Learning Objectives

• How to figure out in which direction a reaction will go (i.e. towards making product, or more reactant)
• Calculating equilibrium concentrations. This may involve knowing equilibrium values for some of the reactants and products and determining the concentration of an unknown.
• Alternatively, we may be provided with the starting concentrations of reactants and products and may be asked to find the equilibrium concentrations

Your ability to interpret the numerical value of a quantity in terms of what it means in a practical sense is an essential part of developing a working understanding of Chemistry. This is particularly the case for equilibrium constants, whose values span the entire range of the positive numbers. Although there is no explicit rule, for most practical purposes you can say that equilibrium constants within the range of roughly 0.01 to 100 indicate that a chemically significant amount of all components of the reaction system will be present in an equilibrium mixture and that the reaction will be *incomplete* or “*reversible*”.

As an equilibrium constant approaches the limits of zero or infinity, the reaction can be increasingly characterized as a one-way process; we say it is “*complete*” or “*irreversible*”. The latter term must of course not be taken literally; the Le Châtelier principle still applies (especially insofar as temperature is concerned), but addition or removal of reactants or products will have less effect.

**Kinetically Hindered Reactions**

Although it is by no means a general rule, it frequently happens that reactions having very large equilibrium constants are kinetically hindered, often to the extent that the reaction essentially does not take place.

The examples in the following table are intended to show that numbers (values of $K$), no matter how dull they may look, do have practical consequences!

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$K$</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$</td>
<td>(5 \times 10^{-31}) at 25°C, 0.0013 at 2100°C</td>
<td>These two very different values of $K$ illustrate very nicely why reducing combustion-chamber temperatures in automobile engines is environmentally beneficial.</td>
</tr>
<tr>
<td>$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$</td>
<td>(7 \times 10^5) at 25°C, 56 at 1300°C</td>
<td>See the discussion of this reaction in the section on the Haber process.</td>
</tr>
</tbody>
</table>
\[ \text{\(H_2(g)\)} \rightleftharpoons 2 \text{\(H_{(g)}\)} \] 10^{-36} \text{ at 25°C,}\] 6 \times 10^{-5} \text{ at 5000°}

Dissociation of any stable molecule into its atoms is endothermic. This means that all molecules will decompose at sufficiently high temperatures.

\[ \text{\(H_2O_{(g)}\)} \rightleftharpoons \text{\(H_{2(g)}\)} + \frac{1}{2} \text{\(O_{2(g)}\)} \] 8 \times 10^{-41} \text{ at 25°C}

You won’t find water a very good source of oxygen gas at ordinary temperatures!

\[ \text{\(CH_3COOH_{(l)}\)} \rightleftharpoons \text{2\(H_2O_{(l)}\)} + \text{2\(C_{(s)}\)} \] \(K_c = 10^{13}\) at 25°C

This tells us that acetic acid has a great tendency to decompose to carbon, but nobody has ever found graphite (or diamonds!) forming in a bottle of vinegar. A good example of a super kinetically-hindered reaction!

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**Do Equilibrium Constants have Units?**

The equilibrium expression for the synthesis of ammonia

\[ \text{\(3\text{\(H_{(g)}\)} + \text{\(N_{2(g)}\)} \rightarrow \text{2\(NH_{3(g)}\)}\)} \tag{15.4.1} \]

can be expressed as

\[ \text{\(K_p = \dfrac{P^2_{NH_3}}{P_{N_2}P^3_{H_2}}\)} \tag{15.4.2} \]

or

\[ \text{\(K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}\)} \tag{15.4.3} \]

so \(\text{\(K_p\)}\) for this process would appear to have units of atm\(^{-1}\), and \(\text{\(K_c\)}\) would be expressed in mol\(^{-2}\) L\(^2\). And yet these quantities are often represented as being dimensionless. Which is correct? The answer is that both forms are acceptable. There are some situations (which you will encounter later) in which \(K\)'s must be considered dimensionless, but in simply quoting the value of an equilibrium constant it is permissible to include the units, and this may even be useful in order to remove any doubt about the units of the individual terms in equilibrium expressions containing both pressure and concentration terms. In carrying out your own calculations, however, there is rarely any real need to show the units.

Strictly speaking, equilibrium expressions do not have units because the concentration or pressure terms that go into them are really ratios having the forms \((n \text{ mol L}^{-1})/(1 \text{ mol L}^{-1})\) or \((n \text{ atm})/(1 \text{ atm})\) in which the unit quantity in the denominator refers to the standard state of the substance; thus the units always cancel out.
Strictly speaking, equilibrium expressions do not have units

For substances that are liquids or solids, the standard state is just the concentration of the substance within the liquid or solid, so for something like $\text{CaF}_2$, the term going into the equilibrium expression is $[\text{CaF}_2]/[\text{CaF}_2]$ which cancels to unity; this is the reason we don’t need to include terms for solid or liquid phases in equilibrium expressions. The subject of standard states would take us beyond where we need to be at this point in the course, so we will simply say that the concept is made necessary by the fact that energy, which ultimately governs chemical change, is always relative to some arbitrarily defined zero value which, for chemical substances, is the standard state.

Summary

The magnitude of the equilibrium constant, $K$, indicates the extent to which a reaction will proceed:

- If $K$ is a large number, it means that the equilibrium concentration of the products is large. In this case, the reaction as written will proceed to the right (resulting in an increase in the concentration of products)
- If $K$ is a small number, it means that the equilibrium concentration of the reactants is large. In this case, the reaction as written will proceed to the left (resulting in an increase in the concentration of reactants)

Knowing the value of the equilibrium constant, $K$, will allow us to determine: (1) the direction a reaction will proceed to achieve equilibrium and (2) the ratios of the concentrations of reactants and products when equilibrium is reached

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