Measuring and calculating equilibrium constants

Clearly, if the concentrations or pressures of all the components of a reaction are known, then the value of $K$ can be found by simple substitution. Observing individual concentrations or partial pressures directly may be not always be practical, however. If one of the components is colored, the extent to which it absorbs light of an appropriate wavelength may serve as an index of its concentration. Pressure measurements are ordinarily able to measure only the total pressure of a gaseous mixture, so if two or more gaseous products are present in the equilibrium mixture, the partial pressure of one may need to be inferred from that of the other, taking into account the stoichiometry of the reaction.

**Problem Example 1**

In an experiment carried out by Taylor and Krist (*J. Am. Chem. Soc.* 1941: 1377), hydrogen iodide was found to be 22.3% dissociated at 730.8°C. Calculate $K_c$ for $2 \text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$.

**Solution:**

No explicit molar concentrations are given, but we do know that for every $n$ moles of HI, $0.223n$ moles of each product is formed and $(1-0.233)n = 0.777n$ moles of HI remains. For simplicity, we assume that $n=1$ and that the reaction is carried out in a 1.00-L vessel, so that we can substitute the required concentration terms directly into the equilibrium expression.
Problem Example 2

Ordinary white phosphorus, P\(_4\), forms a vapor which dissociates into diatomic molecules at high temperatures:

\[ \text{P}_4(g) \rightarrow 2 \text{P}_2(g) \]

A sample of white phosphorus, when heated to 1000°C, formed a vapor having a total pressure of 0.20 atm and a density of 0.152 g L\(^{-1}\). Use this information to evaluate the equilibrium constant \(K_p\) for this reaction.

**Solution:** Before worrying about what the density of the gas mixture has to do with \(K_p\), start out in the usual way by laying out the information required to express \(K_p\) in terms of an unknown \(x\).

<table>
<thead>
<tr>
<th>(\text{P}_4)</th>
<th>(2 \text{P}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial moles:</td>
<td>1</td>
</tr>
<tr>
<td>moles at equilibrium:</td>
<td>(1 - x)</td>
</tr>
<tr>
<td>eq. mole fractions:</td>
<td>(\frac{1 - x}{1 + x})</td>
</tr>
<tr>
<td>eq. partial pressures:</td>
<td>(\left(\frac{1 - x}{1 + x}\right)\cdot P)</td>
</tr>
</tbody>
</table>

Expressing the equilibrium constant in terms of \(x\) gives

\[ K_p = \left(\frac{\text{P}_2}{\text{P}_4}\right) = \left(\frac{2x}{1-x}\right) \frac{(1-x)^2}{(1+x)^2} \]

Now we need to find the dissociation fraction \(x\) of \(\text{P}_4\), and at this point we hope you remember those gas laws that you were told you would be needing later in the course! The density of a gas is directly proportional to its molecular weight, so you need to calculate the densities of pure \(\text{P}_4\) and pure \(\text{P}_2\) vapors under the conditions of the experiment. One of these densities will be greater than 0.152 gL\(^{-1}\) and the other will be smaller; all you need to do is to find where the measured density falls in between the two limits, and you will have the dissociation fraction.

The molecular weight of phosphorus is 31.97, giving a molar mass of 127.9 g for \(\text{P}_4\). This mass must be divided by the volume to find the density; assuming ideal gas behavior, the volume of 127.9 g (1 mole) of \(\text{P}_4\) is given by \(RT/P\), which works out to 522 L (remember to use the absolute temperature here.) The density of pure \(\text{P}_4\) vapor under the conditions of the experiment is then

\[ d = \frac{m}{V} = \frac{128 \text{ g mol}^{-1}}{522 \text{ L mol}^{-1}} = 0.245 \text{ g L}^{-1}. \]

The density of pure \(\text{P}_2\) would be half this, or 0.122 g L\(^{-1}\). The difference between these two limiting densities is 0.123 g L\(^{-1}\), and the difference between the density of pure \(\text{P}_4\) and that of the equilibrium mixture is (0.245 – 0.152) g L\(^{-1}\) or 0.093 g L\(^{-1}\). The ratio 0.093 ÷ 0.123 = 0.76 is therefore the fraction of \(\text{P}_4\) that remains and its fractional dissociation is \((1 - 0.76) = 0.24\). Substituting into the equilibrium expression above gives \(K_p = 1.2\).
This is by far the most common kind of equilibrium problem you will encounter: starting with an arbitrary number of moles of each component, how many moles of each will be present when the system comes to equilibrium? The principal source of confusion and error for beginners at this relates to the need to determine the values of several unknowns (a concentration or pressure for each component) from a single equation, the equilibrium expression. The key to this is to make use of the stoichiometric relationships between the various components, which usually allow us to express the equilibrium composition in terms of a single variable. The easiest and most error-free way of doing this is adopt a systematic approach in which you create and fill in a small table as shown in the following problem example. You then substitute the equilibrium values into the equilibrium constant expression, and solve it for the unknown. This very often involves solving a quadratic or higher-order equation. Quadratics can of course be solved by using the familiar quadratic formula, but it is often easier to use an algebraic or graphical approximation, and for higher-order equations this is the only practical approach. There is almost never any need to get an exact answer, since the equilibrium constants you start with are rarely known all that precisely.

**Problem Example 3**

Phosgene (COCl₂) is a poisonous gas that dissociates at high temperature into two other poisonous gases, carbon monoxide and chlorine. The equilibrium constant $K_p = 0.0041$ at 600°K. Find the equilibrium composition of the system after 0.124 atm of COCl₂ is allowed to reach equilibrium at this temperature.

**Solution:** Start by drawing up a table showing the relationships between the components:

<table>
<thead>
<tr>
<th></th>
<th>COCl₂ →</th>
<th>CO</th>
<th>Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial pressures:</td>
<td>0.124 atm</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change:</td>
<td>−x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>equilibrium pressures:</td>
<td>0.124 − x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Substitution of the equilibrium pressures into the equilibrium expression gives

\[
\frac{x^2}{0.124 - x} = 0.0041
\]

This expression can be rearranged into standard polynomial form $x^2 + 0.0041x - 0.00054 = 0$ and solved by the quadratic formula, but we will simply obtain an approximate solution by iteration. Because the equilibrium constant is small, we know that $x$ will be rather small compared to 0.124, so the above relation can be approximated by

\[
\frac{x^2}{0.124} = 0.0041
\]

which gives $x = 0.0225$. To see how good this is, substitute this value of $x$ into the denominator of the original equation and solve again:

\[
\frac{x^2}{0.124 - 0.0225} = \frac{0.0225^2}{0.124 - 0.0225} = 0.0041
\]

This time, solving for $x$ gives 0.0204. Iterating once more, we get
and $x = 0.0206$ which is sufficiently close to the previous to be considered the final result. The final partial pressures are then 0.104 atm for COCl₂, and 0.0206 atm each for CO and Cl₂.

Note: using the quadratic formula to find the exact solution yields the two roots $-0.0247$ (which we ignore) and 0.0206, which show that our approximation is quite good.

**Problem Example 4**

The gas-phase dissociation of phosphorus pentachloride to the trichloride has $K_p = 3.60$ at 540°C:

$$\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2$$

What will be the partial pressures of all three components if 0.200 mole of PCl₅ and 3.00 moles of PCl₃ are combined and brought to equilibrium at this temperature and at a total pressure of 1.00 atm?

**Solution:**

<table>
<thead>
<tr>
<th></th>
<th>PCl₅</th>
<th>PCl₃</th>
<th>Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial moles:</td>
<td>0.200</td>
<td>3.00</td>
<td>0</td>
</tr>
<tr>
<td>change:</td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>equilibrium moles:</td>
<td>$0.200 - x$</td>
<td>$3.00 + x$</td>
<td>$x$</td>
</tr>
<tr>
<td>eq. partial pressures:</td>
<td>$\frac{(3.00 - x)}{(3.00 + x)}$</td>
<td>$\frac{(3.00 + x)}{(3.00 + x)}$</td>
<td>$\frac{x}{(3.00 + x)}$</td>
</tr>
</tbody>
</table>

The partial pressures in the bottom row were found by multiplying the mole fraction of each gas by the total pressure: $P_i = X_i P_t$. The term in the denominator of each mole fraction is the total number of moles of gas present at equilibrium: $(0.200 - x) + (3.00 + x) + x = 3.20 + x$.

Substituting the equilibrium partial pressures into the equilibrium expression, we have

$$\frac{(3.00 + x)P_t}{(0.200 - x)(3.00 + x)} - 1 = 0$$

whose polynomial form is $4.60x^2 + 13.80x - 2.304 = 0$.

Plotting this on a graphical calculator yields $x = 0.159$ as the positive root:

Substitution of this root into the expressions for the equilibrium partial pressures in the table yields the following values: $P(\text{PCl}_5) = 0.012$ atm, $P(\text{PCl}_3) = 0.94$ atm, $P(\text{Cl}_2) = 0.047$ atm.

**Effects of dilution on an equilibrium**
In the section that introduced the LeChâtelier principle, it was mentioned that diluting a weak acid such as acetic acid CH₃COOH ("HAc") will shift the dissociation equilibrium to the right:

\[ \text{HAc} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Ac}^- \]

Thus a 0.10\text{M} solution of acetic acid is 1.3% ionized, while in a 0.01\text{M} solution, 4.3% of the HAc molecules will be dissociated. This is because as the solution becomes more dilute, the product [H₃O⁺][Ac⁻] decreases more rapidly than does the [HAc] term. At the same time the concentration of H₂O becomes greater, but because it is so large to start with (about 55.5\text{M}), any effect this might have is negligible, which is why no [H₂O] term appears in the equilibrium expression.

For a reaction such as

\[ \text{CH}_3\text{COOH(l)} + \text{C}_2\text{H}_5\text{OH(l)} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5\text{(l)} + \text{H}_2\text{O(l)} \] (in which the water concentration does change), dilution will have no effect on the equilibrium; the situation is analogous to the way the pressure dependence of a gas-phase reaction depends on the number of moles of gaseous components on either side of the equation.

**Problem Example 5**

The biochemical formation of a disaccharide (double) sugar from two monosaccharides is exemplified by the reaction

\[ \text{fructose} + \text{glucose-6-phosphate} \rightarrow \text{sucrose-6-phosphate} \]

(Sucrose is ordinary table sugar.) To what volume should a solution containing 0.050 mol of each monosaccharide be diluted in order to bring about 5% conversion to sucrose phosphate?

**Solution:**

The initial and final numbers of moles are as follows:

<table>
<thead>
<tr>
<th></th>
<th>fructose</th>
<th>glucose-6-P</th>
<th>sucrose-6-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial moles:</td>
<td>0.05</td>
<td>0.05</td>
<td>0</td>
</tr>
<tr>
<td>equilibrium moles:</td>
<td>0.0485</td>
<td>0.0485</td>
<td>0.0015</td>
</tr>
</tbody>
</table>

Substituting into the expression for \( K_c \) in which the solution volume is the unknown, we have

\[
\frac{[\text{sucrose-6-P}]}{[\text{fructose}[\text{glucose-6-P}]]} = \frac{0.0485}{V} = 0.05
\]

Solving for \( V \) gives a final solution volume of 78 mL.

**Phase distribution equilibria**

It often happens that two immiscible liquid phases are in contact, one of which contains a solute. How will the solute tend to distribute itself between the two phases? One’s first thought might be that some of the solute will migrate from one phase into the other until it is distributed equally between the two phases, since this would correspond to the maximum dispersion (randomness) of the solute. This, however, does not take into the account the differing solubilities the solute might have in the two liquids; if such a difference does exist, the solute will preferentially migrate into the
phase in which it is more soluble. For a solute S distributed between two phases a and b the process \( S_a = S_b \) is defined by the distribution law

\[
K_{a,b} = \frac{[S]_a}{[S]_b}
\]

in which \( K_{a,b} \) is the distribution ratio (also called the distribution coefficient) and \([S]_i\) is the solubility of the solute in the phase.

The transport of substances between different phases is of immense importance in such diverse fields as pharmacology and environmental science. For example, if a drug is to pass from the aqueous phase with the stomach into the bloodstream, it must pass through the lipid (oil-like) phase of the epithelial cells that line the digestive tract. Similarly, a pollutant such as a pesticide residue that is more soluble in oil than in water will be preferentially taken up and retained by marine organism, especially fish, whose bodies contain more oil-like substances; this is basically the mechanism whereby such residues as DDT can undergo biomagnification as they become more concentrated at higher levels within the food chain. For this reason, environmental regulations now require that oil-water distribution ratios be established for any new chemical likely to find its way into natural waters. The standard “oil” phase that is almost universally used is octanol, \( \text{C}_8\text{H}_{17}\text{OH} \).

In preparative chemistry it is frequently necessary to recover a desired product present in a reaction mixture by extracting it into another liquid in which it is more soluble than the unwanted substances. On the laboratory scale this operation is carried out in a separatory funnel in which the two phases are brought into intimate contact by shaking. After the two liquids have separated into layers, the bottom layer is drawn off. If the distribution ratio is too low to achieve efficient separation in a single step, it can be repeated; there are automated devices that can carry out hundreds of successive extractions, each yielding a product of higher purity. In these applications our goal is to exploit the LeChâtelier principle by repeatedly upsetting the phase distribution equilibrium that would result if two phases were to remain in permanent contact.

This **separatory funnel** is used to **extract** a substance from one liquid into another in which it is more soluble. The two immiscible liquids are poured into the funnel through the opening at the top. The funnel is then shaken to bring the two phases into intimate contact, and then set aside to allow the two liquids to separate into layers, which are then separated by allowing the more dense liquid to exit through the stopcock at the bottom.

**Problem Example 6**

The distribution ratio for iodine between water and carbon disulfide is 650. Calculate the concentration of \( I_2 \) remaining in the aqueous phase after 50.0 mL of 0.10M \( I_2 \) in water is shaken with 10.0 mL of \( \text{CS}_2 \).

**Solution:**

The equilibrium constant is
Let $m_1$ and $m_2$ represent the numbers of millimoles of solute in the water and CS$_2$ layers, respectively. $K_d$ can then be written as $(m_2/10 \text{ mL}) ÷ (m_1/50 \text{ mL}) = 650$. The number of moles of solute is $(50 \text{ mL}) \times (0.10 \text{ mmol mL}^{-1}) = 5.00 \text{ mmol}$, and mass conservation requires that $m_1 + m_2 = 5.00 \text{ mmol}$, so $m_2 = (5.00 - m_1) \text{ mmol}$ and we now have only the single unknown $m_1$. The equilibrium constant then becomes

$$((5.00 - m_1) \text{ mmol} / 10 \text{ mL}) ÷ (m_1 \text{ mmol} / 50 \text{ mL}) = 650.$$ 

Simplifying and solving for $m_1$ yields $(0.50 - 0.1)m_1 / (0.02 m_1) = 650$, with $m_1 = 0.0382 \text{ mmol}$. The concentration of solute in the water layer is $(0.0382 \text{ mmol}) / (50 \text{ mL}) = 0.000763 \text{ M}$, showing that almost all of the iodine has moved into the CS$_2$ layer.

**Summary**

The six Problem Examples presented above were carefully selected to span the range of problem types that students enrolled in first-year college chemistry courses are expected to be able to deal with. If you are able to reproduce these solutions on your own, you should be well prepared for an examination on this topic.

- The first step in the solution of all but the simplest equilibrium problems is to sketch out a table showing for each component the initial concentration or pressure, the change in this quantity (for example, $+2x$), and the equilibrium values (for example, $0.0036 + 2x$). In doing so, the sequence of calculations required to get to the answer usually becomes apparent.

- Equilibrium calculations often involve quadratic- or higher-order equations. Because concentrations, pressures, and equilibrium constants are seldom known to a precision of more than a few significant figures, there is no need to seek exact solutions. Iterative approximations (as in Problem Example 3) or use of a graphical calculator (Problem Example 4) are adequate and convenient.

- **Phase distribution equilibria** play an important role in chemical separation processes on both laboratory and industrial scales. They are also involved in the movement of chemicals between different parts of the environment, and in the bioconcentration of pollutants in the food chain.