20

Temperature Dependence of K

20.1 Effect of a Change in Temperature

Learning Objectives

• Predict the response of a stressed equilibrium using Le Châtelier's principle

Consistent with the law of mass action, an equilibrium stressed by a change in concentration will shift to re-establish equilibrium without any change in the value of the equilibrium constant, *K*. When an equilibrium shifts in response to a temperature change, however, it is re-established with a different relative composition that exhibits a different value for the equilibrium constant.

To understand this phenomenon, consider the elementary reaction

A≓B

Since this is an elementary reaction, the rates laws for the forward and reverse may be derived directly from the balanced equation's stoichiometry:

$$rate_f = k_f [A]$$
$$rate_r = k_r [B]$$

When the system is at equilibrium,

 $rate_r = rate_f$

Substituting the rate laws into this equality and rearranging gives

$$k_f [A] = k_r [B]$$
$$\frac{[B]}{[A]} = \frac{k_f}{k_r} = K_c$$

The equilibrium constant is seen to be a mathematical function of the rate constants for the forward and reverse reactions. Since the rate constants vary with temperature as described by the Arrhenius equation, is stands to reason that the equilibrium constant will likewise vary with temperature (assuming the rate constants are affected to different extents by the temperature change). For more complex reactions involving multistep reaction mechanisms, a similar but more complex mathematical relation exists between the equilibrium constant and the rate constants of the steps in the mechanism. Regardless of how complex the reaction may be, the temperature-dependence of its equilibrium constant persists.

Predicting the shift an equilibrium will experience in response to a change in temperature is most conveniently accomplished by considering the enthalpy change of the reaction. For example, the decomposition of dinitrogen tetroxide is an endothermic (heat-consuming) process:

$$N_2 O_4(g) \rightleftharpoons 2NO_2(g)$$
 $\Delta H = 57.20 \text{ kJ}$

For purposes of applying Le Chatelier's principle, heat (q) may be viewed as a reactant:

heat + N₂O₄(g)
$$\rightleftharpoons$$
 2NO₂(g)

Raising the temperature of the system is akin to increasing the amount of a reactant, and so the equilibrium will shift to the right. Lowering the system temperature will likewise cause the equilibrium to shift left. For exothermic processes, heat is viewed as a product of the reaction and so the opposite temperature dependence is observed.

20.2 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 K_p is dependent on temperature, the value of K is as well. The form of the temperature dependence can be taken from the definition of the Gibbs function. At constant temperature and pressure

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

Substituting

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

For the two values of $\ln(K)$ and using the appropriate temperatures, yields

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

And simplifying the expression so that only terms involving $-\Delta H^o / R$ 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.



Because of the assumptions made in the derivation of the Gibbs-Helmholtz equation, this relationship only holds if $\Delta H_{rxm}^o = 32.4 kJ / mol$ is independent of temperature over the range being considered. This expression also suggests that a plot of $\Delta H_{rxm}^o = 32.4 kJ / mol$ as a function of

$$\ln\left(\frac{K_2}{0.0260}\right) = -\frac{32400J/mol}{8.314K/(molK)}\left(\frac{1}{310K} - \frac{1}{298K}\right)$$
 should produce a straight line with a slope equal

$$K_2 = 0.0431$$

to P-Cl. Such a plot is known as a **van 't Hoff plot**, and can be used to determine the reaction enthalpy.

Example 20.2.1

A certain reaction has a value of $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ at 25 °C and $\Delta H^o_{rxm} = 32.4 kJ / mol$. Calculate the value of $\Delta H^o_{rxm} = 32.4 kJ / mol$ at 37 °C.

✓ Answer

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

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

$$K_2 = 0.0431$$

- K₁ = 0.0260
- K₂ = ?

So Equation $\boldsymbol{P} = \boldsymbol{C}\boldsymbol{l}$ becomes

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

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 20.2.2

Given the following average bond enthalpies for $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ 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

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

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

✓ Answer

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.

20.2.3 Van 't Hoff plot

For a <u>reversible reaction</u>, the equilibrium constant can be measured at a variety of temperatures. This data can be plotted on a graph with $\ln K_{eq}$ on the *y*-axis and 1/T on the *x-axis*. The data should have a linear relationship, the equation for which can be found by fitting the data using the linear form of the Van 't Hoff equation

$$\ln K_{
m eq} = -rac{\Delta_r H^{\ominus}}{RT} + rac{\Delta_r S^{\ominus}}{R}.$$

This graph is called the "Van 't Hoff plot" and is widely used to estimate the <u>enthalpy</u> and <u>entropy</u> of a <u>chemical reaction</u>. From this plot, $-\Delta_r H/R$ is the slope, and $\Delta_r S/R$ is the intercept of the linear fit.

By measuring the <u>equilibrium constant</u>, K_{eq} , at different temperatures, the Van 't Hoff plot can be used to assess a reaction when the temperature changes.

Knowing the slope and intercept from the Van 't Hoff plot, the enthalpy, and entropy of a reaction can be easily obtained using

$\Delta_r H = -R imes ext{slope}, \ \Delta_r S = R imes ext{intercept}.$

The Van 't Hoff plot can be used to quickly determine the enthalpy of a chemical reaction both qualitatively and quantitatively. This change in enthalpy can be positive or negative, leading to two major forms of the Van 't Hoff plot.

20.2.4 Endothermic reactions

For an <u>endothermic reaction</u>, heat is absorbed, making the net enthalpy change positive. Thus, according to the definition of the slope:

$$ext{slope} = -rac{\Delta_r H}{R},$$

When the reaction is <u>endothermic</u>, $\Delta_r H > 0$ (and the <u>gas constant</u> R > 0), so

$$ext{slope} = -rac{\Delta_r H}{R} < 0.$$

Thus, for an endothermic reaction, the Van 't Hoff plot should always have a negative slope.

Figure 21.1

Van 't Hoff plot for an endothermic reaction



20.2.5 Exothermic reactions

For an <u>exothermic reaction</u>, heat is released, making the net enthalpy change negative. Thus, according to the definition of the slope:

$$ext{slope} = -rac{\Delta_r H}{R},$$

For an <u>exothermic</u> reaction $\Delta_r H < 0$, so

$$ext{slope} = -rac{\Delta_r H}{R} > 0.$$

Thus, for an exothermic reaction, the Van 't Hoff plot should always have a positive slope.

figure 20.2

Van 't Hoff plot for an exothermic reaction



20.2.6 Error propagation

At first glance, using the fact that $\Delta_r G^{\ominus} = -RT \ln K = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$ it would appear that two measurements of K would suffice to be able to obtain an accurate value of $\Delta_r H^{\ominus}$:

$$\Delta_r H^{\ominus} = R rac{\ln K_1 - \ln K_2}{rac{1}{T_2} - rac{1}{T_1}},$$

where K_1 and K_2 are the equilibrium constant values obtained at temperatures T_1 and T_2 respectively. However, the <u>precision</u> of $\Delta_r H^{\circ}$ values obtained in this way is highly dependent on the precision of the measured equilibrium constant values.

The use of <u>error propagation</u> shows that the error in $\Delta_r H^{\odot}$ will be about 76 kJ/mol times the experimental uncertainty in (ln K_1 – ln K_2), or about 110 kJ/mol times the uncertainty in the ln K values. Similar considerations apply to the entropy of reaction obtained from $\Delta_r S^{\odot} = 1/T(\Delta H^{\odot} + RT \ln K)$.

Notably, when equilibrium constants are measured at three or more temperatures, values of $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$ are often obtained by <u>straight-line fitting</u>.

The expectation is that the error will be reduced by this procedure, although the assumption that the enthalpy and entropy of reaction are constant may or may not prove to be correct. If there is significant temperature dependence in either or both quantities, it should manifest itself in nonlinear behavior in the Van t'Hoff plot; however, more than three data points would presumably be needed in order to observe this.

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