

LeChatelier's Principle

LeChatelier's Principle:

If a closed system at equilibrium is subjected to a change, processes will occur that tend to counteract that change.

- "Processes" usually mean that the equilibrium will *shift* to the left or right.
- "Counteract" means that if you do something to a system at equilibrium, the system will shift in such a way as to try to "undo" what you did.
- Remember, equilibrium only occurs in a *closed system*.

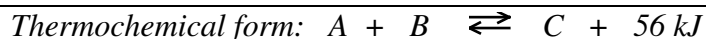
Examples of Counteracting:

- If you *add heat* to a system, it will shift in a way that it tends to "*use up*" the added heat.
- If you *remove heat* from a system, it will shift in a way that it tends to "*produce heat*"
- If you *increase the concentration* of a certain substance in an equilibrium mixture, the system will shift so as to *reduce the concentration* of that substance.
- If you *decrease the concentration* of a certain substance in an equilibrium mixture, the system will shift so as to *increase the concentration* of that substance.
- If you *increase the total pressure* on an equilibrium system involving *gases*, the system will shift in a way that will *reduce the total pressure*.
- If you *decrease the total pressure* on an equilibrium system involving *gases*, the system will shift in a way that will *increase the total pressure*.

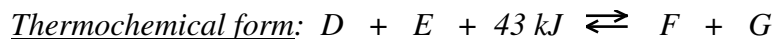
Effect of Changes in Temperature

NOTE: When using LeChatelier's Principle, it is easier to have all reactions with "heat" in "*Thermochemical Form*".

eg.) The reaction: $A + B \rightleftharpoons C \quad \Delta H = -56 \text{ kJ}$
is *exothermic* (ΔH is negative), so heat is given off or written on the *right*.



The reaction: $D + E \rightleftharpoons F + G \quad \Delta H = 43 \text{ kJ}$
 is **endothermic** (ΔH is positive), so heat is absorbed, or written on the left



Let's say we have an *endothermic* reaction:



If we **increase** the temperature of this system, we are **adding heat**. In order to *counteract* our change, the equilibrium will move in such a way as to **use up heat**.

Since heat is on the *left*, the **forward** reaction **uses up heat**, so it will predominate and the equilibrium will **shift toward the right**.

Which means a **new equilibrium** will be established in which there is **more C and D** and **less A and B** than in the original equilibrium.

To summarize: **When the temperature is increased, the equilibrium will shift away from the side with the heat term.**

Now, if the **temperature was decreased**, the equilibrium would shift in such a way that would **produce heat** (to counteract the change).

To do this, it would shift **toward the side with the heat term**. (in other words, produce heat)

To summarize: **When the temperature is decreased, the equilibrium will shift toward the side with the heat term.**

Here are a couple of questions:

- Given the reaction at equilibrium: $A_{(g)} + B_{(g)} + 32.5 \text{ kJ} \rightleftharpoons C_{(g)}$
 - If the temperature was *increased*, which way would this equilibrium shift _____
 - If the temperature was *decreased*, which way would this equilibrium shift: _____

2. Given the reaction: $X_{(g)} + Y_{(g)} \rightleftharpoons W_{(g)} + Z_{(g)} \quad \Delta H = -75 \text{ kJ}$

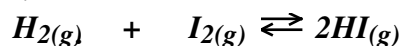
a) Rewrite this as a **thermochemical reaction**

b) If the temperature was *increased*, which way would this equilibrium shift: _____

c) If the temperature was *decreased*, which way would this equilibrium shift: _____

Effect of Changes in Concentration or Partial Pressure

Consider the equilibrium equation:



If we **add some H_2** to a flask containing this mixture at equilibrium, **$[H_2]$ will immediately increase.**

In order to **counteract** this change, the equilibrium will **shift to the right** in order to "use up" some of the extra H_2 . (In other words to decrease the $[H_2]$).

Consider the equilibrium equation: $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

Let's say now that we somehow **take away some I_2** . $[I_2]$ will immediately **decrease**.

In order to **counteract** this change, the equilibrium will **shift to the left** in order to **increase $[I_2]$ again**.

If we were to **add some HI** , the $[HI]$ would immediately _____crease.

In order to **counteract** this change, the equilibrium would shift to the _____.

To answer the last question, adding HI will **increase** $[HI]$. In order to **counteract** this change the equilibrium will **shift to the left**. In shifting to the left, $[H_2]$ and $[I_2]$ will go up and $[HI]$ will go down.

We can summarize the effects of changing concentrations by saying:

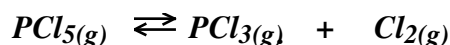
If the concentration of a substance in an equilibrium system is increased by us, the equilibrium will shift toward the other side of the equation, in order to counteract the change.

or

If the concentration of a substance in an equilibrium system is decreased by us, the equilibrium will *shift toward the side of the equation with that substance*, in order to counteract the change.

Some examples:

3. Given the equilibrium equation:



- a) If the $[PCl_5]$ is *increased*, the equilibrium will shift to the
- b) If the $[PCl_5]$ is *decreased*, the equilibrium will shift to the
- c) If the $[PCl_3]$ is *increased*, the equilibrium will shift to the
- d) If the $[PCl_3]$ is *decreased*, the equilibrium will shift to the
- e) If the $[Cl_2]$ is *increased*, the equilibrium will shift to the
- f) If the $[Cl_2]$ is *decreased*, the equilibrium will shift to the

Changing the Partial Pressure of a gas in an equilibrium system has the *same effect* as changing the concentration of that gas.

For example:



If the *partial pressure* of H_2 is *increased*, the equilibrium will shift to the right.

If the *partial pressure* of H_2 is *decreased*, the equilibrium will shift to the left.

If the *partial pressure* of HBr is *increased*, the equilibrium will shift to the left.

If the *partial pressure* of HBr is *decreased*, the equilibrium will shift to the right.

Effect of Changes in Total Pressure or Volume for Gaseous Systems

Recall from the last tutorial that:

The more moles of gas in a certain volume, the higher the pressure.

Also, recall LeChatelier's Principle:

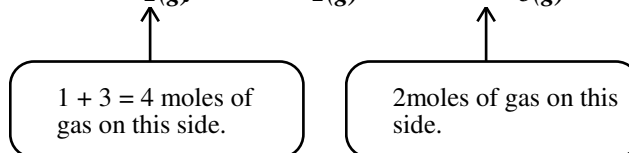
LeChatelier's Principle:
If a closed system at equilibrium is subjected to a change, processes will occur that tend to counteract that change.

Thus:

If the **total pressure** of a system at equilibrium is **increased**, the equilibrium will shift **toward the side with less moles of gas** (as shown by coefficients) in order to **reduce** the total pressure.

For example:

Given the equilibrium equation: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$



If the **total pressure** on this system is **increased**, the equilibrium would **shift to the right** (the side with fewer moles of gas). This *counteracts* the imposed change by *reducing* the pressure.

To review:

A **shift to the right** in this case would mean that once the new equilibrium is established, the $[NH_3]$ would be *higher* than before, the $[N_2]$ and the $[H_2]$ would be *lower* than before.

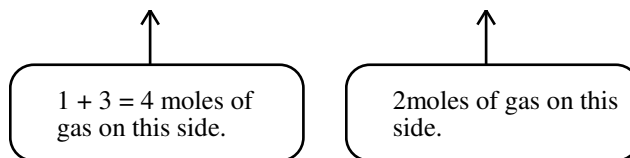
If the **total pressure** on this system is **decreased**, the equilibrium would **shift to the left** (the side with more moles of gas). This *counteracts* the imposed change by *increasing* the pressure.

To see what happens when we change the total volume of the container we must remember that:

Increasing the volume of a closed system with gases will decrease the pressure.
 (the molecules have more room so they exert less pressure on the sides of the container)

So, given changes in volume of the container, just remember that the changes in pressure are just the opposite. For example:

Given the equilibrium equation: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$



If the *total volume* of the container is **increased**, this means that the *total pressure* is **decreased**.

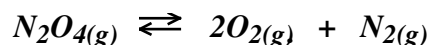
The equilibrium will then shift to the side with **more moles** (to the **left** in this case), in order to counteract the change and try to increase the pressure again.

If the *total volume* of the container is **decreased**, this means that the *total pressure* is **increased**.

The equilibrium will then shift to the side with **less moles** (to the **right** in this case), in order to counteract the change and try to decrease the pressure again.

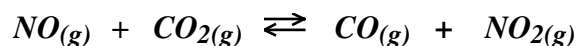
Try the following:

4. Given the equilibrium equation:



- If the total pressure of this system is increased, the equilibrium will shift _____
- If the total pressure of this system is decreased, the equilibrium will shift _____
- If the total volume of this system is increased, the equilibrium will shift _____
- If the total volume of this system is decreased, the equilibrium will shift _____

5. Given the equilibrium equation:



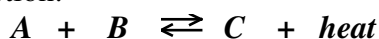
- If the total pressure of this system is increased, the equilibrium will _____
- If the total pressure of this system is decreased, the equilibrium will _____
- If the total volume of this system is increased, the equilibrium will _____
- If the total volume of this system is decreased, the equilibrium will _____

Shifting Equilibrium and Rate of Reaction

Just a little note here about the difference between *rate of reaction* and the *equilibrium shifting right or left*!

First of all, a "shift to the left" means that once the new equilibrium is reached, there will be *more reactants and less products*. It does **not** say anything about the *rate of the reaction*!!

For example, consider the reaction:



If the *temperature* of this system was *increased*, the equilibrium would shift to the *left*.

This does **not** mean that the rate will be slower! It simply means that a new equilibrium will be reached which has *more A and B and less C*.

In fact, as we might recall from Unit 1, *increasing the temperature always increases the rate of a reaction*. (more molecules have the minimum energy necessary for an effective collision.)

Increasing the temperature just causes equilibrium to be reached faster.

Try these:

6. Given the equilibrium equation: $X + Y + \text{heat} \rightleftharpoons Z$

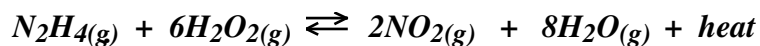
- Increasing the temperature will _____ the rate of reaction.
- Increasing the temperature will cause the equilibrium to shift _____
- Decreasing the temperature will _____ the rate of reaction.
- Decreasing the temperature will cause the equilibrium to shift _____

7. Given the equilibrium equation: $D + E \rightleftharpoons F + \text{heat}$

- Increasing the temperature will _____ the rate of reaction.
- Increasing the temperature will cause the equilibrium to shift _____
- Decreasing the temperature will _____ the rate of reaction.
- Decreasing the temperature will cause the equilibrium to shift _____

More Questions:

1. Given the following equilibrium equation:



Which way will the equilibrium shift when each of the following changes are made?

- The $[\text{NO}_2]$ is increased
 - The $[\text{H}_2\text{O}_2]$ is increased
 - The partial pressure of N_2H_4 is increased
 - The temperature is increased
 - The partial pressure of H_2O_2 is decreased
 - The partial pressure of H_2O is increased
 - The temperature is decreased
 - The total volume of the container is decreased
 - The total pressure of the system is decreased
 - The $[\text{N}_2\text{H}_4]$ is decreased
2. Given the equilibrium equation: $\text{N}_2\text{O}(\text{g}) + \text{NO}_2(\text{g}) + \text{heat} \rightleftharpoons 3\text{NO}(\text{g})$

What effect will each of the following changes have on the equilibrium partial pressure of NO?
(The first question is done as an example.)

- the $[\text{N}_2\text{O}]$ is increased **The partial pressure of NO increases because the equilibrium shifts to the right.**
- the total pressure of the system is decreased
- the temperature is decreased.....
- the partial pressure of NO_2 is decreased.....
- more NO_2 is added
- a catalyst is added

- g) the temperature is increased _____
- h) the total volume of the container is increased _____

The Equilibrium Constant (K_{eq})

What is K_{eq} ?

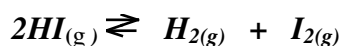
The "K" in K_{eq} stands for "Constant". The "eq" means that the reaction is at equilibrium.

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.

It has been found for the reaction:



that if you take the [H₂], the [I₂] and the [HI] in an *equilibrium mixture* of these at 423 °C, the expression:

$$\frac{[H_2][I_2]}{[HI]^2} = 0.0183$$

↑

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:



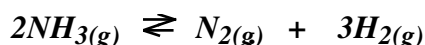
and the K_{eq} expression was:

$$K_{eq} = \frac{[H_2][I_2]}{[HI]^2}$$

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 [HI] in the **K_{eq} expression**. Thus we have $[HI]^2$ in the denominator.

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



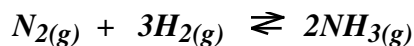
$$K_{eq} =$$

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:



$$K_{eq} =$$

The K_{eq} Expressions for Solids and Liquids

Consider the following reaction:

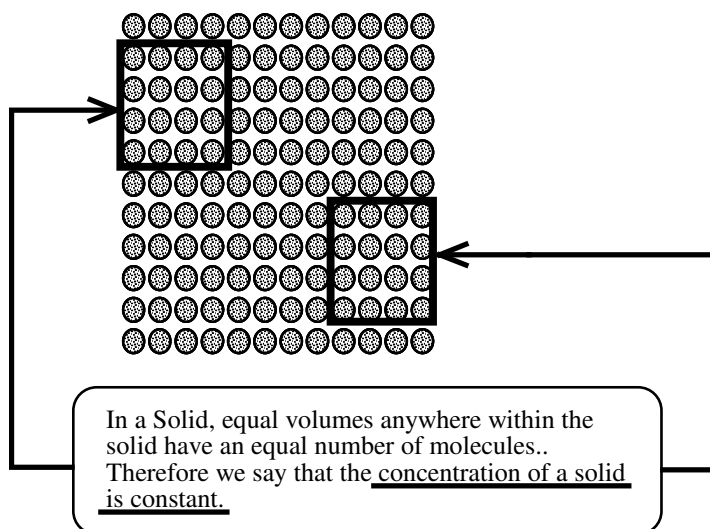


You might expect the K_{eq} expression to be something like:

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

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:



Going back to our example:

Consider the following reaction:



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

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

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

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

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

Now, if we rearrange:

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

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: $K_{eq} = [\text{CO}_2]$

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:



$$K_{eq} =$$

Value of K_{eq} and the Extent of Reaction

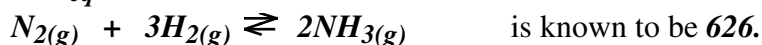
Remember that K_{eq} is a *fraction* (or ratio). The products are on the top and the reactants are on the bottom.

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:



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

Since this ratio is very large (626) at 200°C, we can say that $[\text{NH}_3]^2$ (the numerator) must be quite large and $[\text{N}_2] [\text{H}_2]^3$ (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: $A + B \rightleftharpoons C + D$ $K_{eq} = 1.0$

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:

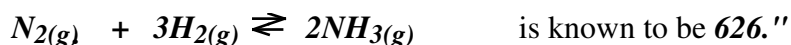
4. For the reaction: $\text{Cu(OH)}_{2(s)} \rightleftharpoons \text{Cu}^{2+}_{(aq)} + 2\text{OH}^{-}_{(aq)}$ $K_{eq} = 1.6 \times 10^{-19}$

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

K_{eq} and Temperature

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:



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

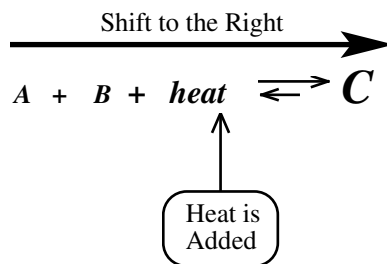
Let's see how this works:

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**:

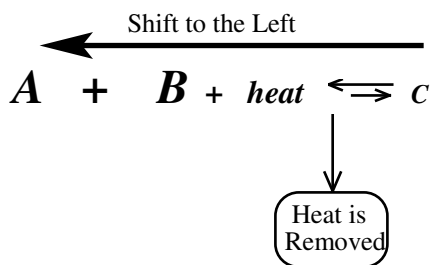
$$K_{eq} = \frac{[C]}{[A][B]} \quad \text{This will make the value of } K_{eq} \text{ larger than it was before.}$$

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:

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

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:

$$K_{eq} = \underline{\hspace{2cm}}$$

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 _____*

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? _____

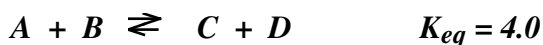
Explain your answer. _____

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:

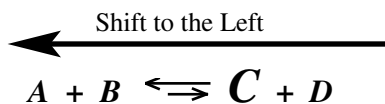
$$K_{eq} = \frac{[C][D]}{[A][B]} = 4.0$$

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.

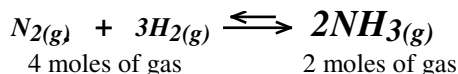
Increasing the pressure will increase the concentrations of all three species the same amount.

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

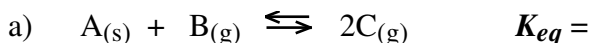
So the ratio:
$$\frac{[NH_3]^2}{[N_2][H_2]^3}$$
 is again equal to 626

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} .

More Questions:

- Write the **Equilibrium Constant Expression** for each of the following reactions. (Be careful of the phases!)





2. A _____ value for K_{eq} means that a reaction has gone close to completion.
3. A _____ value for K_{eq} means that a reaction has not occurred to much of an extent.
4. A value of around 1.0 for K_{eq} means _____

5. Given the equilibrium equation:



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

Explain why _____

6. For the reaction: $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \quad K_{eq} = 2.24 \text{ at } 227^\circ\text{C}$

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

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 _____