

Chemistry 12

Tutorial 3 - Factors Affecting Equilibrium

In Tutorial 3, you will be shown:

1. The *factors* that can cause changes in a system at equilibrium.
2. How *changes* in each factor affect equilibrium.
3. How changes in equilibrium can be explained using the concepts of *reaction kinetics*.
4. How *catalysts* affect a system at equilibrium.

Remember the following?

When a chemical system is at equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction.

As long as no changes are made to conditions of a system at equilibrium, this situation would just go on forever with no changes in macroscopic properties.

This might be nice, but it would be boring! Also, humans like to change and manipulate systems to their advantage. (For example, to produce *more* of a useful product)

In order to disturb an equilibrium all we have to do is change the rate of either the forward or reverse reaction so that they are no longer equal.

Let's do it and see what happens:

Effect of Temperature

Consider the equilibrium system:
$$\text{N}_2\text{O}_4(\text{g}) + \text{heat} \rightleftharpoons 2 \text{NO}_2(\text{g})$$

colourless
brown

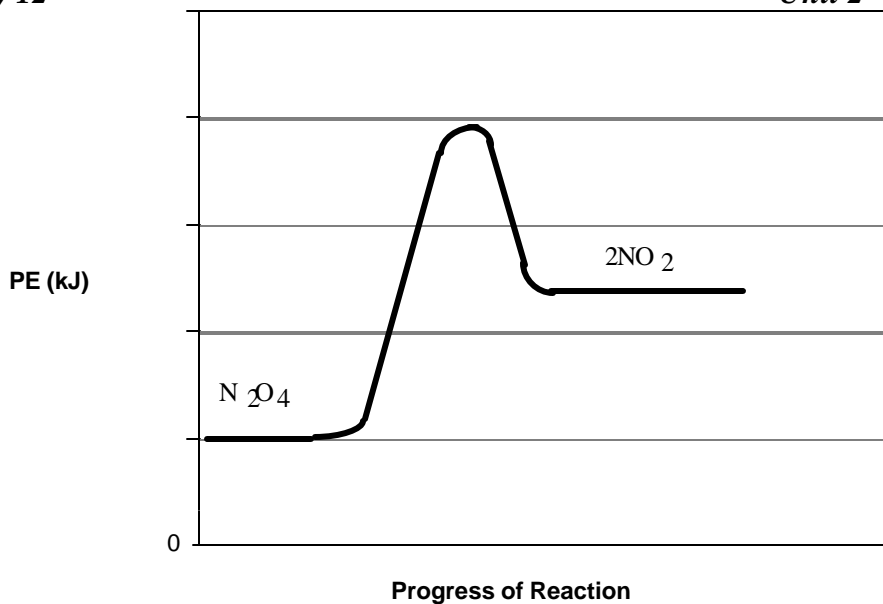
At equilibrium, NO₂ is being formed at the same rate as it is being used up, so its concentration is constant. The system is a medium brown colour at room temperature.

Let's look at a *potential energy diagram* for this reaction (Notice that it is ***endothermic***)

Remember, when the reaction is endothermic, the _____

have higher potential energy than the _____

(fill in these blanks, then look at the graph on the next page. If you were wrong, change your answers)



1. Now, consider the forward reaction and the reverse reaction. Which reaction do you think would be most affected by an increase in temperature? _____

Now check your answer by looking at page 1 of Tutorial 3 - Solutions. Make sure you carefully read the explanation written there!

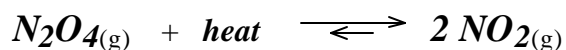
Once you have read the answer and the explanation on Tutorial 3 - Solutions, you will see that **increasing the temperature will speed up the forward reaction more than the reverse:**

One way to look at it is:

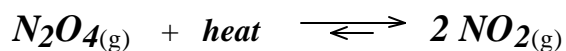


In an endothermic reaction, the forward reaction needs heat, so its rate will be increased more by an increase in temperature.

So, **increasing the temperature**, the **forward reaction** is **faster** than the **reverse reaction** for awhile: (This can be shown by making the forward arrow longer)



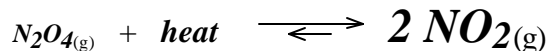
So guess what happens to $[NO_2]$ while the forward reaction is faster than the reverse reaction? _____



The NO_2 is *formed* faster than it is used up, so its concentration **increases**.

The N_2O_4 is *used up* faster than it is formed, so its concentration **decreases**.

This might be shown as follows:



Now, since **more** NO_2 has been formed, what do you think will happen to the rate of the

Reverse Reaction? _____

Since there are now **more** molecules of NO_2 to run into each other,

The rate of the reverse reaction will also speed up.

Because there is less N_2O_4 after awhile, the forward reaction will slow down.

So as you might guess, after awhile, *the rate of the reverse reaction will again equal the rate of the forward reaction and again we have equilibrium!* (a new equilibrium!)

But remember this:

The forward rate was faster than the reverse rate for awhile. (increasing $[NO_2]$ and decreasing $[N_2O_4]$)

But the reverse rate was **never** faster than the forward rate even though it finally caught up.

It may take a little deep thought about this, but :

If NO_2 was being *formed* faster than *being used up* for awhile but never *used up* faster than it was *being formed*, its concentration will be **higher** when the new equilibrium is established.

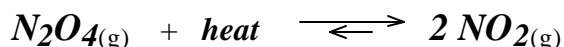
With similar thought, you might also see that the $[N_2O_4]$ will be **lower** in the new equilibrium.

So, to summarize:

1. Original equilibrium:

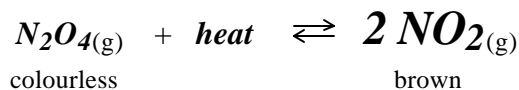


2. Temperature is increased and the endothermic (forward in this case) reaction rate increases:



3. A **new equilibrium** is established in which there is more NO_2 and less N_2O_4 .





When we have *more product(s)* than we had before and *less reactants* we say that:

The equilibrium has shifted to the right

(the stuff on the right has increased and the stuff on the left has decreased)

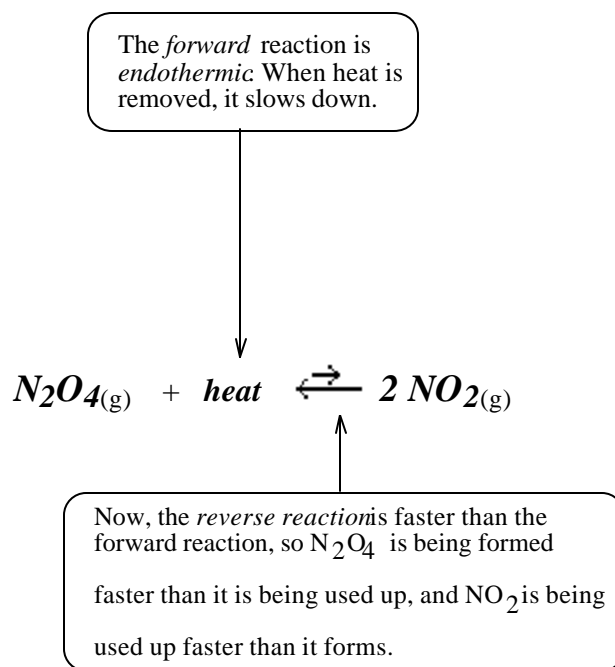
So what will happen to the colour in flask containing the equilibrium mixture when it is put

into boiling water and heated? _____

You're right, of course, it will get *darker*(because of a higher [NO₂] which is *brown*.)

If the flask were placed in *ice water*, the endothermic (forward in this case) reaction would slow down.

You would get a situation like this: (The rate of the forward reaction is slower than the rate of the reverse reaction.)



While the reverse reaction is faster than the forward, the [N₂O₄] will build up and the [NO₂] will decrease...





So what happens now, since $[\text{N}_2\text{O}_4]$ is higher, the rate of the forward reaction will gradually increase and after a certain time, it will again be equal to the rate of the reverse reaction.

At this point, we have a **new equilibrium!**

In this equilibrium $[\text{N}_2\text{O}_4]$ will be *higher* than it was originally (for awhile it was being formed faster than it was being used up), and the $[\text{NO}_2]$ will be *lower* than it was originally. (for awhile it was being used up faster than it was formed.)

We say that **the equilibrium has shifted to the left.** (or shifted toward the *reactant* side)



↑
It's at *equilibrium* again because the rates are equal, even though the amounts are different than in the original equilibrium

To summarize the effect of **temperature:**

When the temperature is **increased**, the *endothermic* reaction will **speed up** and the equilibrium will **shift toward the side without the heat term.**

(A new equilibrium is established in which there is a higher concentration of substances on the side without the heat term and a lower concentration of substances on the side with the heat term.)

When the temperature is **decreased**, the *endothermic* reaction will **slow down** and the equilibrium will **shift toward the side with the heat term.**

(A new equilibrium is established in which there is a lower concentration of substances on the side without the heat term and a higher concentration of substances on the side with the heat term.)

Effect of Concentration and Partial Pressure

Next, we will consider what happens when we change the *concentration* of a reactant or the *partial pressure* of a reactant.

First, we'd better explain the term "partial pressure".

When you have a gas mixture, the pressure exerted by *one* gas in the mixture is called the *partial pressure* of that gas. The *more* of that gas you have, the *greater* its partial pressure.

For example: In a certain gas mixture containing NO and CO₂ gases:

Partial Pressure of NO = 40 kPa (kilopascals-a unit of pressure)

Partial Pressure of CO₂ = 60 kPa

Total Pressure = 40 + 60 = 100 kPa

If you add some NO, its *partial pressure* will go up. For example:

Partial Pressure of NO = 50 kPa (kilopascals-a unit of pressure)

Partial Pressure of CO₂ = 60 kPa

Total Pressure = 50 + 60 = 110 kPa

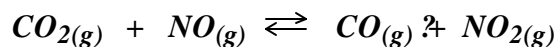
Since a *higher partial pressure* results from putting *more* of a certain gas in the same volume, it is really just another way of saying *concentration*.

That are different quantities in different units (Concentration is in moles/L, Partial pressure is in kPa)

But when one goes up, the other goes up.

From now on, when we mention "*Partial Pressure*" changes, they will have exactly the same effect as *Concentration* changes.

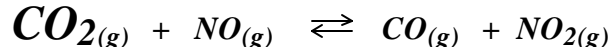
Consider the following system at equilibrium:



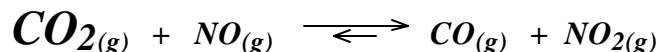
Of course, at equilibrium:

the rate of the forward reaction = the rate of the reverse reaction

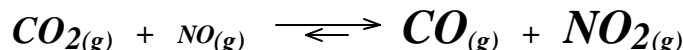
Let's, all of a sudden, **add** some CO_2 to the container that contains all of these. (What we are doing is **increasing** the $[\text{CO}_2]$ or the **partial pressure** of CO_2 .)



Since the $[\text{CO}_2]$, a *reactant* is now *higher*, there will be more *chances of collision* between CO_2 and NO , so the **forward reaction will speed up**.

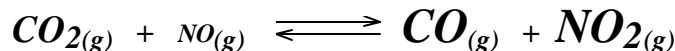


This will cause the $[\text{CO}]$ and the $[\text{NO}_2]$ to **increase** and the $[\text{CO}_2]$ and $[\text{NO}]$ to **decrease**



Because $[\text{CO}]$ and the $[\text{NO}_2]$ have **increased**, the *rate of the reverse reaction will speed up*.

When *the rate of the reverse reaction* is again = *the rate of the forward reaction*, we will again have **equilibrium**. (A **new equilibrium!**)



In this new equilibrium, $[\text{CO}]$ and $[\text{NO}_2]$ will be higher than they were originally and $[\text{CO}_2]$ and $[\text{NO}]$ will be lower than they were after we added the CO_2 .

In this case, the equilibrium is said to have **shifted to the right**. (or shifted to the **product** side.)

NOTE: Remember, we added some CO_2 . In the new equilibrium $[\text{CO}_2]$ is *less than* after we added it, but it doesn't quite go down to the level it was *before* we added any.

$[\text{NO}]$ will be quite low because it goes down and we didn't add any.

Here's a little question for you to do and then check on **Tutorial 3 - Solutions**:

2. Given the equilibrium: $\text{CO}_{2(g)} + \text{NO}_{(g)} \rightleftharpoons \text{CO}_{(g)} + \text{NO}_{2(g)}$

Some NO_2 is added to the system.

The _____ reaction will speed up.

This will cause the $[\text{CO}_2]$ and the $[\text{NO}]$ to _____

Therefore, after awhile, the rate of the _____ reaction will speed up, and there will be a new equilibrium.

Because the rate of the _____ reaction was higher for awhile, in the *new* equilibrium mixture, the $[\text{CO}_2]$ and the $[\text{NO}]$ will be _____ than they were before and the $[\text{CO}]$ and the $[\text{NO}_2]$ will be _____ than after we added the NO_2 .

We can say that adding the NO_2 *shifted* the equilibrium to the _____

After you finish this, check the key on page 2 of Tutorial 3 - Solutions.

Effects of Changing the Volume of the Container or Total Pressure

One thing to remember from Chemistry 11 here is that:

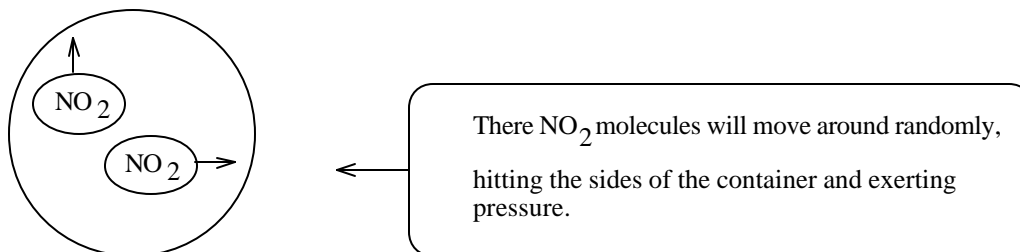
As the volume of a fixed number of moles of gas is *decreased* (the gas is compressed), the pressure will *increase*.

Let's consider the equilibrium:

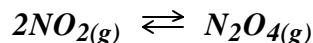
$$2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$$

brown colourless

Let's say that for some strange reason, we had 2 molecules of NO_2 only in a certain volume:



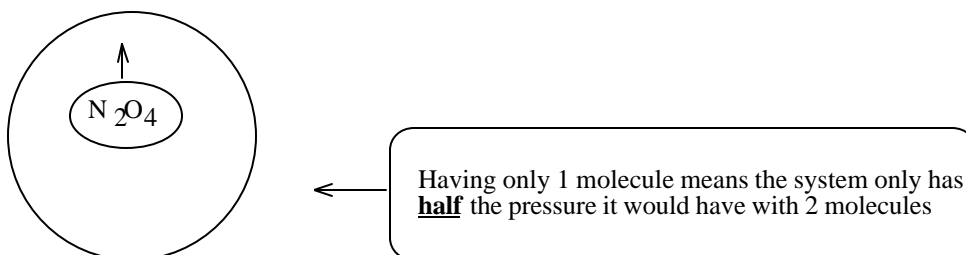
Now, suppose we were to completely convert those two molecules of NO_2 into N_2O_4 :



We would now have only **1** molecule (a molecule of N_2O_4) in the same volume.

This means there are only half as many molecules hitting the sides of the container, and therefore:

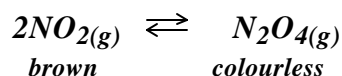
The pressure will be only half of what it was with the 2 molecules of NO₂:



So, to summarize:

The **greater** the number of **moles** (or molecules) of gas in a particular volume, the **greater** the **pressure**.

Now, let's get back to the original equilibrium mixture, where we have some NO₂ and some N₂O₄:



Let's say we have this system in a syringe and we quickly **decrease the volume** by pushing the plunger in.

Recall that **decreasing the volume** is exactly the same thing as **increasing the pressure**.

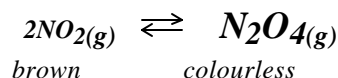
Initially, the colour will go **darker** because everything (including the brown NO₂) is compressed.

However, when you increase the pressure on something, there is a natural tendency for the system to do anything it can in order to offset that increase.

(For example, when you squish a balloon in one place, the air will be forced to another place and the balloon will bulge somewhere else, or the balloon will pop to decrease the pressure!)

When we **increase the pressure** on the $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ system, it can *offset* that increase by:

converting more NO₂ into N₂O₄ !



in other words: **shifting to the side with less moles of gas**. (as shown by the coefficients)

This "*shift to the right*" will *use up* some brown NO_2 converting it to colourless N_2O_4 , and the colour of the system will gradually get *lighter* again.

So, in summary:

When the ***total pressure is increased*** (*volume is decreased*) in an equilibrium system with *gases*, the equilibrium will shift toward the side with ***less moles of gas*** in the equation.

or, as you might guess:

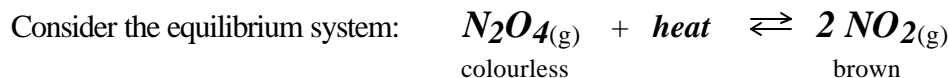
When the ***total pressure is decreased*** (*volume is increased*) in an equilibrium system with *gases*, the equilibrium will shift toward the side with ***more moles of gas*** in the equation.

Now, try the following problem:

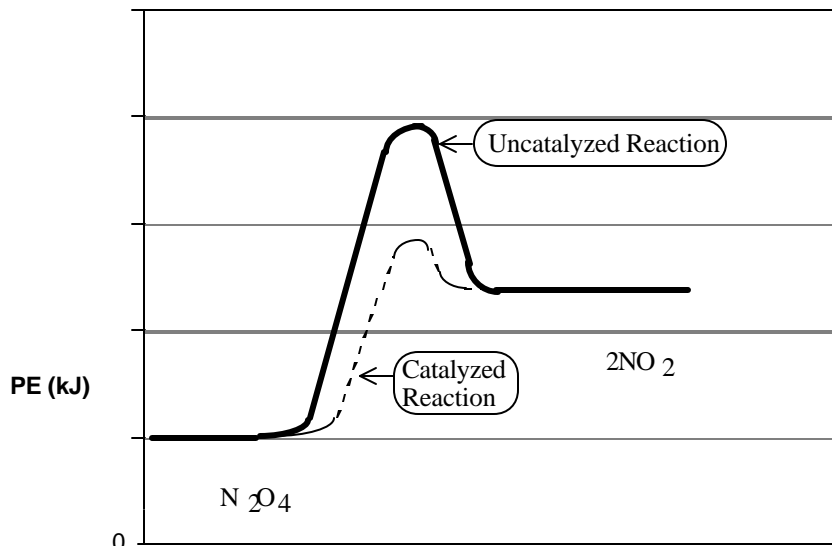
3. Given the equilibrium: $2\text{C}_2\text{H}_6(\text{g}) + 7\text{O}_2(\text{g}) \rightleftharpoons 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$

- a) *Increasing the total pressure* on this system, will cause a shift to the side with _____ moles of gas, which in this case is the _____ side.
- b) *Decreasing the total pressure* on this system, will cause a shift to the side with _____ moles of gas, which in this case is the _____ side.
- c) *Increasing the total volume* on this system (the same as _____ the total pressure) will cause a shift to the side with _____ moles of gas, which in this case is the _____ side.
- d) *Decreasing the total volume* on this system (the same as _____ the total pressure) will cause a shift to the side with _____ moles of gas, which in this case is the _____ side.

Now, check page 2 of Tutorial 3 - Solutions to check your answers. Ask for help if you need it at this point!

Effect of Catalysts

Adding a *catalyst* to this system would **decrease the activation energy** by providing a different route (or mechanism) for the reaction: (see the Potential Energy Diagram on the next page.)



Using a catalyst to provide a route will **decrease the activation energy** for the forward reaction **and for the reverse** reaction by the same amount.

This means the forward reaction will speed up, but so will the reverse reaction.

In fact, the rates of both the forward and reverse reactions will still remain equal to each other (even though they are both faster.)

Therefore, **the equilibrium will not shift!**

Adding a catalyst to a system **not at equilibrium** will simply speed things up so that *equilibrium will be attained faster*. It does **not** alter any of the concentrations etc. at equilibrium!

To summarize, equilibrium is affected by:

1. Temperature - If the temp. is increased, the equilibrium will shift toward the side *without* the heat term.

-If the temp. is decreased the equilibrium will shift toward the side *with* the heat term.

2. Concentration - If the [a reactant] is increased, the equilibrium will shift toward the right (the product side)
 - If the [a product] is increased, the equilibrium will shift toward the left (the reactant side)
3. Partial Pressure of Gases - the same effects as concentration.
4. Total Volume and Total Pressure - If pressure is increased (volume decreased), the equilibrium will shift to the side with less moles of gas.
 - If the pressure is decreased (volume increased), the equilibrium will shift toward the side with more moles of gas.

And lastly, remember:

Catalysts - Have **no effect** on equilibrium. They may help a system reach equilibrium faster, that's all!

Self-Test on Tutorial 3

Do these questions right on this sheet, then check on on page 3 of Tutorial 3 - Solutions for the answers.

1. When a chemical system is at equilibrium, when the temperature is increased, the _____othermic reaction speeds up the most.
2. In the reaction: $A + B \rightleftharpoons C + 43.3 \text{ kJ}$
 - a) When the temperature is increased the (forward/reverse) _____ reaction speeds up more.
 - b) During this time, the [A] and [B] will _____crease and the [C] will _____crease.
 - c) Because [A] and [B] are _____creasing, the rate of the _____ reaction will increase.
 - d) Sooner or later, the forward rate and the reverse rate will again become _____.
At this point a new _____ is established.
 - e) In the new equilibrium, [A] and [B] will be _____er than they were before the temperature is increased.
In the new equilibrium, [C] will be _____er than it was before.

f) In this example, we say that the equilibrium has shifted to the _____

3. Given the reaction: $A + B \rightleftharpoons C + 43.3 \text{ kJ}$

a) When the temperature is decreased the (forward/reverse) _____ reaction will be the faster one.

b) During this time, the [A] and [B] will _____crease and the [C] will _____crease.

c) Because [C] is _____creasing, the rate of the _____ reaction will increase.

d) Sooner or later, the forward rate and the reverse rate will again become _____.

At this point a new _____ is established.

e) In the new equilibrium, [A] and [B] will be _____er than they were before the temperature is increased.

In the new equilibrium, [C] will be _____er than it was before.

f) In this example, we say that the equilibrium has shifted to the _____

4. In the reaction: $A + B + 324 \text{ kJ} \rightleftharpoons C$

a) When the temperature is increased the (forward/reverse) _____ reaction speeds up more.

b) During this time, the [A] and [B] will _____crease and the [C] will _____crease.

c) Because [C] is _____creasing, the rate of the _____ reaction will increase.

d) Sooner or later, the forward rate and the reverse rate will again become _____.

At this point a new _____ is established.

e) In the new equilibrium, [A] and [B] will be _____er than they were before the temperature is increased.

In the new equilibrium, [C] will be _____er than it was before.

f) In this example, we say that the equilibrium has shifted to the _____

5. Given the equilibrium: $B_{(g)} + C_{(g)} \rightleftharpoons D_{(g)} + E_{(g)} + \text{heat}$
- Some B is added to the mixture at equilibrium. The rate of the reaction will increase due to the increase in the [B]. _____
 - While this is happening, the [D] and [E] will gradually _____crease.
 - The _____crease in the [D] and [E] will cause the rate of the reaction to increase. _____
 - When the rates of the forward and reverse reactions are equal, we have a new _____
 - Due to the addition of B, the equilibrium will shift to the _____
[B] and [C] will _____crease and [D] and [E] will _____crease
6. Given the equilibrium: $B_{(g)} + C_{(g)} \rightleftharpoons D_{(g)} + E_{(g)} + \text{heat}$
- Some D is added to the mixture at equilibrium. The rate of the reaction will increase due to the increase in the [D]. _____
 - While this is happening, the [B] and [C] will gradually _____crease.
 - The _____crease in the [B] and [C] will cause the rate of the reaction to increase. _____
 - When the rates of the forward and reverse reactions are equal, we have a new _____
 - Due to the addition of D, the equilibrium will shift to the _____
[B] and [C] will _____crease and [D] and [E] will _____crease.
7. Given the equilibrium: $2A_{(g)} + B_{(g)} \rightleftharpoons 2C_{(g)}$
- If the total pressure on the system is increased, the reaction will speed up the most. _____
 - While this is happening, the [C] will _____crease.
 - This _____crease in [C] will cause the _____reaction to speed up.

- d) When the new equilibrium is reached, the [A] and [B] will be _____er than before and the [C] will be _____ than before.
- e) We say that the increase in total pressure has caused the equilibrium to shift to the ____.
8. Given the equilibrium: $2A_{(g)} + ? B_{(g)} \rightleftharpoons 2C_{(g)}$
- a) If the total pressure on the system is decreased, the _____ reaction will be the faster one.
- b) While this is happening, the [A] and the [B] will _____crease.
- c) This _____crease in [A] and the [B] will cause the _____reaction to speed up.
- d) When the new equilibrium is reached, the [A] and [B] will be _____er than before and the [C] will be _____ than before.
- e) We say that the decrease in total pressure has caused the equilibrium to shift to the ____.
9. Given the equilibrium : $NO_{(g)} + CO_{2(g)} \rightleftharpoons NO_{2(g)} + CO_{(g)}$
- a) Will an increase in total pressure have an affect on the equilibrium? _____
- b) Explain your answer to question (a) _____
10. Given the equilibrium: $2A_{(g)} + B_{(g)} \rightleftharpoons 2C_{(g)}$
- a) If the total **volume** of the system is decreased, the _____ will increase, and the _____reaction will be the faster one.
- b) While this is happening, the [C] will _____crease.
- c) This _____crease in [C] will cause the _____reaction to speed up.
- d) When the new equilibrium is reached, the [A] and [B] will be _____er than before and the [C] will be _____ than before.
- e) We say that the decrease in total **volume** has caused the equilibrium to shift to the ____.

11. Given the equilibrium: $2A_{(g)} + B_{(g)} \rightleftharpoons 2C_{(g)} + \text{heat}$

a) How will this equilibrium be affected if a *catalyst* is added to the mixture? _____

b) Explain your answer to "a" in terms of forward and reverse reaction rates _____

This is the end of Tutorial 3
