Solving Equilibrium Problems

The secret to solving an equilibrium problem is organization (and patience…patience always helps!). Most equilibrium problems begin by providing us with the initial amount of each reactant and each product, and providing us with either the concentration or the change in concentration for one reactant or for one product. From this information we can deduce the change in concentration and the final equilibrium concentration for each species in the equilibrium reaction. As shown in the following examples, a table helps us organize this information and guides us in writing an algebraic equation that we can solve. Beginning an equilibrium problem without this organization can turn a relatively easy problem into one that is difficult to solve.

There are two basic approaches to solving an equilibrium problem: a rigorous approach that relies on an exact algebraic solution to the problem, and a less rigorous approach that uses one or more simplifying assumptions to approximate closely the result of the more rigorous approach. This essay reviews these approaches and provides some hints on how to make and how to evaluate simplifying assumptions. The examples included here are identical to those we discussed in class, which will help you in sorting through your notes.

Rigorous Solutions

Consider the reaction $\mathrm{PCl_3}(g) + \mathrm{Cl_2}(g) \rightleftharpoons \mathrm{PCl_5}(g)$, for which the equilibrium constant is 1000 at an unspecified temperature. If we know the initial concentration for each reactant and product, then we can determine if the system is at equilibrium by calculating the reaction quotient, Q, and comparing it to the equilibrium constant, K. If the system is not at equilibrium, then we can determine the direction in which the reaction will move to reach equilibrium.

> ***Example 1.*** The initial concentrations of $\mathrm{PCl_3}$, $\mathrm{Cl_2}$, and $\mathrm{PCl_5}$ in a mixture are, respectively 0.0220 M, 0.00400 M, and 0.0400 M. Determine if the mixture is at equilibrium. If the system is not at equilibrium, in which direction will it react to establish equilibrium?
>
> ***Solution.*** The reaction quotient is
>
> $$Q = \frac{[\mathrm{PCl_5}]}{[\mathrm{PCl_3}][\mathrm{Cl_2}]} = \frac{0.0400}{(0.0220)(0.004)} = 454.4$$
>
> Because $Q < K$, the system is not at equilibrium and the reaction will move to the right (from reactants-to-products) to reach the equilibrium position. As the concentration of $\mathrm{PCl_5}$ increases and the concentrations of $\mathrm{PCl_3}$ and $\mathrm{Cl_2}$ decrease, the value of Q increases until $Q = K$ and equilibrium is established.

Having established the direction in which equilibrium lies, we need to determine the concentration of each reactant and product when equilibrium is reached. Because only one equation—the equilibrium constant expression—relates the concentrations of our three reactants and products, we must rewrite the equation so that it includes only a single variable.[1] We accomplish this by assigning a variable, such as X, to the change in concentration for any one component and use the reaction's stoichiometry to find the change in concentration for the remaining components in terms of X. A table is a good way to organize our work.

> ***Example 2.*** Continuing with Example 1, express the equilibrium concentrations for all three com-ponents using X as the sole variable.

[1] Recall that a single equation with a single variable has a unique solution, but that a single equation with more than one variable has an infinite number of possible solutions. Thus, the equation $5x + 2 = -8$ has a unique solution ($x = -2$), but the equation $5x + y = -8$ has many possible solutions ($x = -2$, $y = 2$ and $x = 0$, $y = -8$ are two examples). Although this is a trivial point, it is an important point. If you are stuck when solving an equilibrium problem because you find there is more than one unknown term, then stop and ask yourself whether you do, in fact, know the value for one of the unknown terms. Reread the problem carefully because the missing information must be there.

Solution. A table helps us organize information as we work though the problem (we begin with the information shown in bold; all other entries are developed as part of the problem's solution):

	PCl_3(g)	+	$Cl_2(g)$	$\rightleftharpoons$	$PCl_5(g)$
initial	**0.0220**		**0.00400**		**0.0400**
change	$-X$		$-X$		$+X$
equilibrium	$0.0200 - X$		$0.00400 - X$		$0.0400 + X$

The first row of this table, which we call an ICE table (for **i**nitial, **c**hange, and **e**quilibrium), provides each reactant's and each product's initial concentration. We know from Example 1 that the mixture moves toward its equilibrium position by shifting to the right. Because we do not know by how much the concentration of any one species changes, we arbitrarily pick one component and assign it a change of $+X$ if it increases in concentration, or $-X$ if it decreases in concentration. The change in concentration for each of the remaining components is a multiple of X that depends on the reaction's stoichiometry. Although we can assign X to any reactant or product, a judicious choice at this point makes the problem easier by avoiding the use of fractions (such as a change of $\frac{-X}{2}$). For this example, where the stoichiometry is 1:1:1, the assignment is straightforward. Letting $-X$ be the decrease in concentration for PCl_3, we know that the change in concentration for Cl_2 is $-X$ and that for PCl_5 is $+X$.

Having defined each component's equilibrium concentration in terms of the variable X, we are ready to solve the problem. In the rigorous approach to solving an equilibrium problem we substitute the equilibrium concentrations into the equilibrium constant expression and solve for the variable X. In almost all equilibrium problems, finding a rigorous solution is complicated by the presence of an equation that is a second-order (quadratic) or a higher-order polynomial equation in the variable X. Although quadratic equations are relatively easy to solve, higher-order polynomials present a more difficult problem. For now, we will limit problems to those that are second-order in the variable X.

Example 3. Continuing with Example 2, determine the concentration for each component when equilibrium is reached. The equilibrium constant for the reaction is 1000.

Solution. We begin by substituting into the equilibrium constant expression the equilibrium concentrations defined in terms of the variable X (the last row of the ICE table in Example 2); thus

$$K = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{0.0400 + X}{(0.0220 - X)(0.00400 - X)} = 1000$$

Next, we manipulate the equation until it is in the general form of a second-order polynomial equation (i.e., $aX^2 + bX + c = 0$)

$$1000 = \frac{0.0400 + X}{8.8 \times 10^{-5} - 0.026X + X^2}$$

$$0.0400 + X = 0.088 - 26X + 1000X^2$$

$$1000X^2 - 27X + 0.048 = 0$$

The solutions (or roots) for a second-order polynomial are given by the quadratic equation

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

There are two solutions to a second-order polynomial equation, only one of which has chemical significance; the other solution must, therefore, lead to a chemically meaningless result. Continuing, we find that

$$X = \frac{-(-27) \pm \sqrt{(-27)^2 - (4)(1000)(0.048)}}{(2)(1000)} = \frac{27 \pm 23.173}{2000} = 0.0251 \text{ or } 0.00191$$

Of these two results, only one is correct. A value for X of 0.0251 leads to a contradiction as it gives a negative concentration for both reactants; thus, the correct value for X is 0.00191.[2] The equilibrium concentrations for the three components are

$$[\mathrm{PCl_3}] = [\mathrm{PCl_3}]_\mathrm{o} - X = 0.0220 - 0.00191 = 0.0201 \text{ M}$$

$$[\mathrm{Cl_2}] = [\mathrm{Cl_2}]_\mathrm{o} - X = 0.0220 - 0.00191 = 0.0201 \text{ M}$$

$$[\mathrm{PCl_5}] = [\mathrm{PCl_5}]_\mathrm{o} + X = 0.0400 + 0.00191 = 0.0419 \text{ M}$$

Although algebraically intensive, this approach always leads to the correct answer (although if $b^2 \approx 4ac$, then rounding errors may leave you with a negative value under the square root). Many scientific calculators have built in subroutines that will find the roots of any polynomial equation, including those with orders greater than two. Additionally, with a graphing calculator you can plot the function and find the roots by looking for the x-intercepts. These latter two approaches, however, do not always lead to useful answers and, therefore, you must use them with caution.[3]

Approximate Solutions

An alternative approach to solving an equilibrium problem is to find a way to simplify a second-order (or a higher-order) polynomial equation into one that is first-order in the variable X, an equation that is easy to solve. This is possible if we can make a simplifying assumption that introduces no more than a small error into the calculation. An error of less than ±5% generally is considered acceptable due to the uncertainty in published equilibrium constants.

A simplifying assumption is possible if there is at least one term in which the variable X is added to or subtracted from a number. If the value of X is significantly smaller than the number to which it is added or subtracted, then we can safely ignore it; if not, then it is retained. For example, consider this equilibrium constant expression from Example 3

$$K = \frac{[\mathrm{PCl_5}]}{[\mathrm{PCl_3}][\mathrm{Cl_2}]} = \frac{0.0400 + X}{(0.0220 - X)(0.00440 - X)} = 1000$$

which has three terms in which the X is added to or subtracted from a number. If X is significantly smaller than 0.0400 and 0.0220 but larger than 0.00400, then the first term in the denominator simplifies to 0.0220 and the numerator simplifies to 0.0400 without, we hope, introducing any significant error; thus

$$K = \frac{[\mathrm{PCl_5}]}{[\mathrm{PCl_3}][\mathrm{Cl_2}]} = \frac{0.0400}{(0.0220)(0.00440 - X)} = 1000$$

[2] For example, if X is 0.0251 then the concentration of $\mathrm{PCl_3}$ is $0.0220 - 0.0251 = -0.0031$. A negative concentration is impossible.

[3] The limitations here are the calculator's precision, which can lead to calculated concentrations of zero, when X is very large or very small, and to the resolution of the calculator's display.

This equation is now first-order in X and, therefore, easy to solve.

How do we know if a simplifying assumption is reasonable? The short answer is that we cannot be sure without testing the assumption, but we can make an educated guess if we evaluate carefully the values for Q and K. If $Q \approx K$, then we are close to equilibrium and the change in concentration (X) needed to reach equilibrium is small. On the other hand, if the difference between Q and K is large, then the changes in concentration as the system moves toward equilibrium likely are significant.

Example 4. Evaluate the equilibrium constant expression from Example 3 (shown below) and decide whether the value of X is likely to be insignificant for any of the three terms in the equilibrium constant expression.

$$K = \frac{[\mathrm{PCl_5}]}{[\mathrm{PCl_3}][\mathrm{Cl_2}]} = \frac{0.0400 + X}{(0.0220 - X)(0.00440 - X)} = 1000$$

Solution. In Example 1 we showed that the value of Q for this system's initial conditions is 454.5 compared to an equilibrium constant, K, of 1000. Because this difference is quite large we reasonably can assume that X is relatively large and that we probably cannot exclude it from any of the three terms.

The fact that we cannot make a simplifying assumption at this point does not mean we should give up searching for a way to simplify the problem. If the equilibrium constant for a reaction is quite large, then we might treat the reaction as one that first goes to completion and then moves back to its equilibrium position.[4]

Example 5. Return to Example 2, allow the reaction to go to completion, and report the new set of initial concentrations.

Solution. We begin by using a table to organize information (as before, the values in bold are the initial information):

	$\mathrm{PCl_3(g)}$	+	$\mathrm{Cl_2}(g)$	$\rightleftharpoons$	$\mathrm{PCl_5}(g)$
initial	**0.0220**		**0.00400**		**0.0400**
change	−0.00400		−0.00400		+0.00400
new initial	0.0180		0		0.0440

The first row, of course, provides the initial concentrations of the reactants and products. The changes in concentration shown in the second row assume that the reaction goes to completion. The limiting reagent is $\mathrm{Cl_2}$, so we let its concentration change to zero and assign the determine the change in concentration for each remaining component using the reaction's stoichiometry.

Having made this adjustment, we let the reaction move back to its equilibrium position using the variable X to define the extent of that movement.

Example 6. Continue with Example 5 by expressing the equilibrium concentration for each species in terms of a single variable, X, and solve for X.

Solution. Continuing with our table as a means for organizing information, we have

	$\mathrm{PCl_3(g)}$	+	$\mathrm{Cl_2}(g)$	$\rightleftharpoons$	$\mathrm{PCl_5}(g)$
initial	**0.0220**		**0.00400**		**0.0400**
change	−0.00400		−0.00400		+0.00400
new initial	0.0180		0		0.0440
change	$+X$		$+X$		$-X$
equilibrium	$0.0180 + X$		X		$0.0440 - X$

[4] In essence, the composition of the system at equilibrium is independent of the path the system takes to reach equilibrium.

and an equilibrium constant expression of

$$K = \frac{[\mathrm{PCl_5}]}{[\mathrm{PCl_3}][\mathrm{Cl_2}]} = \frac{0.0440 - X}{(0.0180 + X)(X)} = 1000$$

If, as in our example, the equilibrium constant in the forward direction is 1000, then the equilibrium constant in the reverse direction is 0.001. With such a small value, we can reasonably expect that equilibrium is reached with only a very small change in the concentrations of all three species. If true, then we can remove the term X from the numerator and the first term in the denominator by assuming that $0.0440 - X \approx 0.0440$ and that $0.0180 + X \approx 0.180$. Having made these assumptions we find that

$$K = \frac{[\mathrm{PCL_5}]}{[\mathrm{PCl_3}][\mathrm{Cl_2}]} = \frac{0.0440}{(0.0180)(X)} = 1000$$

$$X = 2.44 \times 10^{-3}\ \mathrm{M}$$

Notice how much easier the calculation is! Based on these results, we find that the equilibrium concentrations are:

$$[\mathrm{PCl_3}] = 0.0180 + X = 0.0180 + 2.44 \times 10^{-3} = 0.0204\ \mathrm{M}$$

$$[\mathrm{Cl_2}] = X = 2.44 \times 10^{-3}\ \mathrm{M}$$

$$[\mathrm{PCl_5}] = 0.0440 - X = 0.0440 - 2.44 \times 10^{-3} = 0.0416\ \mathrm{M}$$

Of course, when we make an assumption we introduce errors into our concentrations so we must evaluate whether these errors are acceptable. To determine the error in any concentration, we compare the calculated concentration at equilibrium to our assumption in making the calculation, with the error equal to

$$\%\ \text{error} = \frac{\text{assumed concentration} - \text{calculated concentration}}{\text{assumed concentration}} \times 100$$

If the error for any one concentration is more than 5%, then our assumption is not valid and we need to find an alternative approach to solving the problem.

Example 7. Continuing with Example 6, determine the percent errors and determine if the assumptions are acceptable.

Solution. The percent errors are:

$$\%\ \text{error for PCl}_5 = \frac{0.0440 - (0.0440 - 2.44 \times 10^{-3})}{0.0440} = \frac{0.0440 - 0.0416}{0.0440} \times 100 = 5.5\%$$

$$\%\ \text{error for PCl}_3 = \frac{(0.0180 - (0.0180 + 2.44 \times 10^{-3}))}{0.0180} = \frac{0.0180 - 0.0204}{0.0180} \times 100 = -13.3\%$$

Both errors are too large; thus, our assumptions were not valid.

So, what do we do if our simplifying assumptions fail? One possibility, of course, is to return to the rigorous approach and solve the problem exactly. Another possibility, which often is the better choice, is to continue making approximations. We know, for example, that our initial assumption of 0.0440 M for the equilibrium concentration of PCl_5 was too high and that its original concentration of 0.0400 M is too low. Clearly the equilibrium concentration must lie between these limits and our calculated result from Example 7 of 0.0416 M is as good a choice as any.

> ***Example 8.*** Continue with Example 7, making a new set of simplifying assumptions based upon the results of the first set of assumptions.
>
> ***Solution.*** This time we assume that the calculated equilibrium concentrations for PCl_3 and for PCl_5 from Example 7 are better estimates of their respective equilibrium concentrations than our initial assumptions; thus, for our second iteration we assume equilibrium concentrations of
>
> $$[\mathrm{PCl_5}] = 0.0440 - X \approx 0.0416 \text{ M}$$
>
> $$[\mathrm{PCl_3}] = 0.0180 + X \approx 0.0204 \text{ M}$$
>
> Continuing, we find that
>
> $$K = \frac{[\mathrm{PCl_5}]}{[\mathrm{PCl_3}][\mathrm{Cl_2}]} = \frac{0.0416}{(0.0204)(X)} = 1000$$
>
> $$X = 2.04 \times 10^{-3} \text{ M}$$
>
> For PCl_5, the equilibrium concentration and error are
>
> $$0.0440 - X = 0.0444 - 2.04 \times 10^{-3} = 0.0420 \text{ M}$$
>
> $$\% \text{ error} = \frac{0.0416 - 0.0420}{0.0416} \times 100 = -1.0\%$$
>
> and for PCl_3, the equilibrium concentration and error are
>
> $$0.0180 + X = 0.0180 + 2.04 \times 10^{-3} = 0.0200 \text{ M}$$
>
> $$\% \text{ error} = \frac{0.0204 - 0.0200}{0.0204} \times 100 = +2.0\%$$
>
> These are reasonable errors![5] Comparing the exact concentrations from the rigorous solution to those from this approximate solutions, we find
>
> $$[\mathrm{PCl_3}] = 0.0201 \text{ M vs. } 0.0200 \text{ M}$$
>
> $$[\mathrm{Cl_2}] = 0.00209 \text{ M vs. } 0.00204 \text{ M}$$
>
> $$[\mathrm{PCl_5}] = 0.0419 \text{ M vs. } 0.0420 \text{ M}$$

[5] Note that for this second assumption the percent errors for both species are smaller in magnitude and opposite in sign than for the first assumption. This is a general pattern. With each iteration we switch back-and-fort from overestimating to underestimating the equilibrium concentration, but come closer-and-closer to the actual concentrations.