

## Chapter 52

## EQUILIBRIUM CHANGE

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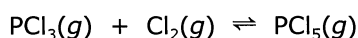
We now start into equilibrium problems which involve changes in the amounts of reagents upon going from a given set of conditions to the point of equilibrium. These problems are a bit more involved and we will bring in some new tools for dealing with these.

Here's a clue to start things off. The most important way to get an equilibrium problem going is to have a balanced equation and a  $K$  expression. Even if you're drawing a blank on the problem, at least set up that much. Then try to take it from there.

## 52.1 Problems of change

We'll continue the numbering of the Examples from the last Chapter.

**Example 3.** At 100. °C,  $K$  for the following equilibrium is 13.



The process is started with 1.00 atm  $\text{PCl}_3$  and 1.00 atm  $\text{Cl}_2$ . The system then proceeds to equilibrium. Find the pressures of  $\text{PCl}_3$ ,  $\text{Cl}_2$  and  $\text{PCl}_5$  at equilibrium.

You are given a balanced equation. From that, set up your  $K$  expression.

$$K = \frac{P(\text{PCl}_5)}{P(\text{PCl}_3) P(\text{Cl}_2)} = 13$$

Now where does that put us?

The problem starts with zero  $\text{PCl}_5$ . Right away, this raises an important point. Whenever you have a zero amount for any component(s) on one side of the balanced equation, then the exergonic direction is to that side of the equation. This means that the present reaction will go to the right.

We start with 1.00 atm  $\text{PCl}_3$  and 1.00 atm  $\text{Cl}_2$  on the left side of the equation. As the reaction proceeds, some  $\text{PCl}_3$  and some  $\text{Cl}_2$  react to form some  $\text{PCl}_5$ . Thus, as the reaction proceeds, the amounts of  $\text{PCl}_3$  and  $\text{Cl}_2$  decrease, while the amount of  $\text{PCl}_5$  increases. We can table this so far as follows.

	$P(\text{PCl}_3)$	$P(\text{Cl}_2)$	$P(\text{PCl}_5)$
Initial:	1.00 atm	1.00 atm	-0-
As reaction proceeds:	decrease	decrease	increase

Now let's get more specific with this.

The system is going to equilibrium. All coefficients in the balanced equation are ones, so everything reacts in a 1:1:1 manner and that simplifies things here. (That won't always be true, as we'll see in later Examples.) We assign 'x' to the amount by which  $P(\text{PCl}_3)$  changes.  $\text{Cl}_2$  reacts 1:1 with  $\text{PCl}_3$ , so  $\text{Cl}_2$  likewise decreases by 'x'.  $\text{PCl}_5$  is formed 1:1 as  $\text{PCl}_3$  reacts, so  $\text{PCl}_5$  is formed in 'x' amount upon reaching equilibrium. We table these changes as follows.

	$P(\text{PCl}_3)$	$P(\text{Cl}_2)$	$P(\text{PCl}_5)$
Initial:	1.00 atm	1.00 atm	-0-
Changes:	-x	-x	+x

Reagents which decrease have a negative change while those which increase have a positive change.

At the point of equilibrium balance, there is no further net change. We can depict the final equilibrium amounts as the initial amount plus the changes.

	$P(\text{PCl}_3)$	$P(\text{Cl}_2)$	$P(\text{PCl}_5)$
Initial:	1.00	1.00	-0-
Changes:	-x	-x	+x
Equilibrium:	1.00 - x	1.00 - x	x

Notice that the atm units were left out in this last table. These numbers are going into  $K$  as activities anyway, so this will simplify matters.

The bottom line of the table shows an algebraic representation for the final amounts at equilibrium. These amounts go into the  $K$  expression.

$$K = \frac{P(\text{PCl}_5)}{P(\text{PCl}_3) P(\text{Cl}_2)} = \frac{x}{(1.00 - x)(1.00 - x)} = 13$$

Now solve for  $x$ . Re-arrange.

$$\begin{aligned} x &= 13(1.00 - x)^2 \\ x &= 13x^2 - 26x + 13 \\ 13x^2 - 27x + 13 &= 0 \end{aligned}$$

This equation can be solved by use of the quadratic equation. For any equation of the form

$$ax^2 + bx + c = 0$$

then the values of  $x$  are given by

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

for which we currently have  $a = 13$ ,  $b = -27$  and  $c = 13$ , which sets up as follows.

$$x = \frac{27 \pm \sqrt{(-27)^2 - 4(13)(13)}}{2(13)}$$

Now, before you go cranking that out on the ole' abacus, let me make a point regarding significant figures.

This equation is quite a mix of arithmetic operations and it would be very tedious to follow our standard sigfig rules here. Furthermore, this equation is another example where rigid adherence to the sigfig rules is not justified. So, we get a shortcut: for our uses of the quadratic equation, go ahead and punch the whole thing out on the calculator and only round off at the end. Round off according to the fewest sigfigs in the values of  $a$ ,  $b$  or  $c$ . (Although there are a 2 and a 4 in the quadratic solution itself, those numbers are exact and do not affect round-off.) Punching out the above gives 0.7584... and 1.3184... as two results for  $x$ . Each of  $a$ ,  $b$  and  $c$  have two sigfigs, so that is where we round. Our final results are 0.76 and 1.3.

You will get two results from the quadratic equation because of the  $\pm$  part but only one of the two is correct. Which one? Fortunately, in many equilibrium problems, one turns out to give a nonsense answer. The other is the one you want. A nonsense answer? Yes, although mathematically correct, one result will typically give something which is chemically nonsensical. Let's consider the two current results for  $x$ .

Plug each quadratic result into the equilibrium amounts from the last line of the table.

$$\begin{aligned} \text{Quadratic result: } x = 0.76 \quad & P(\text{PCl}_3) = 1.00 - x = 0.24 \\ & P(\text{Cl}_2) = 1.00 - x = 0.24 \\ & P(\text{PCl}_5) = x = 0.76 \end{aligned}$$

OK, those numbers seem fine. Now try the other quadratic result.

$$\begin{aligned} \text{Quadratic result: } x = 1.3 \quad & P(\text{PCl}_3) = 1.00 - x = -0.3 \\ & P(\text{Cl}_2) = 1.00 - x = -0.3 \\ & P(\text{PCl}_5) = x = 1.3 \end{aligned}$$

This result gives negative activities (pressures) for  $\text{PCl}_3$  and  $\text{Cl}_2$  at equilibrium, which is nonsense since you can't have a negative pressure. Thus,  $x = 1.3$  is the nonsense result and we eliminate it from further consideration. We keep  $x = 0.76$  as our only valid result. For the final pressures, we append the atm unit.

$$P(\text{PCl}_3) = 0.24 \text{ atm} \quad P(\text{Cl}_2) = 0.24 \text{ atm} \quad P(\text{PCl}_5) = 0.76 \text{ atm}$$

That's it.

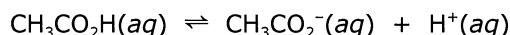
Since problems of this type can get more involved mathematically, these are more vulnerable to making a mistake and it is useful to check your answer in the end. Plug your numbers back into the  $K$  expression, and you should get the value of  $K$  as given originally, or at least close.

$$K = \frac{P(\text{PCl}_5)}{P(\text{PCl}_3) P(\text{Cl}_2)} = \frac{0.76}{(0.24)(0.24)} = 13$$

This one worked out to the exact same number as the given value of  $K$ , but often they come out a bit different. That's OK, but they should be close. If not close, go over your work.

Next.

**Example 4.** The following equilibrium has  $K = 1.8 \times 10^{-5}$  at 25 °C.



The process begins with 0.0962 mol  $\text{CH}_3\text{CO}_2\text{H}$  in 200. mL solution volume. Find the concentration of acetic acid, of acetate, and of hydrogen ion at equilibrium.

First move: spell out  $K$ .

$$K = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = 1.8 \times 10^{-5}$$

OK, this Example starts similarly to Example 3: the initial conditions in the system have some amount of reagents on one side of the equation but none on the other side. The exergonic direction is forward,  $L \rightarrow R$ . We will again set up a table for the initial amounts, the changes in amounts, and the equilibrium amounts and then take it from there. Before we can do that, however, the amount for the given  $\text{CH}_3\text{CO}_2\text{H}$  needs to be in molarity, so we need to calculate that from the given information.

$$\text{initial } [\text{CH}_3\text{CO}_2\text{H}] = \frac{0.0962 \text{ mol}}{0.200 \text{ L}} = 0.481 \text{ M}$$

This amount will decrease as the reaction proceeds; the change will be given by  $x$ . The amounts for  $[\text{H}^+]$  and  $[\text{CH}_3\text{CO}_2^-]$  will increase. Since all coefficients in the balanced equation again are 1:1:1, then all reagents change in 1:1:1 ratios. Thus, the decrease by  $x$  for  $[\text{CH}_3\text{CO}_2\text{H}]$  will give an increase by  $x$  for  $[\text{H}^+]$  and the same for  $[\text{CH}_3\text{CO}_2^-]$ . The table is then set up as follows.

	$[\text{CH}_3\text{CO}_2\text{H}]$	$[\text{H}^+]$	$[\text{CH}_3\text{CO}_2^-]$
Initial:	0.481	-0-	-0-
Changes:	- $x$	+ $x$	+ $x$
Equilibrium:	$0.481 - x$	$x$	$x$

Since these again are activities, I've left the M unit off the amounts. Now, plug the last line into  $K$ .

$$K = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(x)(x)}{0.481 - x} = 1.8 \times 10^{-5}$$

You will need to solve for  $x$ . Re-arrange.

$$x^2 = 1.8 \times 10^{-5} (0.481 - x)$$

This will again end up in quadratic format. The above equation will eventually come to

$$x^2 + 1.8 \times 10^{-5}x - 8.7 \times 10^{-6} = 0$$

for which

$$a = 1 \text{ (exact)} \quad b = 1.8 \times 10^{-5} \quad c = -8.7 \times 10^{-6}$$

and this plugs in as

$$x = \frac{-(-1.8 \times 10^{-5}) \pm \sqrt{(1.8 \times 10^{-5})^2 - 4(1)(-8.7 \times 10^{-6})}}{2(1)}$$

from which you get two results for  $x$ , namely  $-0.0030$  and  $+0.0029$ . One of these is nonsense. Which? Notice in our table above that  $x$  is a concentration for  $[H^+]$  and  $[CH_3CO_2^-]$ . This will rule out the  $-0.0030$  result, since that would give a negative concentration. We work with the  $+0.0029$  result. Plugging this into the expressions for the equilibrium amounts, we get the final values.

$$\begin{aligned} [CH_3CO_2H] &= 0.481 - x = 0.481 - 0.0029 = 0.478 \\ [H^+] &= x = 0.0029 \\ [CH_3CO_2^-] &= x = 0.0029 \end{aligned}$$

We can check this by plugging these values into the  $K$  expression.

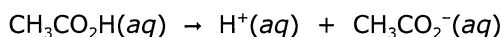
$$K = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{(0.0029)(0.0029)}{0.478} = 1.8 \times 10^{-5}$$

This value of  $K$  matches the given value so we're good. Our final answers will be in molarities.

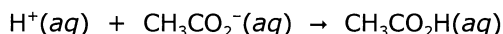
$$[CH_3CO_2H] = 0.478 \text{ M} \quad [H^+] = 0.0029 \text{ M} \quad [CH_3CO_2^-] = 0.0029 \text{ M}$$

Now, pause a minute and look at the result. Acetic acid is a weak acid, as we have discussed ever since Chapter 11. We introduced the equilibrium aspect in Chapter 12. Here are two quotes from Section 12.4.

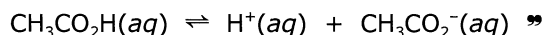
“ Acetic acid dissociates, but not a lot.



The reason is that the backwards reaction also occurs: acetate can react with  $H^+$  to re-form the acid.



Both processes occur at the same time. Some molecules dissociate to ions and some ions recombine to form neutral molecules. This is an equilibrium. We can represent this as



“ These two processes will reach a balance, but that balance is nowhere near even. Depending on conditions, the amount dissociated could be 10% or 1% or 0.1% or etc. The exact numbers aren't important for us at this time, but we'll see their calculations later in Chapter 52. ”

Later is now.

Those percent terms mentioned back in Chapter 12 as applied to a weak acid are called percent dissociation. Percent dissociation tells us the extent to which some compound (such as an acid or a base) has dissociated upon reaching equilibrium. The calculation is fairly straightforward.

$$\%diss = \frac{\text{amount which dissociated}}{\text{starting amount}} \times 100\%$$

For the current Example, we began with 0.481 M of  $CH_3CO_2H$ , of which 0.0029 M dissociated to  $H^+$  and  $CH_3CO_2^-$ .

$$\%diss = \frac{0.0029 \text{ M}}{0.481 \text{ M}} \times 100\% = 0.60\%$$

Be careful with this calculation, because some students get confused by the number to use in the denominator. That number is the starting amount and not the equilibrium amount. Note the distinction.

Here's the significance of this calculation. Percent dissociation is a relative relationship. It's the percent of how much acid did dissociate ( $L \rightarrow R$ ) relative to how much acid was originally present. Keep in mind that the equilibrium is dynamic and the system is still reacting in both directions, so the amounts are the net changes between initial condition and equilibrium. The net change here is only 0.60%, which means that only 0.60% of the original  $CH_3CO_2H$  molecules are dissociated to ions at equilibrium at any point in time; most (99.40%) are still intact, neutral molecules of  $CH_3CO_2H$ . The small value of 0.60% is consistent with the meaning of a weak acid.

We will be doing quite a bit more with percent dissociation when we get more involved in aqueous equilibria beginning in Chapter 54. Also in those Chapters, we will see how percent dissociation changes depending on initial concentrations. That's later. For now, I have simply introduced percent dissociation

as one way to assess how much change actually occurs between initial amounts and equilibrium amounts. Again, this represents a relative amount of change. Some systems, such as in the present Example, do not change much at all. Other systems, such as in the prior Example 3, can change quite a bit. You will see a range of change as you encounter more and more such problems. There is an extra advantage to problem solving when the relative change is small and this leads to a new tool for doing such problems. That tool is approximation.

## 52.2 Approximation

Approximation? As in guessing? Well, no, it's a bit more involved than that. In fact, there are many approximation methods used in chemistry and there are various levels of sophistication involved. The reasons for approximation methods are to simplify calculations and also to make some problems doable which can't be done directly. For now, we will start with a basic approach and we will hone the method as we go into later Chapters.

Approximation works best for equilibrium problems when there is little relative change between the initial amounts and the equilibrium amounts. This is demonstrated with the acetic acid dissociation above, because percent dissociation tells us this directly: there was only 0.60% relative change between initial and final amounts. This outcome is typical for weak acids, although there will be variations. Approximation methods are not limited to weak acids, however, and we will apply them where we can to other equilibria as well. The "where we can" part is important, as you will see.

Here's what you need to know for starting off our approximation methods. We'll call this simple approximation and we'll add to it later.

### Simple Approximation

When there is only a small relative difference between the final equilibrium amounts and the initial amounts for the calculation, then an approximation to  $K$  can frequently be made by leaving one or more initial amounts as "relatively unchanged".

The frequently and "relatively unchanged" parts are important. "Relatively unchanged" really means "not changed enough" for purposes of approximation. In reality, the amounts do change but the relative change is small enough that the approximation still works. The frequently part is really important: this doesn't always work, but checks can be made to see if it is working or not. Again, this is simple level, our intro to approximation.

Let's now apply this to Example 4 and see how this works.

We've already worked out the Example and we know the relative change was small on going to equilibrium. But let's pretend that we haven't yet done the Example, so we don't know the change amounts and we don't know percent dissociation. Let's redo the Example by approximation. Before you do a problem by approximation, remember that the relative change must be small for this to work. Your first clue for a change to be small is the magnitude of  $K$ . The  $K$  for the Example is in the  $10^{-5}$  range which is small, so we can expect that most of the amounts of reagents will lie well to the left side of the equation at equilibrium. Since the Example starts with given amounts only on the left side, then it will indeed change to the right side, but a  $K$  of  $10^{-5}$  says the relative change will be small.

Return to the final equilibrium line of the table.

	$[\text{CH}_3\text{CO}_2\text{H}]$	$[\text{H}^+]$	$[\text{CH}_3\text{CO}_2^-]$
Equilibrium:	$0.481 - x$	$x$	$x$

If we assume the relative change is small, then we are assuming that  $x$  is small relative to 0.481; our approximation then takes the form  $0.481 - x \approx 0.481$ .

HINT: You only approximate where an  $x$  is being added to or subtracted from a substantially bigger number, such as for  $[\text{CH}_3\text{CO}_2\text{H}]$  in the table here. You cannot approximate for an  $x$  which stands by itself, such as for  $[\text{H}^+]$  or  $[\text{CH}_3\text{CO}_2^-]$ .

OK, let's take the approximation into  $K$ .

$$K = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(x)(x)}{0.481 - x} \approx \frac{(x)(x)}{0.481} = 1.8 \times 10^{-5}$$

This becomes

$$x^2 = 1.8 \times 10^{-5} (0.481)$$

and this simplifies things because now you don't need the quadratic equation. Solving will give  $x = \pm 0.0029$ . Only the positive version will work again; this gives the same value for  $x$  (to the allowed sigfigs) as derived from the full-blown quadratic equation shown previously. Thus, the approximation step was fully valid. You would then plug this  $x$  into all of the expressions for equilibrium amounts.

$$\begin{aligned} [\text{CH}_3\text{CO}_2\text{H}] &= 0.481 - x = 0.481 - 0.0029 = 0.478 \\ [\text{H}^+] &= x = 0.0029 \\ [\text{CH}_3\text{CO}_2^-] &= x = 0.0029 \end{aligned}$$

This also gives the same numbers as previously. Note! Although you approximated  $(0.481 - x) \approx (0.481)$  in order to obtain a value of  $x$ , you must still plug this  $x$  back into the final equilibrium line in the table to get your ultimate answer for  $[\text{CH}_3\text{CO}_2\text{H}]$ .

Let me make three points.

First point: Approximation can simplify the mathematical manipulations in many equilibrium problems. Many problems, but not all. The primary requirement for success is for the change amounts to be relatively small, and the first clue for that is the magnitude of  $K$ . On the other hand, approximation will fail if the relative change amounts are sizeable. In Example 4, the  $K$  was small but, in Example 3, the  $K$  was moderate. The change amounts were relatively large in Example 3 and approximation cannot be used. (Go ahead and try it. Approximation fails pathetically.) The solution to Example 3 required the full quadratic equation.

Second point: Approximation is a very handy tool but you won't need it all the time. So don't use it if the problem is straightforward. On the other hand, there will be problems which cannot be solved by direct methods, and you must use approximation. Example 6 later will illustrate this.

Third point: Sigfigs actually play a role in the approximation method. When your answer is limited to fewer sigfigs, then you can get away with approximation more often. Our  $K$ 's and  $x$ 's so far have been limited to two sigfigs, so that has helped. If you need three sigfigs, then you have to be more careful with approximation.

As we go through this and upcoming Chapters, we'll often work with approximation and you will see more of this methodology. We will also be improving upon it as we go.

### 52.3 General steps for change

Examples 3 and 4 are illustrative of the type of equilibrium problem which requires solving for a change in amounts. Remember that these are different from the type in Chapter 51, namely Examples 1 and 2, which dealt with  $K$  or  $Q$  using only the amounts as given. In general, when you are given a problem to do, be sure to distinguish these two types of problems. For clarity, let's spell out the distinction.

Examples 1 and 2 gave some amounts and then asked for  $K$  or  $Q$  with those same amounts. These unchanged amounts were directly plugged into  $K$  or  $Q$ .

Examples 3 and 4 started at some point with some amounts but then asked for amounts at equilibrium. This required changes from the given amounts and the final equilibrium amounts were based on those changes.

The approaches to these two types of problems are different, and the former tend to be much easier than the latter. Some students confuse these two types and they end up turning an easy problem into a nightmare. Again, heed the distinction.

For working with problems involving changes in amounts, there are some General Steps to follow.

#### General Steps to Equilibrium Calculations Which Involve Changes in Amounts

1. Begin with a balanced equation for the equilibrium process.
2. Set up the  $K$  expression.
3. Start a table with the initial amounts (atm, M or mol) which are given for each  $K$  component.
4. For the next line in the table, set up the changes in the amounts (atm, M or mol) for each  $K$  component based on  $x$ 's.
5. For the final line in the table, add the amounts from Steps 3 and 4 to get the equilibrium amounts (atm, M or mol) for each  $K$  component.
6. Plug the expressions for the equilibrium amounts into  $K$  and solve for  $x$ .

7. Plug the value of  $x$  into the final line of the table to solve for the equilibrium amounts.
8. Check your work by plugging the equilibrium amounts into the  $K$  expression and solving for the value of  $K$ .

That's the listing of the Steps. Here are comments for some of them.

Step 1. You must have a balanced equation. You can't do this without one.

Step 3. We had atm in Example 3 and M in Example 4; we'll see the use of mol in Example 7. Remember that only gases and solutes are  $K$  components. Liquids and solids are always unity condition as long as there is some amount of them present.

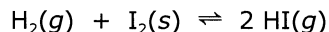
Step 4. This Step requires two things. First, you should know the direction in which the system is heading to reach equilibrium. If no amounts are initially present on one side of the equation, then the system will head to that side. If amounts are initially present for all reagents on both sides of the equation, then you need  $Q$  in order to determine the direction. Knowing the direction allows you to assign a negative  $x$  or a positive  $x$  to the change amounts (although often the math does work out either way). Second, you must take into account the coefficients in the balanced equation. The coefficients in the balanced equation will be the coefficients for the change amounts. This is very important. Examples 3 and 4 had 1:1:1 coefficients and those are the easiest, but life isn't always easy.

Step 6. This is likely to involve some kind of algebraic manipulation, possibly assisted by approximation but not always.

Step 8. This is useful, given the tedious nature of some of the calculations. Your check on  $K$  should be close to the starting value of  $K$  but it does not have to be exact. If it's not even close, then you need to check your math. Also, this check can tell you if an approximation failed.

If you go back over Examples 3 and 4, you will see that we actually followed these Steps. For a new illustration, we will pick up where we left off in Example 1B in the last Chapter. We had completed the Example at that time by determining  $Q$  and the exergonic direction. Now, we'll extend that problem by letting the system go to equilibrium.

**Example 5.** The following reaction has  $K = 0.284$  at 298 K.



Given the following amounts,

0.0418 atm  $\text{H}_2$                       0.00771 mol  $\text{I}_2$                       0.132 atm HI

calculate the pressures of  $\text{H}_2$  and of HI at equilibrium.

This Example is different from Examples 3 and 4 for four reasons: the system starts with amounts for all reagents on both sides; the coefficients in the balanced equation are not all ones; the exergonic direction is reverse; and, a solid is involved. Nevertheless, we still follow the General Steps.

- ▶ Step 1. Balanced equation is provided.
- ▶ Step 2. You'll need the  $K$  expression again.

$$K = \frac{P(\text{HI})^2}{P(\text{H}_2)}$$

- ▶ Step 3. Start a table with the given initial amounts.

	$P(\text{H}_2)$	$P(\text{HI})$
Initial:	0.0418	0.132

Since  $\text{I}_2$  is solid phase and not a  $K$  component, we don't need it here. The mol  $\text{I}_2$  information is irrelevant to the problem.

- ▶ Step 4. Set up the change amounts. In Example 1B, we had determined  $Q = 0.417$  and the exergonic direction was reverse. The system is going  $\text{L} \leftarrow \text{R}$  so watch your signs on your  $x$ 's:  $P(\text{H}_2)$  will increase and  $P(\text{HI})$  will decrease. Also, you now have a catch with the coefficients. You must give each reagent's  $x$  the same coefficient as in the balanced equation. HI has a coefficient of two in the balanced equation, so its  $x$  in the table likewise gets a coefficient of two.

	$P(\text{H}_2)$	$P(\text{HI})$
Initial:	0.0418	0.132
Changes:	+x	-2x

- Step 5. Set up the final equilibrium amounts.

	$P(\text{H}_2)$	$P(\text{HI})$
Initial:	0.0418	0.132
Changes:	+x	-2x
Equilibrium:	0.0418 + x	0.132 - 2x

- Step 6. Plug into  $K$  and solve for  $x$ .

$$K = \frac{P(\text{HI})^2}{P(\text{H}_2)} = \frac{(0.132 - 2x)^2}{0.0418 + x} = 0.284$$

That's a fairly complicated setup. Should we approximate? No, the  $K$  is only 0.284 which is not small enough. The changes could be sizeable. Solve directly.

$$\begin{aligned} (0.132 - 2x)^2 &= 0.284(0.0418 + x) \\ 0.0174 - 0.528x + 4x^2 &= 0.0119 + 0.284x \\ 4x^2 - 0.812x + 0.0055 &= 0 \end{aligned}$$

Plug this into the quadratic equation and you will get 0.0070 and 0.20 for  $x$ .

- Step 7. We need to plug the value of  $x$  into the equilibrium amounts. Which  $x$ ? One is nonsense. If  $x = 0.20$ , then  $0.132 - 2x$  gets you a negative pressure for HI. That won't work. Go instead with  $x = 0.0070$ .

$$\begin{aligned} P(\text{H}_2) &= 0.0418 + x = 0.0488 \\ P(\text{HI}) &= 0.132 - 2x = 0.118 \end{aligned}$$

- Step 8. Check on the math by plugging these back into  $K$ .

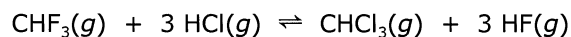
$$K = \frac{P(\text{HI})^2}{P(\text{H}_2)} = \frac{(0.118)^2}{0.0488} = 0.285$$

0.285 is close enough to the original 0.284. All is good. The final answers are in atm.

$$P(\text{H}_2) = 0.0488 \text{ atm} \quad P(\text{HI}) = 0.118 \text{ atm}$$

Finis.

**Example 6.** Consider the following equilibrium.



At 0. °C,  $K = 2.1 \times 10^{-9}$ . The system begins with 0.13 atm  $\text{CHF}_3$  and 0.51 atm HCl. Calculate the pressures of each reactant and of each product at equilibrium.

- Step 1. Balanced equation is provided.  
 ► Step 2.  $K$

$$K = \frac{P(\text{CHCl}_3) P(\text{HF})^3}{P(\text{CHF}_3) P(\text{HCl})^3}$$

- Step 3. Start the table: initial amounts.

	$P(\text{CHF}_3)$	$P(\text{HCl})$	$P(\text{CHCl}_3)$	$P(\text{HF})$
Initial:	0.13	0.51	-0-	-0-

- Step 4. Change amounts. No amounts were given on the right, so the exergonic direction is forward.



	$P(\text{CHF}_3)$	$P(\text{HCl})$	$P(\text{CHCl}_3)$	$P(\text{HF})$
Initial:	0.13	0.51	-0-	-0-
Changes:	-x	-3x	+x	+3x

► Step 5. Final equilibrium amounts.

	$P(\text{CHF}_3)$	$P(\text{HCl})$	$P(\text{CHCl}_3)$	$P(\text{HF})$
Initial:	0.13	0.51	-0-	-0-
Changes:	-x	-3x	+x	+3x
Equilibrium:	$0.13 - x$	$0.51 - 3x$	x	$3x$

► Step 6. Plug into  $K$  and solve.

$$K = \frac{P(\text{CHCl}_3) P(\text{HF})^3}{P(\text{CHF}_3) P(\text{HCl})^3} = \frac{(x) (3x)^3}{(0.13 - x) (0.51 - 3x)^3} = 2.1 \times 10^{-9}$$

OK, this is getting ugly fast. This would be a good time to think about approximating. In fact, you have no choice since the problem will involve fourth power terms and cannot be solved directly. Fortunately,  $K$  is quite small so the relative change should be small.

Assume  $x$  is small relative to 0.13, which means  $0.13 - x \approx 0.13$ . Furthermore, assume  $3x$  is small relative to 0.51, which means  $0.51 - 3x \approx 0.51$ . This simplifies the denominator drastically.

$$\frac{(x) (3x)^3}{(0.13 - x) (0.51 - 3x)^3} \approx \frac{(x) (3x)^3}{(0.13) (0.51)^3} = 2.1 \times 10^{-9}$$

Re-arrange and solve.

$$\begin{aligned} (x) (3x)^3 &= 2.1 \times 10^{-9} (0.13) (0.51)^3 \\ 27x^4 &= 3.62137... \times 10^{-11} \\ x &= \pm 0.0011 \end{aligned}$$

► Step 7. Plug this  $x$  into the equilibrium amounts. The negative version comes out as the nonsense answer. Go with the +0.0011.

$$\begin{aligned} P(\text{CHF}_3) &= 0.13 - x = 0.13 \text{ (atm)} \\ P(\text{HCl}) &= 0.51 - 3x = 0.51 \text{ (atm)} \\ P(\text{CHCl}_3) &= x = 0.0011 \text{ (atm)} \\ P(\text{HF}) &= 3x = 0.0033 \text{ (atm)} \end{aligned}$$

► Step 8.  $K$ -check.

$$K = \frac{P(\text{CHCl}_3) P(\text{HF})^3}{P(\text{CHF}_3) P(\text{HCl})^3} = \frac{(0.0011) (0.0033)^3}{(0.13) (0.51)^3} = 2.3 \times 10^{-9}$$

That value is close enough to the originally provided value of  $2.1 \times 10^{-9}$ . Done.

Notice that the approximation was successful. In the end and to the correct sigfigs,  $0.13 - x = 0.13$  and  $0.51 - 3x = 0.51$ . Thus, the small changes did not even affect the final values for the reactant pressures,  $P(\text{CHF}_3)$  and  $P(\text{HCl})$ .

By the way, you may be wondering what is meant by "close enough" for a  $K$ -check. Typically, if you make a significant mistake in the math, the  $K$ -check will be off quite a bit. When you do the math correctly, you can be a little off and that will depend on the sigfigs, the powers involved, and the specific values provided. Basically, you go with close enough. If you're not sure, check your math again.

Let's do something effervescent.

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**Example 7.** Consider the solubility equilibrium for  $\text{CO}_2(g)$ . Example 6 in Chapter 47 involved a calculation for a system already at equilibrium. Now let's do it differently. A 2 L bottle is partly filled with water and then charged with 0.227 mol  $\text{CO}_2(g)$ . The system then proceeded to equilibrium. The gas volume was 1.46 L and the solution volume was 0.621 L. Calculate the pressure of  $\text{CO}_2(g)$  and the concentration of  $\text{CO}_2(aq)$  at equilibrium at 25 °C, for which  $K = 0.0336$ .

.....

This is different. This is a phase equilibrium problem. We are dealing with  $\text{CO}_2$  as a gas and as a solute. Watch how this works.

- Step 1. Balanced equation.  $\text{CO}_2(g) \rightleftharpoons \text{CO}_2(aq)$   
 ► Step 2.  $K$

$$K = \frac{[\text{CO}_2(aq)]}{P(\text{CO}_2(g))}$$

- Step 3. We are given moles of gas. Some of the gas will dissolve and the system will end up with some moles as solute and some moles still in the gas phase. Since we are dealing with mixed units here (atm and M), it will be best to keep amounts in moles since we can still relate moles as 1:1 as in the balanced equation. We'll do the table in mole amounts.

	mol $\text{CO}_2(g)$	mol $\text{CO}_2(aq)$
Initial:	0.227	-0-

- Step 4. Changes.

	mol $\text{CO}_2(g)$	mol $\text{CO}_2(aq)$
Initial:	0.227	-0-
Changes:	-x	+x

- Step 5. Final equilibrium amounts.

	mol $\text{CO}_2(g)$	mol $\text{CO}_2(aq)$
Initial:	0.227	-0-
Changes:	-x	+x
Equilibrium:	0.227 - x	+x

- Step 6. In order to plug into  $K$ , you have to get the moles into activities based on atm and M. We have a little finagling to do.

For  $\text{CO}_2(g)$ , the pressure at equilibrium is calculated from the ideal gas equation.

$$P(\text{CO}_2(g)) = \frac{nRT}{V} = \frac{(0.227 \text{ mol} - x) (0.08206 \text{ L} \cdot \text{atm}/(\text{mol} \cdot \text{K})) (298 \text{ K})}{1.46 \text{ L}}$$

For  $\text{CO}_2(aq)$ , the concentration at equilibrium is a simple molarity calculation.

$$[\text{CO}_2(aq)] = \frac{\text{mol}}{V} = \frac{x}{0.621 \text{ L}}$$

These relationships go into  $K$  as activities without units.

$$K = \frac{[\text{CO}_2(aq)]}{P(\text{CO}_2(g))} = \frac{\frac{x}{0.621}}{\frac{(0.227 - x) (0.08206) (298)}{1.46}} = 0.0336$$

Approximate? Well, the  $K$  is not real small so the changes are likely to be sizeable. Besides, although this looks downright ugly, it's still an algebra problem and all  $x$ 's are to first power only. Proceed as is.

$$\begin{aligned} \frac{x}{0.621} &= 0.0336 \times \frac{(0.227 - x) (0.08206) (298)}{1.46} \\ x &= 0.0336 \times \frac{(0.227 - x) (0.08206) (298)}{1.46} \times 0.621 \\ x &= 0.0793 - 0.349x \\ x &= 0.0588 \end{aligned}$$

- Step 7. This gives the moles at equilibrium.

$$\begin{aligned}\text{moles CO}_2(g) &= 0.227 - x = 0.227 - 0.0588 = 0.168 \\ \text{moles CO}_2(aq) &= x = 0.0588\end{aligned}$$

The Example wants final pressure and concentration.

$$P(\text{CO}_2(g)) = \frac{nRT}{V} = \frac{(0.168 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/(\text{mol} \cdot \text{K}))(298 \text{ K})}{1.46 \text{ L}} = 2.81 \text{ atm}$$

$$[\text{CO}_2(aq)] = \frac{0.0588 \text{ mol}}{0.621 \text{ L}} = 0.0947 \text{ M}$$

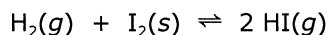
► Step 8. *K*-check.

$$K = \frac{[\text{CO}_2(aq)]}{P(\text{CO}_2(g))} = \frac{0.0947}{2.81} = 0.0337$$

Close enough. Put it to bed. The final pressure of  $\text{CO}_2(g)$  is 2.81 atm and the final concentration of  $\text{CO}_2(aq)$  is 0.0947 M.

Your turn. Repeat Example 5 but with different starting amounts.

.....  
**Example 8.** The following equilibrium has  $K = 0.284$  at 298 K.



The following amounts were present.

$$1.000 \text{ atm H}_2 \quad (\text{some amount of I}_2) \quad 1.000 \text{ atm HI}$$

Calculate the pressures of  $\text{H}_2$  and of  $\text{HI}$  at equilibrium.

.....  
Do the Steps. Do as much as you can without looking at Example 5, but look back if you need to.

► Step 1. Balanced equation is given.

► Step 2.  $K$

► Step 3. Start a table with the initial amounts.

$$P(\text{H}_2) \qquad P(\text{HI})$$

Initial:

► Step 4. Change amounts. Which way is it going? What is the value of  $Q$ ? What does  $Q$  vs.  $K$  tell you?

Changes:

► Step 5. Final equilibrium amounts.

Equilibrium:

► Step 6. Plug into  $K$  and solve for  $x$ . Don't bother approximating.

Somewhere along the way, you should get to here.

$$4x^2 - 4.284x + 0.716 = 0$$

Go quadratic.

- Step 7. Eliminate the nonsense answer and go with the good x.

$$P(\text{H}_2) =$$

$$P(\text{HI}) =$$

- Step 8. Check on the math by plugging these back into  $K$ .

OK? If you want to check your answers, they're in Case A of Chapter 51.

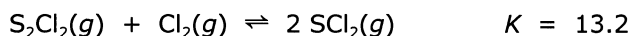
The Examples shown above are a sample of the variety of equilibrium problems. Although the variety can make them seem totally different, they are all fundamentally the same in approach and execution. Some are indeed easier than others, while some can be a bit challenging.

Approximation will often help in these problem types, but not always. Don't worry right now if you're not sure when to use it. You will get much better with this as you get more into equilibrium problems. We will also be stepping up our approximation methods. Try it, see if it works. Sometimes it won't work. On the other hand, sometimes approximation is the only way. Be flexible.

And as with anything which can seem complicated: practice, practice, practice.

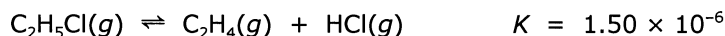
### Problems

1. Consider the following equilibrium system.



The process begins with 1.00 atm of each reagent ( $\text{S}_2\text{Cl}_2$ ,  $\text{Cl}_2$  and  $\text{SCl}_2$ ) and then proceeds to equilibrium. What are the pressures of  $\text{Cl}_2$  and of  $\text{SCl}_2$  at equilibrium?

2. Consider the following equilibrium system.



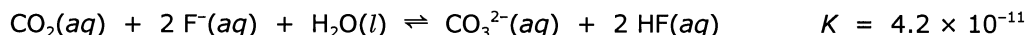
The process begins with 0.482 atm  $\text{C}_2\text{H}_5\text{Cl}$ . What are the pressures of  $\text{C}_2\text{H}_5\text{Cl}$  and of  $\text{C}_2\text{H}_4$  at equilibrium?

3. Consider the following equilibrium system.



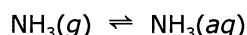
The process begins with  $\text{Cl}_2(g)$  and  $\text{BrCl}(g)$  at 1.00 atm each;  $\text{Br}_2(l)$  is in excess. What are the pressures of  $\text{Cl}_2$  and of  $\text{BrCl}$  at equilibrium?

4. Consider the following equilibrium system.



The process begins with 0.028 M  $\text{CO}_2$  and 0.017 M  $\text{F}^-$ . What are the concentrations of each solute at equilibrium?

5. Consider the solubility equilibrium of  $\text{NH}_3(g)$  in water at 298 K.



a. Calculate  $\Delta G^\circ$ .

b. Calculate  $K$ .

c. A container is partly filled with an  $\text{NH}_3(aq)$  solution which initially contains 0.00937 mol  $\text{NH}_3$ . At equilibrium, the solution volume was 200. mL and the gas space volume was 4.00 L. What are the concentration of  $\text{NH}_3(aq)$  and the pressure of  $\text{NH}_3(g)$  at equilibrium?