dissociation for the reaction



X-Y	D(X-Y) (kJ/mol)
P-Cl	326
Cl-Cl	240

### Solution

The estimated reaction enthalpy is given by the total energy expended breaking bonds minus the energy recovered by the formation of bonds. Since this reaction involves breaking two P-Cl bonds (costing 652 kJ/mol) and the formation of one Cl-Cl bond (recovering 240 kJ/mol), it is clear that the reaction is endothermic (by approximately 412 kJ/mol). As such, an increase in temperature should increase the value of the equilibrium constant, causing the degree of dissociation to be increased at the higher temperature.

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