Factors Affecting Equilibrium

Remember:

> ***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. We can change it though.

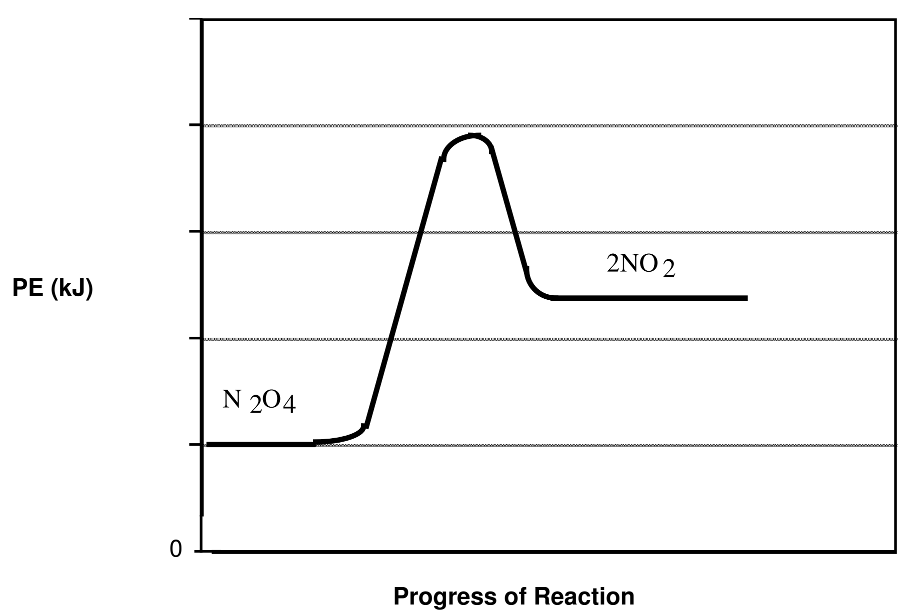
Effect of Temperature

Consider the equilibrium system: $N_2O_{4(g)} + \text{heat} \rightleftarrows 2\,NO_{2(g)}$

colourless — brown

At equilibrium, NO_2 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***)



$$N_2O_{4(g)} + \text{heat} \rightleftarrows 2\,NO_{2(g)}$$

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

<u>increasing the temperature will speed up the forward reaction more than the reverse</u>:

One way to look at it is:

$$N_2O_{4(g)} + heat \rightleftharpoons 2\,NO_{2(g)}$$

In an <u>endothermic</u> reaction, the <u>forward reaction</u> needs heat, so it's 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)

$$N_2O_{4(g)} + heat \rightleftharpoons 2\,NO_{2(g)}$$

The NO_2 is ***formed* faster** than it is used up, so it's concentration ***increases***.
The N_2O_4 is ***used up* faster** than it is formed, so it's concentration ***decreases***.

This might be shown as follows:

$$N_2O_{4(g)} + heat \rightleftharpoons 2\,NO_{2(g)}$$

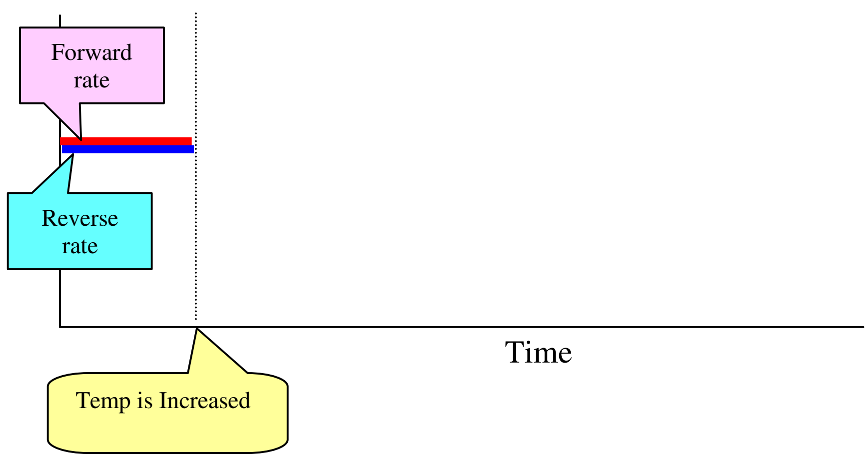
Since there are now ***more*** molecules of NO_2 to run into each other,

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 **<u>equilibrium</u>!**(a new equilibrium!)*

Draw a graph of how you think the forward and reverse rate would vary with time after the temperature has been increased:



<u>But remember this</u>:

The <u>forward</u> rate was faster than the <u>reverse</u> 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.

If NO_2 was being *formed* <u>faster</u> than *being used up* for awhile but never *used up* <u>faster</u> than it was *being formed*, it's concentration will be ***higher*** when the <u>new</u> equilibrium is established. and the [N_2O_4] will be ***lower*** in the new equilibrium.

<u>So, to summarize</u>:

1. Original equilibrium:

$$N_2O_{4(g)} + heat \rightleftarrows 2\ NO_{2(g)}$$

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

$$N_2O_{4(g)} + heat \xrightarrow{\longleftarrow} 2\ NO_{2(g)}$$

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

$$\underset{\text{colourless}}{N_2O_{4(g)}} + heat \rightleftarrows \underset{\text{brown}}{2\ NO_{2(g)}}$$

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

The equilibrium has <u>shifted</u> to the <u>right</u>

(*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? ____

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

$$N_2O_{4(g)} + heat \rightleftarrows 2\ NO_{2(g)}$$

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

The *forward* reaction is *endothermic*. When heat is removed, it slows down.

$$N_2O_{4(g)} + heat \rightleftarrows 2\,NO_{2(g)}$$

Now, the *reverse reaction* is faster than the forward reaction, so N_2O_4 is being formed faster than it is being used up, and NO_2 is being used up faster than it forms.

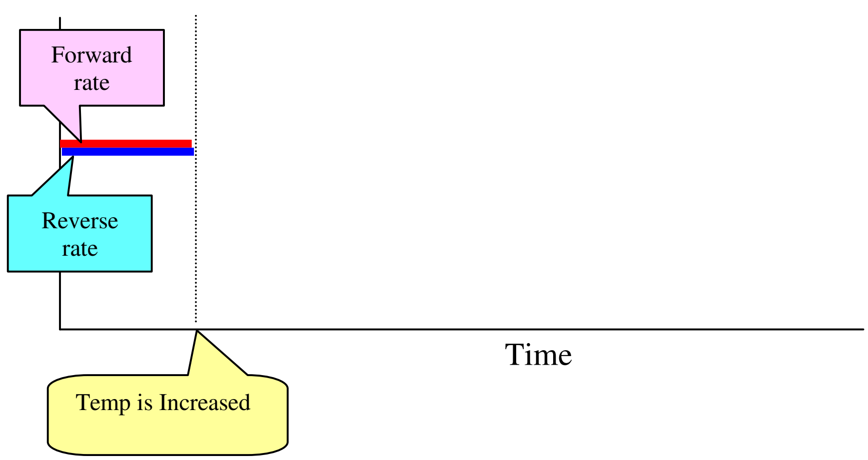
While the reverse reaction is faster than the forward, the $[N_2O_4]$ will build up and the $[NO_2]$ will decrease...

$$N_2O_{4(g)} + heat \rightleftarrows 2\,NO_{2(g)}$$

So what happens now, since $[N_2O_4]$ 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***!

Draw a graph of how you think the forward and reverse rate would vary with time after the temperature has been ***decreased***:



$$N_2O_{4(g)} + heat \rightleftharpoons 2\,NO_{2(g)}$$

In this equilibrium [N_2O_4] will be *higher* than it was originally (for awhile it was being formed faster than it was being used up), and the [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)

$$N_2O_{4(g)} + heat \rightleftharpoons 2\,NO_{2(g)}$$

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.)

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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* it's partial pressure.

For example: In a certain gas mixture containing NO and CO_2 gases:

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

Partial Pressure of CO_2 = 60 kPa

Total Pressure = 40 + 60 = 100 kPa

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

Partial Pressure of NO = **50 kPa**

Partial Pressure of CO_2 = 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:

$$CO_{2(g)} + NO_{(g)} \rightleftarrows CO_{(g)} + NO_{2(g)}$$

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 ***[CO_2]*** or the ***partial pressure*** of CO_2.)

$$CO_{2(g)} + NO_{(g)} \rightleftarrows CO_{(g)} + NO_{2(g)}$$

Since the [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***.

$$CO_{2(g)} + NO_{(g)} \rightleftarrows CO_{(g)} + NO_{2(g)}$$

This will cause the [CO] and the [NO_2] to ***increase*** and the [CO_2] and [NO] to ***decrease***

$$CO_{2(g)} + NO_{(g)} \rightleftarrows CO_{(g)} + NO_{2(g)}$$

Because [CO] and the [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***!)

$$CO_{2(g)} + NO_{(g)} \rightleftarrows CO_{(g)} + NO_{2(g)}$$

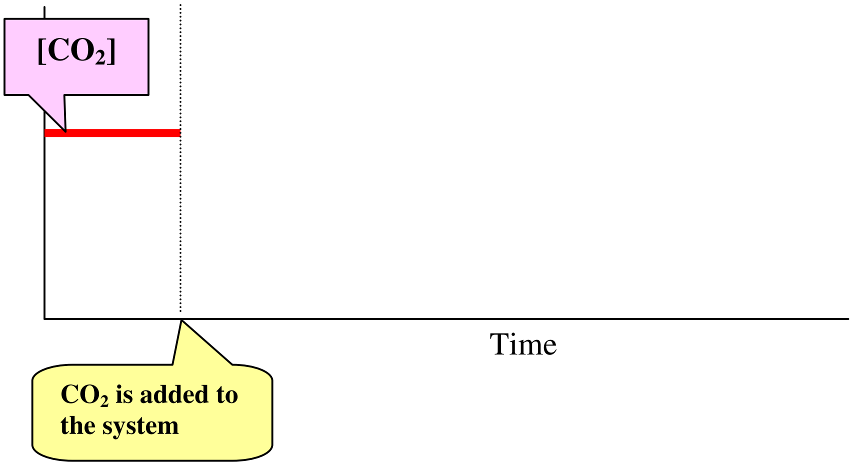
In this new equilibrium, [CO] and [NO_2] will be higher than they were originally and [CO_2] and [NO] will be lower than they were after we added the CO_2.

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 [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.**

[NO] will be quite low because it goes down and we didn't add any.

Try to draw a graph of $[CO_2]$ vs Time, starting at the original equilibrium and ending after we've reached the new equilibrium?



Try this:

Given the equilibruim: $CO_{2(g)} + NO_{(g)} \rightleftarrows CO_{(g)} + NO_{2(g)}$

Some NO_2 is added to the system.

The ____ reaction will speed up.

This will cause the $[CO_2]$ and the [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

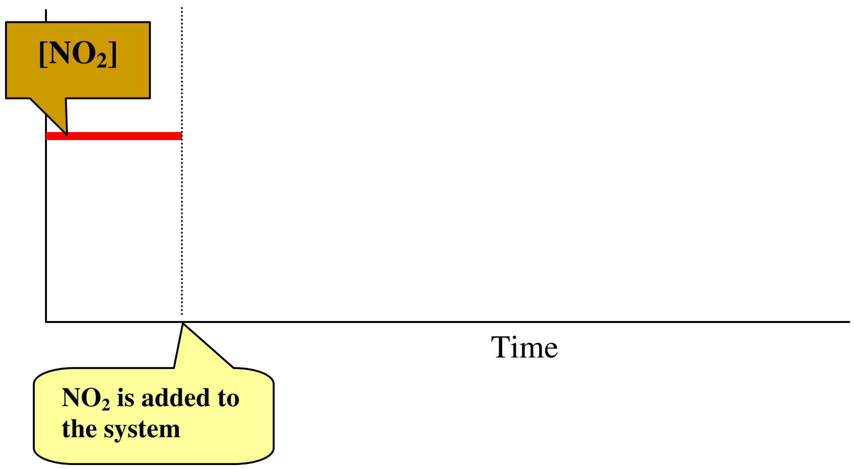
awhile, in the ***new*** equilibrium mixture, the $[CO_2]$ and the [NO] will be _______________

than they were before and the [CO] and the $[NO_2]$ will be _________________________ than after we added the NO_2.

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

Try to draw a graph of $[NO_2]$ vs Time, starting at the original equilibrium and ending after we've reached the new equilibrium?

$$CO_{2(g)} + NO_{(g)} \rightleftarrows CO_{(g)} + NO_{2(g)}$$



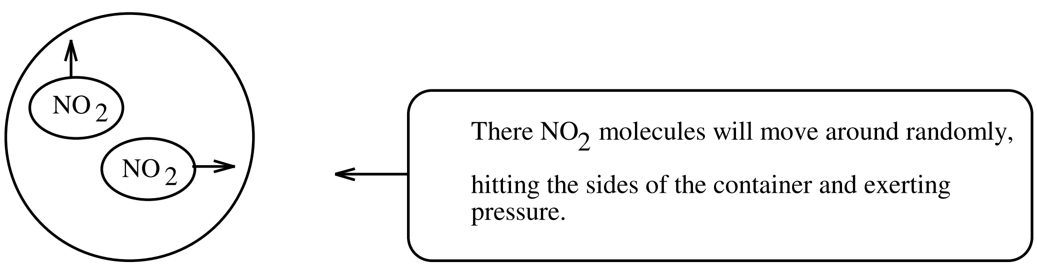
Effects of Changing the Volume of the Container or Total Pressure

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: $2NO_{2(g)} \rightleftarrows N_2O_{4(g)}$
brown colourless

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



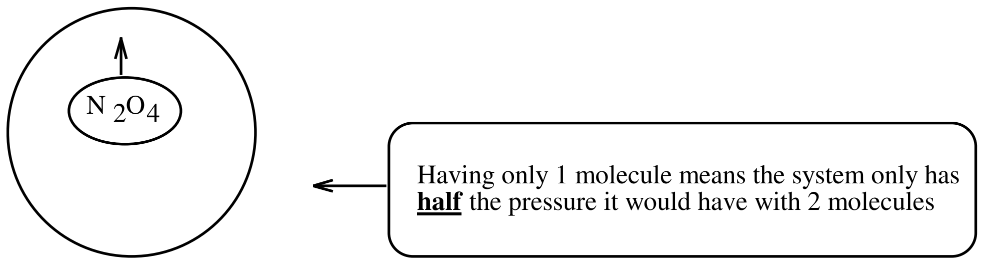
Now, suppose we were to completely convert those two molecules of NO_2 into N_2O_4:

$$2NO_{2(g)} \rightleftarrows N_2O_{4(g)}$$

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 is was with the 2 molecules of NO_2:



So, to summarize:

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

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Now, let's get back to the original equilibrium mixture, where we have some NO_2 and some N_2O_4:

$$\underset{\text{brown}}{2NO_{2(g)}} \rightleftarrows \underset{\text{colourless}}{N_2O_{4(g)}}$$

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 NO_2) 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 $2NO_{2(g)} \rightleftarrows N_2O_{4(g)}$ system, it can ***offset*** that increase by:

converting more NO_2 into N_2O_4 ! (going from 2 mog to 1 mog)

$$2NO_{2(g)} \rightleftarrows N_2O_{4(g)}$$

brown *colourless*

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.

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Now, try the following problem:

Given the equilibrium: $2C_2H_{6(g)} + 7O_{2(g)} \rightleftarrows 4CO_{2(g)} + 6H_2O_{(g)}$

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.

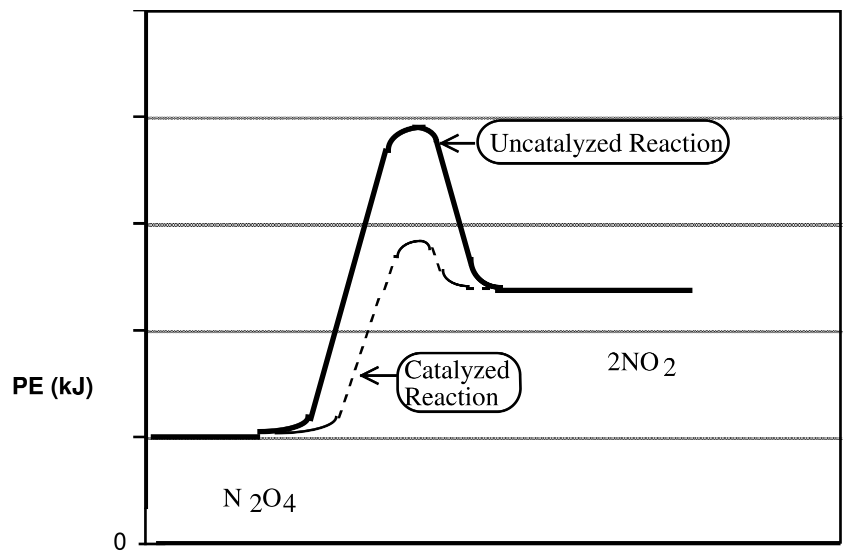
c) *Increasing the total volume* on this system (the same as _________________________ the total pressure) will cause a shift to the side with ____________________________ moles of gas, which in this case is the __________________ side.

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.

Effect of Catalysts

Consider the equilibrium system: $N_2O_{4(g)}$ + ***heat*** $\rightleftarrows$ $2\ NO_{2(g)}$
colourless brown

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.**

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

Here are some questions:

1. When a chemical system is at equilibrium, when the temperature is increased, the

   ___________othermic reaction speeds up the most.

2. In the reaction: $\mathbf{A + B \rightleftarrows C + 43.3\ kJ}$

   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.

$A + B \rightleftarrows C + 43.3\ kJ$

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: **$A + B \rightleftarrows C + 43.3\ kJ$**

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: **$A + B + 324\ kJ \rightleftarrows C$**

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.

A + B + 324 kJ ⇄ C

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: $\mathbf{B_{(g)} + C_{(g)} \rightleftarrows D_{(g)} + E_{(g)} +}$ **heat**

a) Some B is added to the mixture at equilibrium. The rate of the ____________________ reaction will increase due to the increase in the [B].

b) While this is happening, the [D] and [E] will gradually ___________crease.

c) The ______crease in the [D] and [E] will cause the rate of the ____________________ reaction to increase.

d) When the rates of the forward and reverse reactions are equal, we have a new ____

e) 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: $\mathbf{B_{(g)} + C_{(g)} \rightleftarrows D_{(g)} + E_{(g)} +}$ **heat**

a) Some D is added to the mixture at equilibrium. The rate of the ____________________ reaction will increase due to the increase in the [D].

b) While this is happening, the [B] and [C] will gradually ________crease.

c) The ______crease in the [B] and [C] will cause the rate of the ___________________ reaction to increase.

d) When the rates of the forward and reverse reactions are equal, we have a new ____

$$\mathbf{B_{(g)} + C_{(g)} \rightleftarrows D_{(g)} + E_{(g)} + heat}$$

e) 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: $\mathbf{2A_{(g)} + B_{(g)} \rightleftarrows 2C_{(g)}}$

a) If the total pressure on the system is increased, the ______________________________ reaction will speed up the most.

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 increase in total pressure has caused the equilibrium to shift to the ____________.

8. Given the equilibrium**:** $\mathbf{2A_{(g)} + B_{(g)} \rightleftarrows 2C_{(g)}}$

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 : $\mathbf{NO_{(g)} + CO_{2(g)} \rightleftarrows NO_{2(g)} + CO_{(g)}}$

a) Will an increase in total pressure have an affect on the equilibrium?________________

b) Explain your answer to question (a) ____

10. Given the equilibrium: $\mathbf{2A_{(g)} + B_{(g)} \rightleftarrows 2C_{(g)}}$

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: $\mathbf{2A_{(g)} + B_{(g)} \rightleftarrows 2C_{(g)}}$ **+ 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** ____

____