

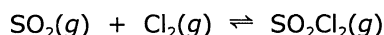
We now start into equilibrium problems which involve changes in the amounts of reagents upon going from a given set of conditions to the point of equilibrium. These problems are a bit more involved and we will bring in some new tools for dealing with these.

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 25 °C, K for the following equilibrium is 61.4.



The process is started with 0.600 atm SO_2 and 0.600 atm Cl_2 . The system then proceeds to equilibrium. Find the pressures (in atm) of SO_2 , Cl_2 and SO_2Cl_2 at equilibrium.

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

$$K = \frac{P(\text{SO}_2\text{Cl}_2)}{P(\text{SO}_2) P(\text{Cl}_2)} = 61.4$$

Now where does that put us?

The problem starts with zero SO_2Cl_2 . 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. KNOW THIS. For this Example, the reaction will go to the right.

We start with 0.600 atm SO_2 and 0.600 atm Cl_2 on the left side of the equation. As the reaction proceeds, some SO_2 and some Cl_2 react to form some SO_2Cl_2 ; thus, the amounts of SO_2 and Cl_2 decrease, while the amount of SO_2Cl_2 increases. We can table this so far as follows.

	$P(\text{SO}_2)$	$P(\text{Cl}_2)$	$P(\text{SO}_2\text{Cl}_2)$
Initial:	0.600 atm	0.600 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 $P(\text{SO}_2)$ changes. Cl_2 reacts 1:1 with SO_2 , so Cl_2 likewise decreases by 'x'. SO_2Cl_2 is formed 1:1 as SO_2 reacts, so SO_2Cl_2 is formed in 'x' amount upon reaching equilibrium. We table these changes as follows.

	$P(\text{SO}_2)$	$P(\text{Cl}_2)$	$P(\text{SO}_2\text{Cl}_2)$
Initial:	0.600 atm	0.600 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.

	$P(\text{SO}_2)$	$P(\text{Cl}_2)$	$P(\text{SO}_2\text{Cl}_2)$
Initial:	0.600	0.600	-0-
Changes:	-x	-x	+x
Equilibrium:	0.600 - x	0.600 - 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. By the way, these tables are sometimes called ICE tables for Initial/Changes/Equilibrium.

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

$$K = \frac{P(\text{SO}_2\text{Cl}_2)}{P(\text{SO}_2) P(\text{Cl}_2)} = \frac{x}{(0.600 - x)(0.600 - x)} = 61.4$$

Now solve for x . Re-arrange.

$$\begin{aligned} x &= 61.4 (0.600 - x)^2 \\ x &= 61.4x^2 - 73.7x + 22.1 \\ 61.4x^2 - 74.7x + 22.1 &= 0 \end{aligned}$$

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

$$a x^2 + b x + c = 0$$

then the values of x are given by

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

for which we currently have $a = 61.4$, $b = -74.7$ and $c = 22.1$, which sets up as follows.

$$x = \frac{74.7 \pm \sqrt{(-74.7)^2 - 4(61.4)(22.1)}}{2(61.4)}$$

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 0.50779... and 0.70881... as two results for x . Each of a , b and c have three sigfigs, so we round to three. Our final results are 0.508 and 0.709.

You will get two results from the quadratic equation due to 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.

$$\begin{aligned} \text{Quadratic result: } x = 0.508 & & P(\text{SO}_2) &= 0.600 - x = 0.092 \\ & & P(\text{Cl}_2) &= 0.600 - x = 0.092 \\ & & P(\text{SO}_2\text{Cl}_2) &= x = 0.508 \end{aligned}$$

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

$$\begin{aligned} \text{Quadratic result: } x = 0.709 & & P(\text{SO}_2) &= 0.600 - x = -0.109 \\ & & P(\text{Cl}_2) &= 0.600 - x = -0.109 \\ & & P(\text{SO}_2\text{Cl}_2) &= x = 0.709 \end{aligned}$$

This result gives negative activities (pressures) for SO_2 and Cl_2 at equilibrium, which is nonsense since you can't have a negative pressure. Thus, $x = 0.709$ is the nonsense result and we eliminate it from further consideration. We keep $x = 0.508$ as our only valid result. For the final pressures, we append the atm unit.

$$P(\text{SO}_2) = 0.092 \text{ atm} \quad P(\text{Cl}_2) = 0.092 \text{ atm} \quad P(\text{SO}_2\text{Cl}_2) = 0.508 \text{ atm}$$

That's it.

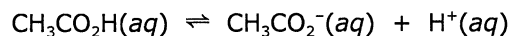
Since problems of this type can get more involved mathematically, these are more vulnerable to making a mistake and it is useful to check your answer in the end. Plug your numbers back into the K expression, and you should get the value of K as given originally, or at least close.

$$K = \frac{P(\text{SO}_2\text{Cl}_2)}{P(\text{SO}_2) P(\text{Cl}_2)} = \frac{0.508}{(0.092)(0.092)} = 60.$$

This is decent agreement to the given value of 61.4. A slight difference is not unusual at this stage of the game, but the values need to 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 concentrations (in M) 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.

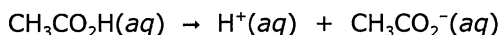
$$K = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{(0.0029)(0.0029)}{0.478} = 1.8 \times 10^{-5}$$

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

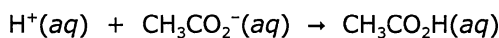
$$[CH_3CO_2H] = 0.478 \text{ M} \quad [H^+] = 0.0029 \text{ M} \quad [CH_3CO_2^-] = 0.0029 \text{ M}$$

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.

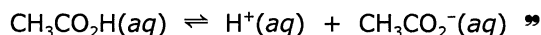
“ Acetic acid dissociates, but not a lot.



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 further develop 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 of the acid. 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" to interfere with 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. The K and x in this Example were limited to two sigfigs, so that has helped. If three sigfigs are involved, 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 or M) which are given for each K component.
4. For the next line in the table, set up the changes in the amounts (atm or M) 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 or M) 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. 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 solutes and gases 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 sometimes 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.

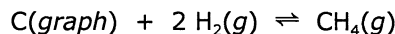
Step 6. This is likely to involve some kind of algebraic manipulation, possibly assisted by approximation but not always.

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.

Let's take a look at three more Examples.

Example 5. The following reaction has $K = 1.38$ at 800. K.



Given the following amounts,

0.119 mol C 0.270 atm H₂ 0.206 atm CH₄

calculate the pressures (in atm) of H₂ and of CH₄ 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 (as you will see in Step 4 below); 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.

$$K = \frac{P(\text{CH}_4)}{P(\text{H}_2)^2}$$

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

	$P(\text{H}_2)$	$P(\text{CH}_4)$
Initial:	0.270	0.206

Since graphite is solid phase and not a K component, we don't need it here. It stays unity activity. The amount given for mol C is irrelevant to the problem.

- ▶ Step 4. Set up the changes in amounts. Which way is this going? We need Q . Plugging in the initial pressures gives you $Q = 2.83$; since this is larger than K , the exergonic direction is 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 $P(\text{CH}_4)$ 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. H₂ has a coefficient of two in the balanced equation, so its x in the table likewise gets a coefficient of two.

	$P(\text{H}_2)$	$P(\text{CH}_4)$
Initial:	0.270	0.206
Changes:	+2x	-x

- Step 5. Set up the final equilibrium amounts.

	$P(\text{H}_2)$	$P(\text{CH}_4)$
Initial:	0.270	0.206
Changes:	+2x	-x
Equilibrium:	0.270 + 2x	0.206 - x

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

$$K = \frac{P(\text{CH}_4)}{P(\text{H}_2)^2} = \frac{0.206 - x}{(0.270 + 2x)^2} = 1.38$$

That's a fairly complicated setup. Should we approximate? No, the K is only 1.38 which is not large or small enough. The changes are likely to be sizeable. Solve directly.

$$\begin{aligned} 0.206 - x &= 1.38 (0.270 + 2x)^2 \\ 0.206 - x &= 0.101 + 1.49x + 5.52x^2 \\ 5.52x^2 + 2.49x - 0.105 &= 0 \end{aligned}$$

Plug this into the quadratic equation and you will get 0.0388 and -0.490 for x .

- Step 7. We need to plug the value of x into the equilibrium amounts. Which x ? One is nonsense. If $x = -0.490$, then you'll get a negative pressure for H_2 . That won't work. Go instead with $x = 0.0388$.

$$\begin{aligned} P(\text{H}_2) &= 0.270 + 2x = 0.348 \\ P(\text{CH}_4) &= 0.206 - x = 0.167 \end{aligned}$$

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

$$K = \frac{P(\text{CH}_4)}{P(\text{H}_2)^2} = \frac{0.167}{0.348^2} = 1.38$$

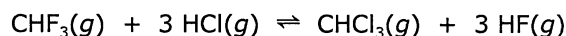
The calculated K checks out perfectly with the given K . All is good. The final answers are in atm.

$$P(\text{H}_2) = 0.348 \text{ atm} \quad P(\text{CH}_4) = 0.167 \text{ atm}$$

Finis.

Next.

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Example 6. Consider the following equilibrium.



At 0. °C, $K = 4.5 \times 10^{-11}$. The system begins with 0.13 atm CHF_3 and 0.51 atm HCl . Calculate the pressures (in atm) of each reactant and of each product at equilibrium.

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 ► 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. Set up the changes in 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.

$$K = \frac{P(\text{CHCl}_3) P(\text{HF})^3}{P(\text{CHF}_3) P(\text{HCl})^3} = \frac{(x) (3x)^3}{(0.13 - x) (0.51 - 3x)^3} = 4.5 \times 10^{-11}$$

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 terms up to fourth power and this cannot be solved readily. Fortunately, K is very 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.

$$\frac{(x) (3x)^3}{(0.13 - x) (0.51 - 3x)^3} \approx \frac{(x) (3x)^3}{(0.13) (0.51)^3} = 4.5 \times 10^{-11}$$

Re-arrange and solve.

$$\begin{aligned} (x) (3x)^3 &= 4.5 \times 10^{-11} (0.13) (0.51)^3 \\ 27x^4 &= 7.7600\dots \times 10^{-13} \\ x &= \pm 4.1 \times 10^{-4} \end{aligned}$$

► Step 7. Plug this x into the equilibrium amounts. The negative version comes out as the nonsense answer. Go with the $+4.1 \times 10^{-4}$.

$$\begin{aligned} P(\text{CHF}_3) &= 0.13 - x = 0.13 \text{ (atm)} \\ P(\text{HCl}) &= 0.51 - 3x = 0.51 \text{ (atm)} \\ P(\text{CHCl}_3) &= x = 4.1 \times 10^{-4} \text{ (atm)} \\ P(\text{HF}) &= 3x = 0.0012 \text{ (atm)} \end{aligned}$$

► Step 8. K -check.

$$K = \frac{P(\text{CHCl}_3) P(\text{HF})^3}{P(\text{CHF}_3) P(\text{HCl})^3} = \frac{(4.1 \times 10^{-4}) (0.0012)^3}{(0.13) (0.51)^3} = 4.1 \times 10^{-11}$$

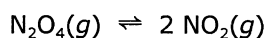
That value is close enough to the originally provided value of 4.5×10^{-11} . Done.

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.

You've probably been waiting to take a turn at this. Here it is.

Example 7. The following equilibrium has $K = 0.148$ at 25 °C.

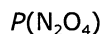


The system begins with 1.00 atm of each gas. Calculate the pressures of each gas at equilibrium.

Do the Steps.

- ▶ Step 1. Balanced equation is given.
- ▶ Step 2. K

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



Initial:

- ▶ Step 4. Set up the changes in amounts. Which way is the system 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 trying to approximate.

Somewhere along the way, you should get to here.

$$4x^2 - 4.15x + 0.85 = 0$$

Go quadratic.

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

$$P(\text{N}_2\text{O}_4) =$$

$$P(\text{NO}_2) =$$

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

Here's a clue for the final answers: the sum of the two pressures is 1.72 atm.

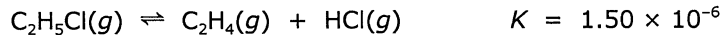
The Examples shown above are a sample of the variety of equilibrium problems. Although the variety can make them seem totally different, they are all fundamentally the same in approach and execution. Some are indeed easier than others, while some can be a bit challenging.

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.



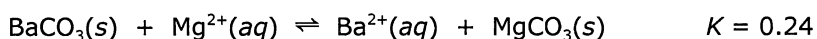
The process begins with 0.482 atm $\text{C}_2\text{H}_5\text{Cl}$. What are the pressures (in atm) of each gas at equilibrium?

2. Consider the following equilibrium system.



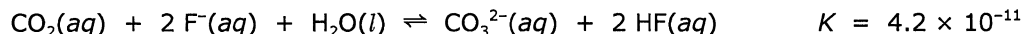
The process begins with $\text{Cl}_2(g)$ and $\text{BrCl}(g)$ at 1.00 atm each; $\text{Br}_2(l)$ is in excess. What are the pressures (in atm) of Cl_2 and of BrCl at equilibrium?

3. An aqueous solution contains 0.00400 M Mg^{2+} and 0.00200 M Ba^{2+} . Excess amounts of the solids MgCO_3 and BaCO_3 are added to give a heterogeneous mixture. This gives rise to the following equilibrium.



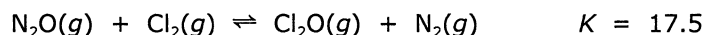
What are the concentrations (in M) of Mg^{2+} and of Ba^{2+} at equilibrium?

4. Consider the following equilibrium system.



The process begins with 0.028 M CO_2 and 0.017 M F^- . What are the concentrations (in M) of each solute at equilibrium?

5. Consider the following equilibrium system.



The following amounts were present initially.



What are the pressures (in atm) of each gas at equilibrium?