Two examples of an equilibrium constant dealt with in other sections, namely:

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

for the reaction

\[ \text{cis-C}_2\text{H}_2\text{F}_2 \rightleftharpoons \text{trans-C}_2\text{H}_2\text{F}_2 \]

In the equation above, notice that both sides have the same molecular formula, yet in the image below, the elements involved are arranged differently. These molecules are called isomers and to learn more about them, check out the following site: [https://www.thoughtco.com/geometric-isomerism-cis-and-trans-608702](https://www.thoughtco.com/geometric-isomerism-cis-and-trans-608702).
\[K_c = \frac{[\text{ NO}_2]^2}{[\text{ N}_2\text{O}_4]}\]

for the reaction
\[\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2\]

In the equation above, we see the decomposition of N\textsubscript{2}O\textsubscript{4} (the clear gas pictured below) into NO\textsubscript{2}, which is the brownish red gas seen below. As you can see in the molecular structure above, this decomposition of N\textsubscript{2}O\textsubscript{4} occurs when the middle bond holding N\textsubscript{2}O\textsubscript{4} together is broken, leaving two NO\textsubscript{2} molecules. For more information on this specific equilibrium, check out the page on *The Effect of a Change in Temperature*.

Both the trans-cis transition of C\textsubscript{2}H\textsubscript{2}F\textsubscript{2} and the decomposition of N\textsubscript{2}O\textsubscript{4} are particular examples of a more general law governing chemical equilibrium in gases. If we write an equation for a gaseous equilibrium in general in the form
\[aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g) \quad \text{\eqref{1}}\]
then the equilibrium constant defined by the equation
\[K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{\eqref{2}}\]
is found to be a constant quantity depending only on the temperature and the nature of the reaction. This general result is called the **law of chemical equilibrium**, or the **law of mass action**.

Example \( \PageIndex{1} \): Equilibrium Constant

Write expressions for the equilibrium constant for the following reactions:

a. \[2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)\]
b. \[\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)\]
c. \[\text{O}_2(g) + 4\text{HCl}(g) \rightleftharpoons 2\text{H}_2\text{O}(g) + 2\text{Cl}_2(g)\]
Solution

a. \[ K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} \]

b. \[ K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \]

c. \[ K_c = \frac{[\text{H}_2\text{O}]^2[\text{Cl}_2]^2}{[\text{O}_2][\text{HCl}]^4} \]

Example (PageIndex(2)): Methane and Steam Equilibrium Constant

A mixture containing equal concentrations of methane and steam is passed over a nickel catalyst at 1000 K. The emerging gas has the composition [CO] = 0.1027 mol dm\(^{-3}\), [H\(_2\)] = 0.3080 mol dm\(^{-3}\), and [CH\(_4\)] = [H\(_2\)O] = 0.8973 mol dm\(^{-3}\). Assuming this mixture is at equilibrium, calculate the equilibrium constant \(K_c\) for the reaction

\[ \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g) \]

Solution

The equilibrium constant is given by the following equation:

\[ K_c = \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]} = \frac{0.1027 \text{ mol dm}^{-3} \times (0.3080 \text{ mol dm}^{-3})^3}{0.8973 \text{ mol dm}^{-3} \times 0.8973 \text{ mol dm}^{-3}} \]

\[ = 3.727 \times 10^{-3} \text{ mol}^2 \text{ dm}^{-6} \]

Note: The yield of H\(_2\) at this temperature is quite poor. In the commercial production of H\(_2\) from natural gas, the reaction is run at a somewhat higher temperature where the value \(K_c\) is larger.

As the above example shows, the equilibrium constant \(K_c\) is not always a dimensionless quantity. In general it has the units (mol dm\(^{-3}\))\(^{\Delta n}\), where \(\Delta n\) is the increase in the number of molecules in the equation. In the above case \(\Delta n = 2\), since 4 molecules (3 H\(_2\) and 1CO) have been produced from 2 molecules (CH\(_4\) and H\(_2\)O). Only if \(\Delta n = 0\), as is the case for the cis-trans isomerization considered above, is the equilibrium constant a dimensionless quantity.

We can also apply the equilibrium law to reactions which involve pure solids and pure liquids as well as gases. We find in such cases that as long as some solid or liquid is present, the actual amount does not affect the position of equilibrium. Accordingly, only the concentrations of gaseous species are included in the expression for the equilibrium constant. For example, the equilibrium constant for the reaction

\[ \text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g) \]

Notice below the molecular representation of the above reaction, with the ionic structure of CaCO\(_3\) 'breaking apart' to form the simpler ionic structure CaO as well as gaseous CO\(_2\).
is given by the expression
\[
\text{K}_c = [\text{CO}_2]
\]
in which only the concentration of the gas appears. Equation (4) suggests that if we heat CaCO₃ to a high temperature so that some of it decomposes, the concentration of CO₂ at equilibrium will depend only on the temperature and will not change if the ratio of amount of solid CaCO₃ to amount of solid CaO is altered. Experimentally this is what is observed.

Example \(\PageIndex{3}\) : Equilibrium Constant Expression

Write expressions for the equilibrium constants for the following reactions:

a. \[
\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g)
\]
b. \[
\text{C}(s) + \text{CO}_2(g) \rightleftharpoons 2\text{CO}(g)
\]
c. \[
\text{Fe}_3\text{O}_4(s) + \text{H}_2(g) \rightleftharpoons 3\text{FeO}(s) + \text{H}_2\text{O}(g)
\]

Solution

Since only gaseous species need be included, we obtain

a. \[
\text{K}_{c} = \frac{[\text{ CO }] [\text{ H}_2]}{[\text{ H}_2\text{O}]}
\]
b. \[
\text{K}_{c} = \frac{[\text{ CO }]^2}{[\text{ CO}_2]}
\]
c. \[
\text{K}_{c} = \frac{[\text{ H}_2\text{O}]}{[\text{ H}_2]}
\]

The equilibrium law can be shown experimentally to apply to dilute liquid solutions as well as to mixtures of gases, and the equilibrium-constant expression for a solution reaction can be obtained in the same way as for a gas-phase reaction. In solution only the concentrations of species in the liquid phase need be included. In some solution reactions, the solvent may be a reactant or product. Acetic acid, for example, reacts as follows when it dissolves in water:
\[
\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+
\]

Notice in the figure below how the white hydrogen attached to the red oxygen on the acetic acid molecule is transferred to water, forming acetate (acetic acid minus a hydrogen) and a hydronium ion. Symbolically in the equation above, we can see this same transfer, except hydrogen is represented as an H rather than a white ball.
As long as the solution is dilute, however, the concentration of the solvent is hardly affected by addition of solutes, even if they react with it. (The concentration of pure water may be calculated from the density:

\[
c_{\text{H}_2\text{O}} = \frac{1.0 \text{ g}}{1 \text{ cm}^3} \times \frac{10^3 \text{ cm}^3}{1 \text{ dm}^3} \times \frac{1 \text{ mol}}{18.0 \text{ g}} = 55.5 \text{ mol dm}^{-3}
\]

Even if 0.1 mol dm$^{-3}$ of acetic acid were added, the concentration of water would be affected by much less than 1 percent.)

Because the concentration of solvent remains essentially constant, it is usually incorporated into the equilibrium constant. Following the usual rules, Equation (5) would give

\[
K_a = K_c \times 55.5 \text{ mol dm}^{-3} = \frac{[\text{ CH}_3\text{COO}^-][\text{ H}_3\text{O}^+]}{[\text{ CH}_3\text{COOH}][\text{ H}_2\text{O}]}\]

This can be rearranged to

\[
\text{K}_a = \frac{[\text{ CH}_3\text{COO}^-][\text{ H}_3\text{O}^+]}{[\text{ CH}_3\text{COOH}][\text{ H}_2\text{O}]}
\]

Thus the concentration of water is conventionally included in the equilibrium constant $K_a$ for a reaction in aqueous solution. Since it applies to a weak acid, $K_a$ is called an acid constant. (The $a$ stands for acid.) Other equilibrium constants which contain a constant concentration in this way are the base constant, $K_b$, for ionization of a weak base and the solubility product constant, $K_{sp}$, for dissolution of a slightly soluble compound.

Example 4: Ionic Equilibria

Write out expressions for the equilibrium constants for the following ionic equilibria in dilute aqueous solution:

a. \[
\text{HF}(aq) + \text{H}_2\text{O} \rightleftharpoons \text{F}^-(aq) + \text{H}_3\text{O}^+(aq)
\]

b. \[
\text{H}_2\text{O} + \text{NH}_3(aq) \rightleftharpoons \text{OH}^-(aq) + \text{NH}_4^+(aq)
\]

c. \[
\text{H}_2\text{O} + \text{CO}_3^{2-}(aq) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq)
\]

d. \[
\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq)
\]

Solution

We leave out the concentration of H$_2$O in the first three examples and the concentration of solid BaSO$_4$ in the fourth.

a. \[
\text{K}_a = \frac{[\text{ F}^-][\text{ H}_3\text{O}^+]}{[\text{ HF}][\text{ H}_2\text{O}]}
\]

b. \[
\text{K}_b = \frac{[\text{ NH}_4^+][\text{ OH}^-]}{[\text{ NH}_3][\text{ H}_2\text{O}]}
\]

c. \[
\text{K}_b = \frac{[\text{ HCO}_3^-][\text{ OH}^-]}{[\text{ CO}_3^{2-}][\text{ H}_2\text{O}]}
\]

d. \[
\text{K}_{sp} = \frac{[\text{ Ba}^{2+}][\text{ SO}_4^{2-}]}{[\text{ BaSO}_4]}
\]
Example 

Measurements of the conductivities of acetic acid solutions indicate that the fraction of acetic acid molecules converted to acetate and hydronium ions is

a. 0.0296 at a concentration of 0.020 00 mol dm\(^{-3}\)
b. 0.5385 at a concentration of 2.801 \times 10^{-5} \text{ mol dm}^{-3}

Use these data to calculate the equilibrium constant for Equation (5) at each concentration.

Solution

Consider first 1 dm\(^3\) of solution a. This originally contained 0.02 mol CH\(_3\)COOH of which the fraction 0.0296 has ionized. Thus \((1 - 0.0296)\times 0.02\) mol undissociated CH\(_3\)COOH is left, while \(0.0296 \times 0.02\) mol H\(_3\)O\(^+\) and CH\(_3\)COO\(^-\) have been produced. In tabular form

<table>
<thead>
<tr>
<th>Substance</th>
<th>Original Amount</th>
<th>Amount Produced</th>
<th>Equilibrium Amount</th>
<th>Equilibrium Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)COOH</td>
<td>0.02 mol</td>
<td>-0.0296\times0.02 mol</td>
<td>(0.02-0.000 592) mol</td>
<td>0.0194 mol dm(^{-3})</td>
</tr>
<tr>
<td>H(_3)O(^+)</td>
<td>0 mol</td>
<td>+0.0296\times0.02 mol</td>
<td>0.000 592 mol</td>
<td>5.92\times10^{-4} mol dm(^{-3})</td>
</tr>
<tr>
<td>CH(_3)COO(^-)</td>
<td>0 mol</td>
<td>+0.0296\times0.02 mol</td>
<td>0.000 592 mol</td>
<td>5.92\times10^{-4} mol dm(^{-3})</td>
</tr>
</tbody>
</table>

Substituting into the expression for \(K_a\) gives

\[
K_a = \frac{[\text{ CH}_3\text{COO}^-][\text{ H}_3\text{O}^+]}{[\text{ CH}_3\text{COOH}]} = \frac{(5.92 \times 10^{-4} \text{ mol dm}^{-3})^2}{0.0194 \text{ mol dm}^{-3}} = 1.81 \times 10^{-5} \text{ mol dm}^{-3}
\]

A similar calculation on the second solution yields

\[
K_a = \frac{(1.5083 \times 10^{-5} \text{ mol dm}^{-3})^2}{1.2926 \times 10^{-5} \text{ mol dm}^{-3}} = 1.760 \times 10^{-5} \text{ mol dm}^{-3}
\]

Note

The two values of the equilibrium constant are only in approximate agreement. In more concentrated solutions the agreement is worse. If the concentration is 1 mol dm\(^{-3}\), for instance, \(K_a\) has the value \(1.41 \times 10^{-5} \text{ mol dm}^{-3}\). This is the reason for our statement that the equilibrium law applies to dilute solutions.
Acknowledgements

tolview.org was used to create the molecular representations found on this webpage. Check out the site at the following link: Molview.