

Some Thoughts on Solving Equilibrium Problems

The secret to solving an equilibrium problem is organization and planning. Most equilibrium problems begin by stating the initial amount of each reactant and product and either the concentration or change in concentration for one reactant or product. From this information you can deduce the change in concentration and the final equilibrium concentration for each species in the equilibrium reaction. As shown in the following worked examples, using a table to organize this information helps guide this process.

Beginning an equilibrium problem without planning a method of attack can turn a relatively easy problem into one that is difficult to solve. There are two basic approaches to solving equilibrium problems: a rigorous approach that relies on an exact algebraic solution to the problem, and an less rigorous approach that uses one or more simplifying assumptions to approximate closely the result of the more rigorous approach. This tutorial reviews these approaches and provides some hints on making and evaluating simplifying assumptions. The example used in this tutorial is identical to that discussed in class, which will help you in sorting through your notes.

Rigorous Solution. Consider the reaction $\text{PCl}_3 + \text{Cl}_2 \rightleftharpoons \text{PCl}_5$, for which the equilibrium constant is 1000 at an unspecified temperature. If we know the initial concentration for each component, then we can evaluate whether 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, we can determine the direction in which the reaction will move to reach equilibrium.

Example 1. The initial concentrations of PCl_3 , Cl_2 , and PCl_5 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?

Solution. The reaction quotient is

$$Q = \frac{(\text{PCl}_5)_o}{(\text{PCl}_3)_o(\text{Cl}_2)_o} = \frac{(0.0400)}{(0.0220)(0.00400)} = 454.5$$

Because $Q < K$, the system is not at equilibrium. The reaction must proceed from reactants-to-products to reach the equilibrium position. As the concentration of PCl_5 increases and the concentrations of PCl_3 and 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 species when equilibrium is reached. Because only one equation, the equilibrium constant expression, relates the concentrations of our three reactants and products, we must rewrite it 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 this variable. A table is a good way to keep this organized.

¹ Recall that a single equation with one 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 (e.g., $x = -2, y = 2$; $x = 0, y = -8$). Although this is a trivial point, it is important. Should you become stuck when solving an equilibrium problem because you find that there is more than one unknown term, 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.

Example 2. Continuing with Example 1, express the equilibrium concentrations for all three components using X as the sole variable.

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

	PCl_3	$+ \text{Cl}_2$	$\rightleftharpoons \text{PCl}_5$
<u>Initial</u>	0.0220	0.00400	0.0400
<u>Change</u>	$-X$	$-X$	$+X$
<u>Equilibrium</u>	$0.0220-X$	$0.00400-X$	$0.0400+X$

The first row of this table, which we call an ICE table, provides each reactant's and each product's initial concentration. We know from the previous example that the mixture will move toward its equilibrium position by shifting to the right. Because we do not know by how much the concentration of any one species will change, we arbitrarily pick one component and assign it a change of $+X$ if it is known to increase in concentration, or $-X$ if it is known to decrease in concentration. The change in concentration for each remaining component is a multiple of X that depends on the reaction's stoichiometry. Although we can assign X to any component, a judicious choice at this point makes the problem easier by avoiding the possibility that one or more species has a change in concentration that is fractional multiple of X . 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 $+X$.

After defining each component's equilibrium concentration in terms of the variable X , we are ready to finishing solving the problem. In the rigorous approach to solving equilibrium problems 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 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 table in Example 2); thus

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{(0.0400 + X)}{(0.0220 - X)(0.00400 - X)} = 1000$$

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

$$\begin{aligned} \frac{(0.0400 + X)}{8.8 \times 10^{-5} - 0.026X + X^2} &= 1000 \\ 0.0400 + X &= 0.088 - 26X + 1000X^2 \\ 1000X^2 - 27X + 0.048 &= 0 \end{aligned}$$

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

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

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

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

$$X = 0.0251 \text{ or } X = 0.00191$$

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 reactants²; thus, the correct value for X is 0.00191 and the equilibrium concentrations for the three components are

$$[\text{PCl}_3] = [\text{PCl}_3]_0 - X = 0.0220 - 0.00191 = 0.0201 \text{ M}$$

$$[\text{Cl}_2] = [\text{Cl}_2]_0 - X = 0.0220 - 0.00191 = 0.0201 \text{ M}$$

$$[\text{PCl}_5] = [\text{PCl}_5]_0 + X = 0.0400 + 0.00191 = 0.0419 \text{ M}$$

Although algebraically intensive, this approach always leads to the correct answer. Keep in mind that many scientific calculators have built in subroutines for finding the roots of polynomial equations. Additionally, with many scientific calculators you can graph 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, must be used cautiously.³

Approximate Solutions. An alternative approach to solving equilibrium problems is to find a way to simplify the second-order (or higher-order) polynomial equation into one that is first-order in the variable X . 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 $\pm 5\%$ generally is considered acceptable due to the uncertainty in published equilibrium constants.

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

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{(0.0400 + X)}{(0.0220 - X)(0.00400 - X)} = 1000$$

which has three terms in which the variable X is added to or subtracted from a number. If X is significantly smaller than 0.0220 but larger than 0.00400, then the first term in the denominator

² For example, if X is 0.0251 then the concentration of PCl_3 becomes $0.0220 - 0.0251 = -0.0031$. A negative concentration is impossible.

³ The limitation with using a calculator's subroutine to find the roots of a polynomial occurs when rounding the values of a , b , and c makes the quantity $b^2 - 4ac$ negative. The limitation with using a calculator's graphing capabilities is in the resolution of the resulting graph.

simplifies to 0.0220 and the numerator simplifies to 0.0400 without, we hope, introducing any significant error; thus

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{(0.0400)}{(0.0220)(0.00400 - X)} = 1000$$

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

How do we know whether a simplifying assumption is reasonable? The short answer is we are not certain, but we can make an educated guess by carefully examining the values for Q and K . If $Q \approx K$, then we are close to equilibrium and the change in concentration 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 is significant.

Example 4. Evaluate the example 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.

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{(0.0400 + X)}{(0.0220 - X)(0.00400 - X)} = 1000$$

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 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. Here is where planning helps. If the equilibrium constant for a reaction is quite large, then we might treat the reaction as one that goes to completion and then let it move back to its equilibrium position.

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

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

	PCl_3	+	Cl_2	\rightleftharpoons	PCl_5
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 Cl_2 , so we assume its concentration decreases to zero and assign 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 .

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

	PCl_3	$+$	Cl_2	\rightleftharpoons	PCl_5
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		$0.0440 - X$

and an equilibrium expression of

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{(0.04400 - X)}{(0.0180 + X)(X)} = 1000$$

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 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

$$0.0180 + X \approx 0.0180$$

Applying these assumptions reduces the problem to one that is first-order in X .

Example 7. Continue with Example 6 by making the assumptions described above and completing the algebraic solution.

Solution. Having made the assumptions we find that

$$\frac{(0.0440)}{(0.0180)(X)} = 1000$$

$$X = 2.444 \times 10^{-3}$$

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

$$[\text{PCl}_3] = 0.0180 + X = 0.0180 + 2.444 \times 10^{-3} = 0.0204 \text{ M}$$

$$[\text{Cl}_2] = X = 2.444 \times 10^{-3} \text{ M}$$

$$[\text{PCl}_5] = 0.0440 - X = 0.0440 - 2.444 \times 10^{-3} = 0.0416 \text{ M}$$

Of course, making an assumption introduces the possibility of error so we must evaluate whether the errors in this case are acceptable. Errors are determined by comparing the calculated concentrations at equilibrium to those assumed 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 concentration is greater than 5%, then the assumptions are invalid.

Example 8. Continuing with Example 7, determine the percent errors and determine if the assumptions are acceptable.

Solution. The percent errors are:

$$\begin{aligned}\% \text{error for } \text{PCl}_5 &= \frac{0.0440 - 0.0416}{0.0440} \times 100 = 5.5\% \\ \% \text{error for } \text{PCl}_3 &= \frac{0.0180 - 0.0204}{0.0180} \times 100 = -13.3\%\end{aligned}$$

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

So, what do we do if our simplifying assumptions fail? One solution, of course, is to return to the rigorous solution and solve the problem exactly. Another solution, which often is the better choice, is to continue making approximations. We know, for example, that the assumed equilibrium concentration for PCl_5 of 0.0440 M is too high and that its original concentration of 0.0400 M is too low. Clearly the equilibrium concentration must lie within these limits and the calculated result from Example 8 of 0.0416 M is as good a choice as any.

Example 9. Continue with Example 8, 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 concentrations for PCl_3 and PCl_5 from Example 8 are better estimates of their respective equilibrium concentrations than the initial assumptions; thus, for our second iteration we assume that

$$0.0440 - X \approx 0.0416 \qquad 0.0180 + X \approx 0.0204$$

Continuing, we find that

$$\begin{aligned}\frac{(0.0416)}{(0.0204)(X)} &= 1000 \\ X &= 2.039 \times 10^{-3}\end{aligned}$$

For PCl_5 , the equilibrium concentration and error are

$$\begin{aligned}0.0440 - X &= 0.0440 - 2.039 \times 10^{-3} = 0.0420 \\ \% \text{error} &= \frac{0.0416 - 0.0420}{0.0416} \times 100 = -1.0\%\end{aligned}$$

For PCl_3 , the equilibrium concentration and error are

$$\begin{aligned}0.0180 + X &= 0.0180 + 2.039 \times 10^{-3} = 0.0200 \\ \% \text{error} &= \frac{0.0204 - 0.0200}{0.0204} \times 100 = 2.0\%\end{aligned}$$

These are reasonable errors! Comparing the exact concentrations from the rigorous solution to those from this approximate solutions, we find

$$\begin{aligned}[\text{PCl}_3] &= 0.0201 \text{ M vs. } 0.0200 \text{ M} & [\text{Cl}_2] &= 0.00209 \text{ M vs. } 0.00204 \text{ M} \\ [\text{PCl}_5] &= 0.0419 \text{ M vs. } 0.0420 \text{ M}\end{aligned}$$