Chapter 19 Chemical Equilibrium
Up to now we have assumed that reactions only go in one direction, products → reactants. In the last chapter, I hinted once or twice that the reverse reaction, products → reactants could occur. In this chapter we will study what happens when you both the forward and reverse reactions occur, and you give both reactions enough time that they come to an equilibrium situation where the rate of the forward reaction = the rate of the backward reaction.

I have some problems with how McQuarrie organizes this chapter and where he has you do some of the problems. I will skip around a little in this chapter to present the information in a different order. I’ll try to let you know when and where I skip

19-1 Dynamic Equilibrium
Let’s look at the reaction \( \text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2 \)

Initially there is only \( \text{N}_2\text{O}_4 \) so the rate of this decomposing is high, but then it tapers off as the \( \text{N}_2\text{O}_4 \) drops
Initially there is 0 \( \text{NO}_2 \) so the rate of the reverse reaction is initially zero, it’s rate increases as the \([\text{NO}_2]\) increases

At some point the rate of the forward and reverse reaction becomes the same so the concentrations don’t change. At this point we have achieved equilibrium

The equilibrium we achieve is termed a dynamic equilibrium to emphasize the fact that the reaction hasn’t stopped. Reactants are still changing to products, and products are still changing to reactants, it is just that rates of the two reaction are equal so there is no net change in the system

The dynamics of the system can be illustrated in figure 19.3

Here we have the equilibrium \( \text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2 \). If we let the system come to equilibrium so nothing is changing, but add some radioactive \( \text{CaCO}_3 \), you can detect the radioactivity entering the \( \text{CO}_2 \). Even though its concentration is not changing!

19-2 Attainment of Equilibrium
As shown in table 19.1 you can achieve equilibrium in many different ways, you can start with all products, you can start with all reactants, you can start with a mix of both, all situations will come to equilibrium.

Sample equilibrium concentration problem
One type of problem you may have to deal with using reaction stoichiometry to determine concentrations of all reactants and products at equilibrium

Say we focus on the third line in table 19.1 In this line we start with \([\text{NO}_2] = 2\text{M}\) and \([\text{N}_2\text{O}_4] = 0\). If you are given the equilibrium concentration of \([\text{NO}_2] = .4\), can
you determine the equilibrium concentration of $[N_2O_4]$?

If $[NO_2]$ is initially 2 but drops to .4 at equilibrium then 2-.4 or 1.6M NO$_2$ was used up in the back reaction

using stoichiometry

$$1.6 \text{ M NO}_2 \times \frac{1 \text{N}_2\text{O}_4}{2 \text{NO}_2} = .8 \text{ M N}_2\text{O}_4$$

The more interesting thing is the last column of this table. Here we have achieved equilibrium 5 different way with 5 sets of concentrations. Yet if you take $[NO_2]^2/[N_2O_4]$ you get the same number .2!

19-3 Equilibrium Constant expressions (I will skip around a bit here!)

The above relationship, that at equilibrium, any set of equilibrium concentrations can give you the same ratio was discovered by Guldberg & Waage in the late 1800’s

Let’s look at that ratio a little more

Here I will take a very generic chemical reaction

$$aA(g) + bB(aq) + cC(s) \rightleftharpoons dD(g) + eE(aq) + fF(l)$$

The ratio is:


or products/reactants, where the product and reactant concentrations or partial pressures are raised to stoichiometric coefficient found in the balanced equation

Key concept/definition

We call the ratio of products over reactants the Equilibrium constant -$K_c$ if you use concentrations, $K_p$ if you use partial pressures.

We call the expression of product concentration terms divided by reactant concentration terms the equilibrium expression

Later, in chapter 23 we shall see the thermodynamics behind this expression, but for now we will just take it and use it.
Example problems possible clicker questions
Write the equilibrium expression corresponding to the stoichiometric equations:

\[ 4\text{NH}_3 + 7\text{O}_2 \rightleftharpoons 4\text{NO}_2 + 6\text{H}_2\text{O} \]

\[ K_C = \frac{[\text{NO}_2]^4[H_2\text{O}]^4}{[\text{NH}_3]^4[\text{O}_2]^7} \]

\[ \text{P}_4 + 5\text{O}_2 \rightleftharpoons \text{P}_4\text{O}_{10} \]

\[ K_C = \frac{[\text{P}_4\text{O}_{10}]}{[\text{P}_4][\text{O}_2]^5} \]

**Solid and liquids in equilibrium expressions**
Go back to my original generic equation. Notice solid and liquids DO NOT APPEAR IN the Equilibrium constant expression. Never include solids or liquids!

Example Problem
Write the equilibrium expression corresponding to the stoichiometric expression:

\[ \text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g) \]

\[ K_P = P_{\text{CO}_2} \text{ or } K_C = [\text{CO}_2] \]

**Units**
As a ration of concentrations, a \( K_C \) or a \( K_P \) should have units, and the units will be different for every \( K_C \) or \( K_P \)

In chapter 23 we will define a more fundamental equilibrium constant \( K \) (No subscript) that will be a unitless number

**Important points**
1. In the equilibrium expression the equilibrium product concentrations appear in the numerator, and the equilibrium reactant concentrations appear in the denominator
2. The equilibrium concentration of each product or reactant is raised to a power equal to the stoichiometric coefficient of that species in the balanced chemical equation
3. Reactants or products that are liquids or solids do not appear in the equilibrium expression
4. The value of \( K_C \) or \( K_P \) for a stated chemical equation is equal to a constant at a given temperature
5. The equilibrium state is a dynamic state: When a system reaches equilibrium products and reactants are still being created or destroyed, but there is no net change in concentrations because the rate of the forward reaction = the rate of the reverse reaction


**What the K tells us about the reaction**
If K is products/ reactants

Key Concept:
- \( K \gg 1 \) say the reaction strongly favors the products and is favorable
- \( K \ll 1 \) say the reaction strongly favors the reactants and says the reaction is not favorable

**Equilibrium constants for related reactions**
McQuarrie makes an important point, but maybe a nit-picky point in this section..
“ There is no such thing as an equilibrium constant for a reaction. There is only an equilibrium constant for the chemical equation that represents a reaction”

What he is trying to say is that if there were a true constant for a reaction, it wouldn’t matter how you wrote the reaction, a constant would be a constant. In reality you get a different constant for the same reaction, depending on how you write the balanced reaction!

For instance look at the data in table 19.1 again. We used have used the equation \( \text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2 \), obtained the ratio of \( [\text{NO}_2]/[\text{N}_2\text{O}_4] = .2 \)
Another person might have used the balanced equation \( \frac{1}{2} \text{N}_2\text{O}_4 \rightarrow 1\text{NO}_2 \)
obtained the ratio of \( [\text{NO}_2]/[\text{N}_2\text{O}_4]^{1/2} = .45 \)

Because you can write different balanced equations for the same reaction, you need to be able to know how to convert the equilibrium constant corresponding to one balanced equation to the equilibrium constant for another balanced equation. This is something McQuarry covers in section 19.6 so I will skip forward to that section

19-6 Equilibrium constants for related reaction equations

Let’s start with the reaction written in forward and reverse directions:
If the equilibrium expression of the forward reaction
\[
j\text{A} + k\text{B} \rightarrow l\text{C} + m\text{D}
\]
is:
\[
K = \frac{[C]^l[D]^m}{[A]^j[B]^k}
\]

What do you think the expression for the reverse reaction
\[
l\text{C} + m\text{D} \rightarrow j\text{A} + k\text{B}
\]
is? 
\[
K_{\text{rev}} = [A][B]^j /[C][D]^m = 1/K_{\text{forward}}
\]
What happens if you combine equations?
\[ \text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g); \quad K_1 = [\text{CO}][\text{H}_2]/[\text{H}_2\text{O}] \]

And
\[ \text{CO}_2(g) + 2\text{H}_2(g) \rightleftharpoons 2\text{H}_2\text{O}(g) + \text{C}(s); \quad K_2 = [\text{H}_2\text{O}]^2/[\text{CO}_2][\text{H}_2]^2 \]

If you add the two equations you get
\[ \text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g) \quad K_{\text{net}} = [\text{CO}][\text{H}_2\text{O}]/[\text{CO}_2][\text{H}_2] \]

When you add reactions you multiply the K’s
\[ K_1K_2 = [\text{CO}][\text{H}_2][\text{H}_2\text{O}]^2/[\text{H}_2\text{O}][\text{CO}_2][\text{H}_2] \]
\[ = [\text{CO}][\text{H}_2\text{O}]/[\text{CO}_2][\text{H}_2] \]

This logically leads to what happens when you multiply the balances equation by a number:

\[ \text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3; \quad K = [\text{NH}_3]^2/[\text{N}_2][\text{H}_2]^3 = 3.8 \times 10^4 \text{ L}^2/\text{mol}^2 \]

Suppose we want the equilibria expression of the reaction

\[ 2\text{N}_2 + 6\text{H}_2 \rightleftharpoons 4\text{NH}_3 \text{ instead?} \]
\[ [\text{NH}_3]^4/[\text{N}_2]^2[\text{H}_2]^6 = 2(\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3) = ([\text{NH}_3]^2/[\text{N}_2][\text{H}_2]^3)^2 = K^2 \]

We see that we simply take the K for the expression and take it to the power of the coefficient.

Key Equations:
1. The equilibrium constant for a reverse reaction is the reciprocal of that of the forward reaction. \( K_{\text{rev}} = 1/K_{\text{forward}} \)
2. When you add two or more equations together the K for the combined equation = multiplying the K’s together
3. When a balanced equation for a reaction is multiplied by a factor, \( n \), the equilibrium expression for that reaction is raised to the power of \( n \), and the equilibrium Constant for that reaction is also raised to the power of \( n \).

Example Problems:
The reaction
\[ \text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{CH}_3\text{COO}^-(aq) + \text{H}^+(aq) \]
has a \( K_C \) of \( 1.75 \times 10^{-4} \) M

What is \( K_C \) for the reaction: \( \text{CH}_3\text{COO}^-(aq) + \text{H}^+(aq) \rightleftharpoons \text{CH}_3\text{COOH} \)?
This is the reverse reaction so \( K_R = 1/K_F \)
\[ = 1/1.75 \times 10^{-4} = 5714 \text{ M}^{-1} \]
What is $K_{C}$ for the reaction: $2\text{CH}_3\text{COOH}(aq) \rightleftharpoons 2\text{CH}_3\text{COO}^-(aq) + 2\text{H}^+(aq)$

Reaction New = 2(old reaction)

$K_N = K_{old}^2$

$= 3.06 \times 10^{-8} \text{ M}^2$

Returning to section 19.3

**Introduction to Equilibrium calculations**

Given the initial concentrations of all species, and the final concentration of 1 species, we can calculate the $K_c$ using basic stoichiometry.

In problems like this is it useful to use a table called an ICE table, where ICE stands for Initial, Change and Equilibrium

**Example calculation**

If the reaction: $\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$
starts with the concentrations of

$[\text{CO}] = 1.75 \text{ M}, [\text{H}_2] = .8 \text{ M}$ and $[\text{CH}_3\text{OH}] = .65 \text{ M}$

and. At equilibrium $[\text{CO}]$ is 1.6M what is the $K_c$ for this reaction

**ICE table**

$\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$

<table>
<thead>
<tr>
<th>Initial</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.75$</td>
<td>$.8$</td>
<td>$.65$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Filling in initial</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$</td>
</tr>
<tr>
<td>Initial</td>
</tr>
<tr>
<td>$1.75$</td>
</tr>
</tbody>
</table>
Adding the one known equilibrium #

\[
\text{CO(g) + 2H}_2\text{(g)} \rightleftharpoons \text{CH}_3\text{OH(g)}
\]

Initial  \[1.75\] \[.8\] \[.65\]
Change   \[-.15\] \[-.3\]  \[+.15\]
Equilibrium  \[1.6\]  \[.5\]  \[.8\]

We first figure out that the change in CO must be 1.75-1.6 = .15
And put this into the table

\[
\text{CO(g) + 2H}_2\text{(g)} \rightleftharpoons \text{CH}_3\text{OH(g)}
\]

Initial  \[1.75\] \[.8\] \[.65\]
Change   \[-.15\] \[-.3\]  \[+.15\]
Equilibrium  \[1.6\]  \[.5\]  \[.8\]

Now using stoichiometry

\[-.15 \text{ CO} \times \frac{2\text{H}_2}{1 \text{CO}} = -.3 \text{H}_2\]

\[\text{CH}_3\text{OH is a product so it is a positive number}\]

\[+.15 \text{ CO} \times \frac{1\text{CH}_3\text{OH}}{1 \text{CO}} = +.15 \text{CH}_3\text{OH}\]

Filling in the table with this data

<table>
<thead>
<tr>
<th></th>
<th>CO(g) + 2H_2(g) ⇌ CH_3OH(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1.75 [.8] [.65]</td>
</tr>
<tr>
<td>Change</td>
<td>-.15 [-.3] [+.15]</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>1.6 [.5]  [.8]</td>
</tr>
</tbody>
</table>

And doing the math written on the table

\[
\text{And going to the equilibrium expression:} \]

\[
[\text{CH}_3\text{OH}] / [\text{CO}]^2 [\text{H}_2]^2 = 0.8 / 1.6 (0.5)^2 = 2 \text{ M}^2
\]

19-4 Pressure Equilibrium constants

When dealing with gases it is often convenient to use \(K_p\), an equilibrium constant expressed in partial pressure of a gas rather than \(K_c\), an equilibrium expression that deals with concentration of a gas.

For most reaction \(K_p \neq K_c\), so you need to be able to convert from one to the other. The way we do this is through the good old PV=nRT.

If \(n/V = \text{concentration}\) then \(P = nRT/V = n/V(\text{RT})\)

So \(P_{\text{gas A}} = [\text{gas A}] \cdot \text{RT}\).
So if we have the reaction \( \text{C(s)} + \text{CO}_2(g) \rightarrow 2\text{CO(g)} \) and know that
\[
K_p = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}}
\]

Plugging in the above expression
\[
K_p = \frac{([\text{CO}]RT)^2}{([\text{CO}_2]RT)}
\]
\[
K_p = K_c(RT)
\]

But this expression only works for this reaction. If you change the stoichiometry, you change the relationship between \( K_p \) and \( K_c \).

Without deriving it lets jump to the key equation:

Key Equation:
For the reaction:
\[
aA(g) + bB(g) \rightarrow cC(g) + dD(g)
\]
\[
K_p = K_c(RT)^{\Delta n} \quad \text{where} \ \Delta n = (c+d)-(a+b)
\]

Example problem 1.
\( 2\text{NO(g)} + \text{Cl}_2(g) \rightarrow 2\text{NOCl(g)} \)

\[
K_c = \frac{[\text{NOCl}]^2}{[\text{NO}]^2[\text{Cl}_2]}
\]
\[
K_p = K_c(RT)^{\Delta n} ; \quad \Delta n = (2) - (2+1) = -1
\]
\[
K_p = K_c(RT)^{-1}
\]
\[
K_p = K_c /RT
\]

Example Problem 2
If \( K_c \) is 170 \( \text{M}^{-2} \) for the reaction \( \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \) at 225°C, what is \( K_p \) at this temperature

\[
K_p = K_c(RT)^{\Delta n}
\]
\[
\Delta n = 2-(1+3) = -2, \quad T = 225 + 273 = 498K
\]
\[
K_p = 170 \text{ M}^{-2} \cdot (0.08206 \cdot 498K)^{-2}
\]
\[
= .102 \text{ atm}^{-2}
\]
19-5 Equilibrium Calculations
In the calculations we did first semester we always assumed that the reaction went to 100% completion. This can only happen when you have very large K values. So how do you do calculations with reaction that have smaller K values and you cannot assume 100% completion?

VERY CAREFULLY!

As you will see the key is to keep using the ice table and reaction stoichiometry to work your way through a problem.

Before we can use the ICE table though, you have to be able to tell whether the reaction will go forward or backward. To so this we must skip forward to section 19.9

19-9 The Reaction Quotient

Key Definition:
The Reaction Quotient Q is a quantity that has exactly the same algebraic form as the equilibrium constant expression, but uses the current concentrations found in the system, not the equilibrium concentrations

When you plug the equilibrium concentrations into the equilibrium expression you get the equilibrium constant. When you plug the set of concentrations that you currently have in your system you get a number that is called the Reaction Quotient (Q). The reaction quotient tells you if you are at equilibrium, and if you aren’t at equilibrium, which way your concentrations will change to get there.

Very simply if Q=K, you are at equilibrium.
What does it mean if Q>K
Q>K ; K = product/reactants, so product in excess, will shift toward reactants
Q<K K=product/reactants Product < reactants, will shift toward products

Example Problem
For the reaction: \( K = \frac{[NH_3]^2}{[N_2][H_2]^3} \) \( K_c = 6.0 \times 10^{-2} \)
Say we have the following sets of concentrations

<table>
<thead>
<tr>
<th></th>
<th>[NH₃]</th>
<th>[N₂]</th>
<th>[H₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.0 × 10⁻³</td>
<td>1.0 × 10⁻⁵</td>
<td>2.0 × 10⁻³</td>
</tr>
<tr>
<td>B</td>
<td>2.0 × 10⁻⁴</td>
<td>1.5 × 10⁻⁵</td>
<td>3.54 × 10⁻¹</td>
</tr>
<tr>
<td>C</td>
<td>1.0 × 10⁻⁴</td>
<td>5.0</td>
<td>1.0 × 10⁻²</td>
</tr>
</tbody>
</table>

Which reactions are at equilibrium? If you aren’t at equilibrium, which way will the reaction go, toward products or reactant?
For Reaction A
Q = $\left[ \text{NH}_3 \right]_0 / \left[ \text{N}_2 \right]_0 \left[ \text{H}_2 \right]_0$
=$\left(1.0 \times 10^{-3}\right)^2 / \left[1.0 \times 10^{-5}\right] \left(2.0 \times 10^{-3}\right)^3$ = $1.3 \times 10^7$ L$^2$/mol$^2$

For filling in the entire table:

<table>
<thead>
<tr>
<th></th>
<th>[NH$_3$]</th>
<th>[N$_2$]</th>
<th>[H$_2$]</th>
<th>Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$1.0 \times 10^{-5}$</td>
<td>$2.0 \times 10^{-3}$</td>
<td>$1.3 \times 10^7$</td>
</tr>
<tr>
<td>B</td>
<td>$2.0 \times 10^{-4}$</td>
<td>$1.5 \times 10^{-5}$</td>
<td>$3.54 \times 10^{-1}$</td>
<td>$6.01 \times 10^{-2}$</td>
</tr>
<tr>
<td>C</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$5.0$</td>
<td>$1.0 \times 10^{-2}$</td>
<td>$2 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

K was $6.0 \times 10^{-2}$

So in case A, Q>K so conc of product will DECREASE
In case B K=Q so you are at equilib
In C Q < K will move towards product (to the right)

What happens when you have a zero concentration?
What will happen to our Expression if the concentration of a product is 0?
0/X =0; Q=0; Q<K will shift toward products
If a reactant conc is 0? Q =X/0, Q = $\infty$, Q>K will shift toward reactants.

**Bottom line: if either product or reactant is 0, reaction will shift to give that substance a non-zero conc.**

Now that we have a tool to tell us which way a given set of conditions will shift, we can Return to section 19-5 to find how to do equilibrium calculations

There are hundreds of different problems that can be set up, so Let's just work through a few so you can get a feel for how to do these kinds of problems. Let me start by giving you a complete procedure.

**Key Procedure for solving equilibrium problems:**
1. Write the balanced reaction
2. Write the equilibrium expression that corresponds to the balanced reaction
3. list initial concentrations and start your ICE table
4. Calculate Q to determine what direction(if any) the reaction will shift
5. using a single variable(X), define change for each concentration needed to reach equilibrium using X.
6. Substitute modified concentration terms into the equilibrium expression
7. Solve the equilib. expression for the unknown.
8. Plug final values back in to see if they check out.

This is a long procedure, and once you are good at it you can skip steps. But for now I advise you to follow it closely
Example problem 1

Let’s start out with the reaction: \( \text{CO}(g) + \text{H}_2\text{O}(g) ⇌ \text{CO}_2(g) + \text{H}_2(g) \)

If \(K_c = 5.10\) (no units) and all concentrations are with 2.0 mol/L, what are the equilibrium concentrations of all products and reactants?

Step 1: \( \text{CO}(g) + \text{H}_2\text{O}(g) ⇌ \text{CO}_2(g) + \text{H}_2(g) \)

Step 2: \(K_c = [\text{CO}_2][\text{H}_2] / [\text{CO}][\text{H}_2\text{O}]\)

Note: why doesn’t water drop out?? This is a gas phase reaction, not dealing with liquid water

Step 3: ICE table

\[
\begin{array}{c|cccc}
& \text{CO}(g) & \text{H}_2\text{O}(g) & \text{CO}_2(g) & \text{H}_2(g) \\ 
\text{Initial} & 2 & 2 & 2 & 2 \\
\text{Change} & -X & -X & X & X \\
\text{Equilibrium} & 2-X & 2-X & 2+X & 2+X \\
\end{array}
\]

Step 4: \(Q = \frac{2(2)}{2(2)} = 1\)

\(Q < K; \) Not enough products, reaction will shift to right

Step 5: Will make the change = \(+XM \text{ CO}_2\)

With nice 1:1:1:1 stoichiometry that makes our ICE table

\[
\begin{array}{c|cccc}
& \text{CO}(g) & \text{H}_2\text{O}(g) & \text{CO}_2(g) & \text{H}_2(g) \\ 
\text{Initial} & 2 & 2 & 2 & 2 \\
\text{Change} & -X & -X & X & X \\
\text{Equilibrium} & 2-X & 2-X & 2+X & 2+X \\
\end{array}
\]

Step 6: Putting this into the equilibrium expression:

\[
\begin{align*}
K &= \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]}, \\
5.10 &= (2.0+x)(2.0+x) \div (2.0-x)(2.0-x) = (2.0+x)^2 / (2.0-x)^2 = [(2+x)/(2-x)]^2 \\
\sqrt{5.10} &= 2.26 = (2+x)/(2-x) \\
2.26(2-x) &= 2+x \\
4.52 - 2.26x &= 2+x \\
4.52 - 2 &= X + 2.26X \\
2.52 &= 3.26X \\
X &= 2.52/3.26 = .773 \text{ M} \\
\text{so } [\text{CO}_2]_i &= [\text{H}_2\text{O}]_i = 2+.773 = 2.773 \text{ mol/L} \\
\text{and } [\text{CO}]_i &= [\text{H}_2]_i = 2-.773 = 1.227 \text{ mol/L}
\end{align*}
\]
Example 2.
We want to synthesize HF form \( \text{H}_2 \) and \( \text{F}_2 \). Say we start with 4 moles of \( \text{H}_2 \) and 2 moles of \( \text{F}_2 \) in a 3.0 L container.

1. Balance Reaction
   \[ \text{H}_2 + \text{F}_2 \rightarrow 2\text{HF} \]

2. Equilib expression
   \[ K_c = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = 1.15 \times 10^2 \] (Must be looked up)

3.
   \[ [\text{H}_2] = \frac{4 \text{ mol}}{3.0 \text{ L}} = 1.333 \text{ M} \]
   \[ [\text{F}_2] = \frac{2 \text{ mol}}{3.0 \text{ L}} = 0.667 \text{ M} \]
   \[ [\text{HF}] = 0 \]
   **ICE Table**
   \[
   \begin{array}{ccc}
   \text{H}_2 & + & \text{F}_2 & \rightarrow & 2\text{HF} \\
   \text{Initial} & 1.333 & 0.667 & 0 \\
   \text{Change} & -X/2 & -X/2 & +X \\
   \text{Equilibrium} & 1.333-X/2 & 0.667-X/2 & X \\
   \end{array}
   \]

4. Calculate Q
   Actually is not needed. Since \([\text{HF}] = 0\) know equilib will shift to right to form HF

5. X will be amount of HF formed
   So Change in \([\text{HF}] = X\)

   Change in \([\text{H}_2] = ?\)
   If \([\text{HF}] = X\), the mole conversion factor based on the equation is:
   \( X \text{ mole HF} \times \frac{1 \text{ mole } \text{H}_2}{2 \text{ moles HF}}\)
   So change in \([\text{H}_2] = -X/2\)

   Change in \([\text{F}_2] = ?\)
   Again, \( X \text{ mole HF} \times \frac{1 \text{ mole } \text{F}_2}{2 \text{ moles HF}}\)
   So change in \([\text{F}_2] = -X/2\)

   **ICE table**
   \[
   \begin{array}{ccc}
   \text{H}_2 & + & \text{F}_2 & \rightarrow & 2\text{HF} \\
   \text{Initial} & 1.333 & 0.667 & 0 \\
   \text{Change} & -X/2 & -X/2 & +X \\
   \text{Equilibrium} & 1.333-X/2 & 0.667-X/2 & X \\
   \end{array}
   \]

6.
   \[ 1.15 \times 10^2 = \frac{X^2}{[(1.33-.5X)(.667-.5X)]} \]

7. Solve the above equation for X. Notice this problem gets hairy (as do most real problems)
\[ 1.15 \times 10^2 = X^2 / (0.887 - 0.999X + 0.25X^2) \]
\[ 1.15 \times 10^2 (0.887 - 1.0X + 0.25X^2) = X^2 \]
\[ 1.02 \times 10^2 - 1.15 \times 10^2 X + 0.2875 \times 10^2 X^2 = X^2 \]
\[ 102 - 115X + 28.75X^2 = X^2 \]

Remember how to solve this? The quadratic Equation? If you have

\[ aX^2 + bX + c = 0 \]

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

So we have to get the above equation into this form

\[ 27.75 X^2 - 115X + 102 = 0 \]

\[ x = 115 \pm \sqrt{(115^2 - 4 \times 27.75 \times 102)} / 2(27.75) \]
\[ = 115 \pm \sqrt{(13,225 - 11,320)} / 55.5 \]
\[ = 115 \pm \sqrt{1905} / 59.5 \]
\[ = 115 \pm 43.6 / 59.5 \]

(115 + 43.6) / 59.5 = 2.858 mol/L
and
(115 - 43.6) / 59.5 = 1.286 mol/L

Which of these answers is correct? Let’s keep going

If \([HF] = 2.858\) M then
\([H_2] = 1.33 - 1/2X = 1.33 - (2.858/2) = 1.33 - 1.429 = \text{Negative number}\)

This can’t exist so this must be the wrong root.

Let’s try the other

If \([HF] = 1.286\)
Then \([H_2] = 1.33 - 1.286/2 = 1.33 - .643 = .687\ M\)
and
\([F_2] = .667 - 1.286/2 = .667 - .643 = .024\ M\)

8. Check to see if these concentrations really work
\(K = (1.286)^2 / 0.687 \cdot 0.024 = 100\) Not exactly correct, but round off errors are usually pretty significant in this kind of problem.
**Treating systems with very large or small K's**

As you can see the last problem got pretty hairy because we had a large K and so we ended up having to use a quadratic equation to get it solved. If you have a small K, you can sometimes make some assumptions that simplify the problem and make it easier to solve.

**Example Problem**

If you start with 1.5 mol of NOCl in a 1L flask, and the NOCl undergoes the equilibrium reaction: \(2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g)\) with a \(K_c\) of \(1.6 \times 10^{-5}\) mol/L

What are the equilibrium concentrations of all the reactants and products at equilibrium?

\[
K = \frac{\text{[NO]}^2 \text{[Cl]} }{\text{[NOCl]}^2} = 1.6 \times 10^{-5}\ 	ext{mol/L}
\]

Where does this equilibrium lay? Does it favor products or reactants? 
\((K<1,\text{ favors reactants, very little product formed})\)

Let's say we start out with 1.5 mol of NOCl in a 1L flask. What are the concentrations of the various components after the reaction has come to equilibrium?

\[
\text{[NOCl]}_i = 1.5 \text{ mol in } 1\text{L} = 1.5 \text{ M} \\
\text{[NO]}_i = 0 \text{ M} \\
\text{[Cl}_2]\_i = 0 \text{M}
\]

Initially no products present so reaction will go to right to form products. Let's call the amount of Cl\(_2\) formed \(X\).

\(\text{mole [NO]} \times 2 \text{ mole NO/1 mol Cl}_2 = \text{Mole Cl}_2 \times 2 = 2X\)

\(\text{Mole NOCl used} = 2 \text{ mole [NOCl]}/1 \text{ mole Cl}_2 = 2X\)

ICE table

<table>
<thead>
<tr>
<th></th>
<th>2NOCl(g)</th>
<th>2NO(g)</th>
<th>Cl(_2)(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>-2X</td>
<td>+2X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>1.5-2X</td>
<td>2X</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

Our equilibrium expression is then

\[
K = 1.6 \times 10^{-5} = \frac{\text{[NO]}^2 \text{[Cl]} }{\text{[NOCl]}^2} \\
= \frac{(2X)^2(X)}{(1.5-2X)^2} \\
= 4X^3/(1.5-2X)^2
\]

You can see that we will have a term with \(X^3, X^2\), etc in the numerator so this is going to get very ugly.
However, let’s think about the fact that we have such a small K. This means that the reaction really doesn’t favor the product very much, so you really don’t expect much product to be formed. This also means that not much of the reactant will be used up.

If we start out with 1.5M reactant, and very little of this reactant will be used up, we can make the assumption mathematically that

\[ 1.5 - 2X \approx 1.5 \]

Plugging this in to the equation we have

\[ K = \frac{4X^3}{(1.5)^2} \]

1.6x10^-6 = 4X^3/2.25
3.6x10^-6 = 4X^3
9x10^-6 = X^3
X = (9x10^-6)^(1/3) = .0208

Our equilibrium concentration are then:

\[ [\text{NO}] = 0 + 2X = .0416 \]
\[ [\text{Cl}_2] = 0 + X = .0208 \]
\[ [\text{NOCl}] = 1.5 - 2X = 1.5 - .0416 = 1.458 \text{ M} \]

Let’s check these by plugging in to the equilibrium expression

\[ \frac{[\text{NO}] [\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(.0416)^2 (.0208)}{1.458^2} = 1.7x10^{-5} \]

So our answer is reasonably close

**Bottom line when the value of K is small you can often make some assumptions that simplify solving the problem.**

Note: if you are good with your calculator, there is a solver function that solves the original equation exactly. When I use that solver I get \( X = .0204 \), so our Q&D answer is off by \( (.0204 - .0208)/.0204 x 100 \) or 2%

19-6 Properties of equilibrium Constants
Covered earlier when I shuffled sections!

19-7 Le Châtelier’s Principle
If we have a reaction that is initially at equilibrium, and then change something, we can predict which way the reaction will go (- or -) by simple logic rather than doing a Q calculation. This logic was outlined by Le Châtelier in the late 1800’s and is not called LeChâtelier’s Principle
Key Concept

**Le Châtelier’s principle** says that when a system that is at equilibrium is changed, after the change the system will return to equilibrium by shifting in a manner that tends to reduce the change.

**The Effect of a Change in Concentrations**

Let’s look at the NOCl system again. We have just calculated that at equilibrium we have (2NOCl $\rightleftharpoons$ 2NO + Cl₂)

- $[\text{NO}] = 4.2 \times 10^{-2}$ M
- $[\text{Cl}_2] = 2.1 \times 10^{-2}$ M
- $[\text{NOCl}] = 1.46$ M

What happens to the equilibrium if we pump NOCl into the system and increase its concentration to 3M does the equilibrium move toward the product or the reactants (is more product formed?)

Well the way you have been handling this is to attack it with a Q calculation

$$Q = \frac{[\text{NO}]^2[\text{Cl}_2]^2}{[\text{NOCl}]^2} = \frac{(4.2 \times 10^{-2})^2(2.1 \times 10^{-2})}{3^2} \text{ (new value)}$$

$$Q = 4.1 \times 10^{-6} \ ; K = 1.6 \times 10^{-6} \ ; Q>K \ ; \text{Reaction moved toward product}$$

Now that we proved this with math, Let’s think if we could have predicted this without the math

Have reactants and products in equilibrium. Increase concentration of reactant. More reactant forward rate of reaction increases, start to make more product. After a while product builds up so reverse reaction catches up to forward reaction, but overall equilib has shifted toward product.

Now Using Le C’s. Increase reactant, the relieve this change will form more product.

The Le C principle also work in the other direction. Say we had some special way we could get rid of NOCl, say by making it react in a second different reaction, so the concentration goes to .5M instead of the 1.46M we have at equilibrium

By Le C, we have lowered the con of reactants in the system, so the system will respond by shifting the equilib toward the reactants trying to relieve the change on the system. (You might confirm this with a Q calculation)
Key Concept
If a reactant or product is added to a system at equilibrium, the system will shift away from that component. If a product or reactant is removed from a system the system will respond by shifting toward the missing component.

**The effect of pressure**
If we are working in the gas phase we can change the overall pressure in the system as well as the concentration of the individual components. We can do this by either adding an inert gas to the system that increases the overall pressure or by changing the volume of the container we are doing the reaction in.

The effect of changes in pressure on gas phase reactions can also be understood using Le C\’s Principle

Case 1 addition of inert gas
When we change the pressure in a system by adding an inert gas we do not change either the K of the reaction or the concentration of the components or the partial pressure of the components. Thus nothing significant changes and you remain at equilibrium

Key Concept
Adding an inert gas will not affect a gas phase equilibrium

Case 2 Change in volume
When the volumes change, the concentrations change. Once concentrations change we have to start all over on our Q calculations to predict what will happen. However, if we are clever, we don\’t have to do all that work.

Let\’s focus on the volume of the system and look at how the volume of the system may be used in LeC Principle

If we change the volume of the system, LeC \’s principle say that the system will respond to try to minimize that change

Key Concept:
If the pressure in a system is decreased by increasing volume, the equilb will shift in a manner that increases the total volume of the system. If the pressure in increased by decreasing the volume of the system, the system will respond in a way to decreases the overall vol of the system
OK that sounds good, but how do we tell how whether a shift in equilibrium favors an increased volume or a decreased volume? Remember PV=nRT?

\[ V = \frac{nRT}{P} \]

if T and P are constant, then V is directly proportional to n

i.e. volume is proportion to number of molecules (DUH)

Thus all you have to do is to look at the total number of reactant gas molecules and product gas molecules to see if a reaction increases in volume or decreases in volume.

In our example 2NOCl $\rightarrow$ 2NO + Cl₂ we have 2 gas molecule as reactants and 3 as product, so the volume here increases with the reaction. If we increase the size of the container we will favor the product, if we decrease the volume we will favor the reactants

How about an even earlier example

\[ N_2(g) + 3H_2(g) \rightarrow 3NH_3(g) \]

How will this change with a change in volume?

(4 molecules of reactants, 3 of product, product has smaller vol than reactant, decrease vol favor product, increase vol favor reactants

**The effect of Temp**

In studying the effect of temp, vol and $\Delta$ conc on a reaction we change the conditions under which a reaction occurs but we don't change the actual K of the reaction.

If we change the temperature at which a reaction occurs, then the K of the reaction changes, so you technically have to start over and determine a new K

However, to a first approximation you can make a good guess as to what will happen to K if you treat heat like a reactant or a product.

Remember the concept of Enthalpy or heat of reaction? We found that many reaction release heat to the surroundings ($-\Delta H$), while other reaction absorb heat from the surroundings($+\Delta H$).

We can apply Le C's principle to the heat in a reaction to predict which way K will move. If we add heat to a system, the system will respond by trying to minimize the added heat. If we remove heat form the system, the system will respond by trying to generate heat to minimize the change.

Let's take the ammonia example
\[ \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 3\text{NH}_3(\text{g}) \]

This reaction is exothermic and releases 92 kJ of heat, \((\Delta H = -92\text{kJ})\)

Let’s add this heat to the appropriate side of the reaction

\[ \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 3\text{NH}_3(\text{g}) + 92 \text{kJ} \]
\[ \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 3\text{NH}_3(\text{g}) + \text{heat} \]

If we heat the system, the system response is to remove the added heat, so it will decrease the amount of product, so \(K\) will be reduced.

Let’s try some other examples

\[ \text{Heat} + \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) \quad \Delta H = +181 \text{ (endothermic)} \]
\[ 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g}) + \text{heat} \quad \Delta H = -198 \text{ (exothermic)} \]

If the temp increases, the \(K\) of reaction 1 will increase while the \(K\) of reaction 2 will decrease.

**Key Concept**

If \(\Delta H_{\text{rxn}}\) is \(+\) (endothermic) then as \(T\uparrow\), \(K\downarrow\) (Reaction \(-\)) and as \(T\downarrow\) \(K\uparrow\) (Reaction \(+\))

If \(\Delta H_{\text{rxn}}\) is \(-\) (exothermic) then as \(T\uparrow\), \(K\downarrow\) (Reaction \(-\)) and as \(T\downarrow\) \(K\uparrow\) (Reaction \(+\))

**19-8 Quantitative Application of Le C’s Principle**

Here McQuarrie does some more equilibrium calculations to show that Le C’s principle actually works, but I don’t see any new principles or ideas so we will skip this section

**19-9 Approach to Equilibrium**

Covered in an earlier section when I shuffled the order.