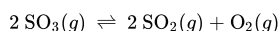


## 15.4: Expressing the Equilibrium Constant in Terms of Pressure

So far, we have expressed the equilibrium constant only in terms of the *concentrations* of the reactants and products. For gaseous reactions, the partial pressure of a particular gas is proportional to its concentration. Therefore, we can also express the equilibrium constant in terms of the *partial pressures* of the reactants and products. Consider the gaseous reaction:



From this point on, we designate  $K_c$  as the equilibrium constant with respect to concentration in molarity. For the reaction just given, we can express  $K_c$  using the law of mass action:

$$K_c = \frac{[\text{SO}_2]^2 [\text{O}_2]}{[\text{SO}_3]^2}$$

We now designate  $K_p$  as the equilibrium constant with respect to partial pressures in atmospheres. *The expression for  $K_p$  takes the form of the expression for  $K_c$ , except that we use the partial pressure of each gas in place of its concentration.* For the  $\text{SO}_3$  reaction, we write  $K_p$  as:

$$K_p = \frac{(P_{\text{SO}_2})^2 P_{\text{O}_2}}{(P_{\text{SO}_3})^2}$$

where  $P_A$  is the partial pressure of gas A in units of atmospheres.

Because the partial pressure of a gas in atmospheres is not the same as its concentration in molarity, the value of  $K_p$  for a reaction is not necessarily equal to the value of  $K_c$ . However, as long as the gases are behaving ideally, we can derive a relationship between the two constants. The concentration of an ideal gas A is the number of moles of A ( $n_A$ ) divided by its volume ( $V$ ) in liters:

$$[A] = \frac{n_A}{V}$$

From the ideal gas law, we can relate the quantity  $n_A/V$  to the partial pressure of A as follows:

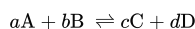
$$\begin{aligned} P_A V &= n_A R T \\ P_A &= \frac{n_A}{V} R T \end{aligned}$$

Since  $[A] = n_A/V$ , we can write:

[15.1]

$$P_A = [A] R T \quad \text{or} \quad [A] = \frac{P_A}{R T}$$

Now consider the following general equilibrium chemical equation:



According to the law of mass action, we write  $K_c$  as follows:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Substituting  $[X] = P_X/RT$  for each concentration term, we get:

$$K_c = \frac{\left(\frac{P_C}{RT}\right)^c \left(\frac{P_D}{RT}\right)^d}{\left(\frac{P_A}{RT}\right)^a \left(\frac{P_B}{RT}\right)^b} = \frac{P_C^c P_D^d \left(\frac{1}{RT}\right)^{c+d}}{P_A^a P_B^b \left(\frac{1}{RT}\right)^{a+b}} = \frac{P_C^c P_D^d}{P_A^a P_B^b} \left(\frac{1}{RT}\right)^{c+d-(a+b)}$$

$$= K_p \left(\frac{1}{RT}\right)^{c+d-(a+b)}$$

Rearranging,

$$K_p = K_c (RT)^{c+d-(a+b)}$$

Finally, if we let  $\Delta n = c + d - (a + b)$  which is the sum of the stoichiometric coefficients of the gaseous products minus the sum of the stoichiometric coefficients of the gaseous reactants, we get the following general result:

[15.2]

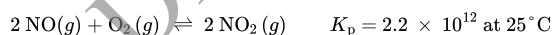
$$K_p = K_c (RT)^{\Delta n}$$

Notice that if the total number of moles of gas is the same after the reaction as before,  $\Delta n = 0$  and  $K_p$  is equal to  $K_c$ .

In the equation  $K_p = K_c (RT)^{\Delta n}$  the quantity  $\Delta n$  represents the difference between the number of moles of gaseous products and gaseous reactants.

### Example 15.3 Relating $K_p$ and $K_c$

Nitrogen monoxide, a pollutant in automobile exhaust, is oxidized to nitrogen dioxide in the atmosphere according to the equation:



Find  $K_c$  for this reaction.

**SORT** You are given  $K_p$  for the reaction and asked to find  $K_c$ .

**GIVEN:**  $K_p = 2.2 \times 10^{12}$

**FIND:**  $K_c$

**STRATEGIZE** Use Equation 15.2 to relate  $K_p$  and  $K_c$ .

**EQUATION**  $K_p = K_c (RT)^{\Delta n}$

**SOLVE** Solve the equation for  $K_c$ .

Calculate  $\Delta n$ .

Substitute the required quantities to calculate  $K_c$ . The temperature must be in kelvins. The units are dropped when reporting  $K_c$  as described below.

**SOLUTION**

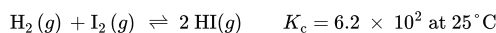
$$\begin{aligned}
 K_c &= \frac{K_p}{(RT)^{\Delta n}} \\
 \Delta n &= 2 - 3 = -1 \\
 K_c &= \frac{2.2 \times 10^{12}}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298 \text{ K}\right)^{-1}} \\
 &= 5.4 \times 10^{13}
 \end{aligned}$$

**CHECK** The most straightforward way to check this answer is to substitute it back into Equation 15.2 and confirm that you get the original value for  $K_p$ .

$$\begin{aligned}
 K_p &= K_c (RT)^{\Delta n} \\
 &= 5.4 \times 10^{13} \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298 \text{ K}\right)^{-1} \\
 &= 2.2 \times 10^{12}
 \end{aligned}$$

### FOR PRACTICE 15.3

Consider the following reaction and corresponding value of  $K_c$ :



What is the value of  $K_p$  at this temperature?

## Units of $K$

Throughout this book, we express concentrations and partial pressures within the equilibrium constant expression in units of molarity and atmospheres, respectively. When expressing the value of the equilibrium constant, however, we have not included the units. Formally, the values of concentration or partial pressure that we substitute into the equilibrium constant expression are ratios of the concentration or pressure to a reference concentration (exactly 1 M) or a reference pressure (exactly 1 atm).

For example, within the equilibrium constant expression, a pressure of 1.5 atm becomes:

$$\frac{1.5 \text{ atm}}{1 \text{ atm}} = 1.5$$

Similarly, a concentration of 1.5 M becomes:

$$\frac{1.5 \text{ M}}{1 \text{ M}} = 1.5$$

As long as concentration units are expressed in molarity for  $K_c$  and pressure units are expressed in atmospheres for  $K_p$ , we skip this formality and enter the quantities directly into the equilibrium expression, dropping their corresponding units.

### Conceptual Connection 15.3 The Relationship between $K_p$ and $K_c$

Interactive

*Not for Distribution*