

Chemistry 12
Tutorial 5
The Equilibrium Constant (K_{eq})

In this Tutorial you will be shown:

1. What is meant by the equilibrium constant K_{eq} .
2. How to write the **expression** for K_{eq} given a balanced equilibrium equation.
3. How to write the K_{eq} **expression** for equations involving liquids and solids
4. How the *extent* of a reaction is related to the *value* of K_{eq}
5. How the *value* of K_{eq} changes with **temperature** in an exothermic or endothermic reaction
6. That the *value* of K_{eq} is **not affected** by:
 - changes in *concentration*,
 - *total volume* or
 - *pressure* or by addition of a *catalyst*.

What is K_{eq} ?

The "K" in K_{eq} stands for "Constant". The "eq" means that the reaction is at equilibrium.

Very roughly, K_{eq} tells you the **ratio** of Products/Reactants for a given reaction at *equilibrium* at a certain temperature.

$$K_{eq} = \frac{[\text{Products}]}{[\text{Reactants}]}$$

It's not quite this simple when we deal with real substances. Let's take an example.

(see the next page)

It has been found for the reaction:



that if you take the $[\text{H}_2]$, the $[\text{I}_2]$ and the $[\text{HI}]$ in an *equilibrium mixture* of these at $423\text{ }^\circ\text{C}$, the expression:

$$\frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = 0.0183$$

↑
 The K_{eq}
 expression

↑
 The value of K_{eq}

The value of this ratio stays at 0.0183 *regardless of what we might try to do with the concentrations*.

The **only** thing that changes the *value* of K_{eq} for a given reaction is the **temperature**!

Writing K_{eq} Expressions

In the example just above this, the equation was:



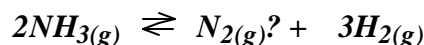
and the K_{eq} expression was:

$$K_{\text{eq}} = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$$

Notice a couple of things here. The concentrations of the **products** are on the **top** (numerator) and the concentration of the **reactant** is on the **bottom**. (denominator).

Also, notice that the **coefficient "2"** in the "**2HI**" in the **equation** ends up as an **exponent** for $[\text{HI}]$ in the **K_{eq} expression**. Thus we have $[\text{HI}]^2$ in the denominator.

1. With this in mind, see if you can write the K_{eq} expression for the following reaction:



$$K_{\text{eq}} =$$

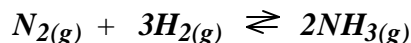
Go to page 1 of Tutorial 5 - Solutions to check your answer to this.

Notice that in the Equilibrium Constant Expression (K_{eq}), whatever is written on the **right** of the arrow in the equation (products) is on **top** and whatever is written on the **left** of the arrow in the equation (reactants) is on the **bottom**.

This is always the case in a K_{eq} expression, regardless of which reaction (forward or reverse) predominates at a certain time.

Try this one:

2. Write the K_{eq} expression for the following reaction:



$K_{eq} =$

Go to page 1 of Tutorial 5 - Solutions to check your answer to this.

The K_{eq} Expressions for Solids and Liquids

Consider the following reaction:



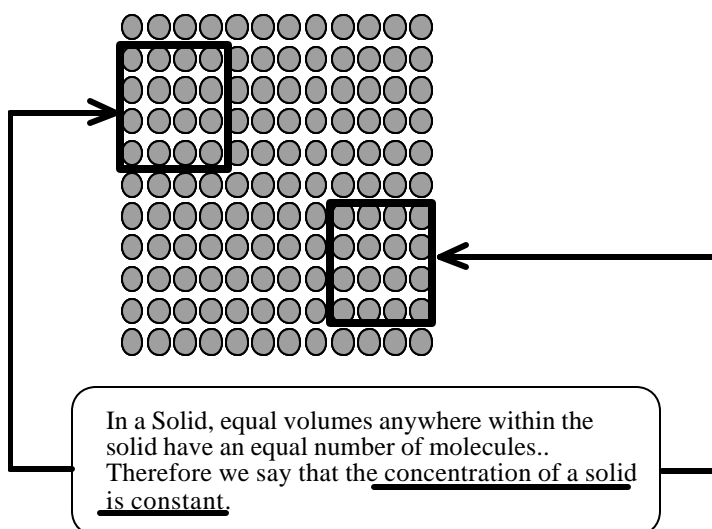
You might expect the K_{eq} expression to be something like:

$$? \quad K_{eq} = \frac{[CaO_{(s)}] [CO_{2(g)}]}{[CaCO_{3(s)']}}$$

But when you consider a solid, the number of moles per litre or molecules in a certain volume is constant.

The molecules everywhere in the solid are about the same distance apart and are the same size:

See the diagram on the next page...



Going back to our example:

Consider the following reaction:



You might expect the K_{eq} expression to be something like:

$$K_{\text{eq}} = \frac{[\text{CaO}_{(s)}] [\text{CO}_{2(g)}]}{[\text{CaCO}_{3(s)}]}$$

Since CaO and CaCO₃ are solids, we can assume that their concentrations are constant.

We can therefore rewrite the K_{eq} expression as follows:

$$? \quad K_{\text{eq}} = \frac{(\text{a constant}) [\text{CO}_{2(g)}]}{(\text{a constant})}$$

Now, if we rearrange:

$$? \quad K_{\text{eq}} \frac{(\text{a constant})}{(\text{a constant})} = [\text{CO}_{2(g)}]$$

You'll notice that now, on the left side, we have an expression which consists of only constants.

Chemists simply combine all these constants on the left and call it the *equilibrium constant* (K_{eq})

In other words, the *concentrations of the solids* are incorporated into the value for K_{eq} .

Therefore, the K_{eq} expression for the equation:



is simply: $K_{eq} = [CO_2]$

The bottom line is:

When we write the K_{eq} expression for a reaction with solids, we simply leave out the solids.

Liquids also have a fairly constant concentration. They don't expand or contract that much even with changes in temperature.

The same argument that was used for *solids* can also be used for *liquids*. Thus, we can expand the last statement:

When we write the K_{eq} expression for a reaction with solids or liquids, we simply leave out the solids and the liquids.

Gases and *aqueous solutions* do undergo changes in concentration so they are always included in the K_{eq} expression.

Try the following:

3. Write the K_{eq} expression for the following reaction:



$K_{eq} =$

Check your answer on page 2 of Tutorial 5 - Solutions.

Value of K_{eq} and the Extent of Reaction

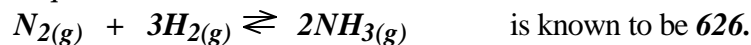
Remember that K_{eq} is a *fraction* (or ratio). The products are on the top and the reactants are on the bottom.

Remember that in a fraction:

The *larger* the numerator \rightarrow the *larger* the value of the fraction.

The *larger* the denominator \rightarrow the *smaller* the value of the fraction.

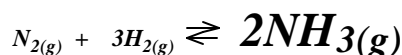
At 200 °C, the K_{eq} for the reaction:



K_{eq} is equal to the ratio:

$$\frac{[NH_3]^2}{[N_2] [H_2]^3}$$

Since this ratio is very large (626) at 200°C, we can say that $[NH_3]^2$ (the numerator) must be quite large and $[N_2] [H_2]^3$ (the denominator) must be small:



In other words, a **large** value for K_{eq} means that at equilibrium, there is **lots of product** and **very little reactant** left.

Even another way to say this is:

The larger the value for K_{eq} the closer to completion the reaction is at equilibrium.

(NOTE: "Completion" means reactants have been completely converted to products.)

A **very small** value for K_{eq} means that there is **very little product** and **lots of reactant** at equilibrium.

In other words, a **very small** value for K_{eq} means that the reaction has **not occurred to a very great extent** once equilibrium is reached.

Consider the following reaction: $A + B \rightleftharpoons C + D \quad K_{eq} = 1.0$

The K_{eq} expression is:

$$K_{eq} = \frac{[C] [D]}{[A] [B]} = 1.0$$

In this case the ratio of [C] [D] to [A] [B] is 1.0.
This means that there is about the same amount of products as reactants. At equilibrium, this reaction has proceeded to "about half way" to completion.

Here's another question:

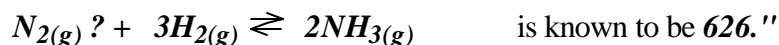
4. For the reaction: $Cu(OH)_{2(s)} \rightleftharpoons Cu^{2+}_{(aq)} + 2OH^{-}_{(aq)} \quad K_{eq} = 1.6 \times 10^{-19}$

Describe the extent of the reaction and the relative amounts of reactant and product at equilibrium.

Check the answer to this on page 2 of Tutorial 5 - Solutions

You probably couldn't help but notice that in some of the examples above when the K_{eq} was given, the temperature was also mentioned

eg.) "At 200 °C, the K_{eq} for the reaction:



You probably wondered, "What's the 200 °C got to do with it and what should I do with the "200"?"

Well, here's something you need to know:

When the temperature changes, the value of K_{eq} also changes.

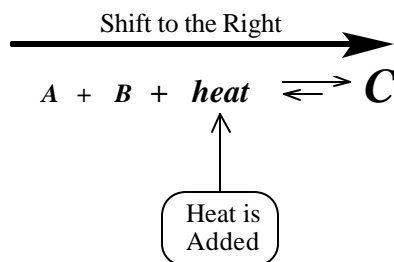
Let's see how this works:

Consider the following *endothermic* reaction: $A + B + \text{heat} \rightleftharpoons C$

The K_{eq} expression for this is:

$$K_{eq} = \frac{[C]}{[A][B]}$$

Now, let's say that we *increase the temperature* of this system. By LeChatelier's Principle, adding heat to an endothermic reaction will make it *shift to the right*:



Because it *shifts to the right*, a new equilibrium is established which has a *higher* $[C]$ and a *lower* $[A]$ and $[B]$.

Therefore the K_{eq} will have a *larger numerator* and a *smaller denominator*:

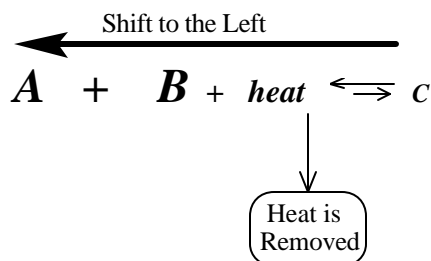
$$K_{eq} = \frac{[C]}{[A][B]} \quad \text{This will make the value of } K_{eq} \text{ larger than it was before.}$$

So we can summarize by saying:

When the temperature is increased in an *endothermic* reaction, the equilibrium will shift to the right and the value of K_{eq} will increase.

For an **endothermic** reaction, *decreasing the temperature* would make the equilibrium shift to the **left**.

This would cause $[C]$ to *decrease* and the $[A]$ and $[B]$ to *increase*:



Now, in the K_{eq} expression, the numerator would be smaller and the denominator would be larger:

$$K_{eq} = \frac{[C]}{[A][B]}$$

This will make the value of K_{eq} **smaller** than it was before.

So we can say:

When the *temperature is decreased* in an **endothermic** reaction, the equilibrium will **shift to the left** and the *value of K_{eq} will decrease*.

Try this question:

5. Given the equation for an **exothermic** reaction: $C + D \rightleftharpoons E + \text{heat}$

a) Write the K_{eq} expression for this reaction:

$$K_{eq} = \text{-----}$$

b) If the *temperature* of this exothermic reaction is **increased**, the equilibrium will shift ____

c) The shift will make $[E]$ _____er, and $[C]$ and $[D]$ _____er than they were before.

d) Since the numerator is _____er and the denominator is _____er, the value of the K_{eq} will be _____er than it was before.

e) If the temperature of this system is **decreased**, the equilibrium will shift to the _____, and the value of K_{eq} will _____

f). Fill in the following blanks:

When the *temperature is increased* in an *exothermic* reaction, the equilibrium will
shift to the _____ and the *value of K_{eq} will _____*.

and

When the *temperature is decreased* in an *exothermic* reaction, the equilibrium will
shift to the _____ and the *value K_{eq} will _____*.

Check your answers on page 3 of Tutorial 5 - Solutions

Here's another good question for you:

6. The reaction: $X + Y \rightleftharpoons Z$ has a $K_{eq} = 235$ at 100°C .

When the temperature is raised to 200°C , the value for $K_{eq} = 208$

Is this reaction endothermic or exothermic? _____

Explain your answer. _____

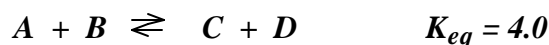
Check your answer on page 4 of Tutorial 5 - Solutions

Changes in Concentration and K_{eq}

Now, as you know, changing the concentration of one of the reactants or products will cause the reaction to shift right or left. *But this does not change the value for K_{eq} as long as the temperature remains constant.*

How can this be?

Let's have a look:
Consider the reaction:



The K_{eq} expression is:

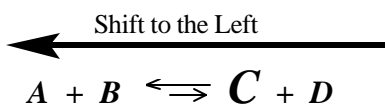
$$K_{eq} = \frac{[C][D]}{[A][B]} = 4.0$$

Let's say we quickly add some C to the system at equilibrium.

Of course [C] would increase, and temporarily equilibrium would be destroyed.

Since [C] is so large, the ratio: $\frac{[C][D]}{[A][B]}$ would be > 4.0 (the high [C] makes the numerator large)

But, of course, things don't stay like this. When [C] has been increased, the equilibrium will shift to the *left* (by LeChatelier's Principle)



In the shift to the left [A] and [B] will get a little larger and the big [C] will get smaller and [D] will get smaller.

This will decrease the value of the numerator and increase the value of the denominator until the ratio:

$$\frac{[C][D]}{[A][B]} \text{ is again} = 4.0$$

As long as the temperature is not changed, the equilibrium will always shift just enough to keep the ratio equal to the value of the equilibrium constant (K_{eq})!

Effect of Catalysts on the Value of K_{eq}

As we saw in the Tutorial on LeChatelier's Principle:

Addition of a *catalyst* speeds up the forward reaction and the reverse reaction *by the same amount*. Therefore, it does not cause any shift of the equilibrium.

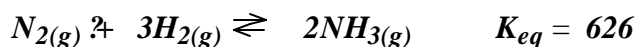
Because there is no shift, the value of the K_{eq} will also remain unchanged.

Addition of a catalyst to a system at equilibrium does not change the value of K_{eq} !

Effect of Pressure or Volume on the Value of K_{eq}

Like changes in concentration, changes in the total pressure or volume can cause an equilibrium to shift left or right. (If there is a different number of moles of gas on each side.)

For example: Given the reaction:



So the ratio:

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = 626$$

Let's say the volume of the container is decreased. This increases the total pressure of the system.

Increasing the pressure will increase the concentrations of all three species the same amount.

Since there are more moles of gas ($N_{2(g)} + 3H_{2(g)}$) on the left side, there is more "stuff" increased in the denominator of the ratio, so the value of the ratio will temporarily go down:

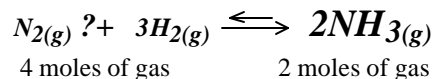
So the ratio:

$$\frac{[NH_3]^2}{[N_2][H_2]^3} \text{ will be } < 626$$



There are two substances in the denominator that are increased, so the whole denominator goes up more than the numerator.

But, by LeChatelier's Principle, **increased pressure** will cause the equilibrium to shift to the **right**:



This will bring $[NH_3]$ up, so the numerator of the ratio ($[NH_3]^2$) will increase.

Thus, the value of the ratio increases again. And guess what?

It increases until it just reaches 626 again. The ratio is now equal to K_{eq} and equilibrium has again been achieved!

So the ratio: $\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$ is again equal to 626

So, to summarize:

A change in total volume or total pressure does not change the value of the equilibrium constant K_{eq} . The equilibrium will shift to keep the ratio equal to K_{eq} .

Self-Test on Tutorial 5

- Write the **Equilibrium Constant Expression** for each of the following reactions. (Be careful of the phases!)
 - $\text{A}_{(s)} + \text{B}_{(g)} \rightleftharpoons 2\text{C}_{(g)} \quad K_{eq} =$
 - $\text{COCl}_{2(g)} \rightleftharpoons \text{CO}_{(g)} + \text{Cl}_{2(g)} \quad K_{eq} =$
 - $\text{Zn}_{(s)} + 2\text{HCl}_{(aq)} \rightleftharpoons \text{H}_{2(g)} + \text{ZnCl}_{2(aq)} \quad K_{eq} =$
- A _____ value for K_{eq} means that a reaction has gone close to completion.
- A _____ value for K_{eq} means that a reaction has not occurred to much of an extent.
- A value of around 1.0 for K_{eq} means _____

- Given the equilibrium equation:

$$2\text{NO}_{2(g)} \rightleftharpoons \text{N}_2\text{O}_{4(g)} + \text{heat} \quad K_{eq} = 1.20 \text{ at } 55^\circ\text{C}$$

What will happen to the value of K_{eq} if the temperature is increased? _____

Explain why _____

6. For the reaction: $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$ $K_{eq} = 2.24$ at 227°C

$$K_{eq} = 33.3 \text{ at } 487^\circ\text{C}$$

Is this reaction endothermic or exothermic? _____

Explain your answer _____

7. If the temperature remains constant in an equilibrium:

a) Will changing the **concentration** of one of the substances change the value of K_{eq} ?

Answer _____

b) Will changing the **total pressure** of the system change the value of K_{eq} ?

Answer _____

c) Will changing the **total volume** of the system change the value of K_{eq} ?

Answer _____

d) Will adding a **catalyst** change the value of K_{eq} ?

Answer _____

8. The K_{eq} for the reaction: $2\text{HI}_{(g)} \rightleftharpoons \text{H}_{2(g)} + \text{I}_{2(g)}$ is 85 at 25°C

Determine the value of K_{eq} for the reaction: $\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$ at 25°C

Answer _____

Check answers for the Self-Test starting on page 4 of Tutorial 5 - Solutions