

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)



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:



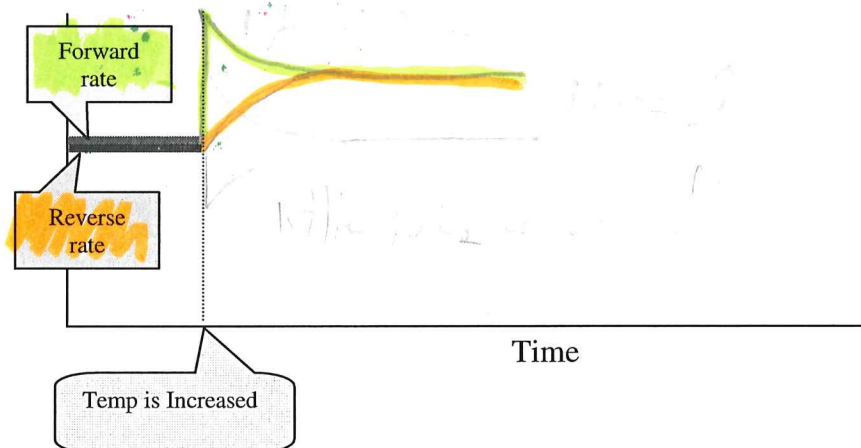
Since there are now *more* molecules of NO_2 to run into each other,

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!)

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



But remember this:

The forward rate was faster than the reverse rate for awhile. (increasing $[\text{NO}_2]$ and decreasing $[\text{N}_2\text{O}_4]$)

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

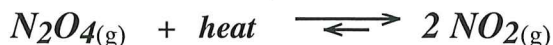
If NO_2 was being *formed faster* than *being used up* for awhile but never *used up faster* than it was *being formed*, its concentration will be *higher* when the new equilibrium is established. and the $[\text{N}_2\text{O}_4]$ will be *lower* in the new equilibrium.

So, to summarize:

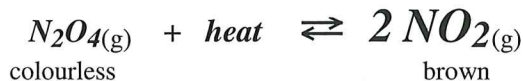
1. Original equilibrium:



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

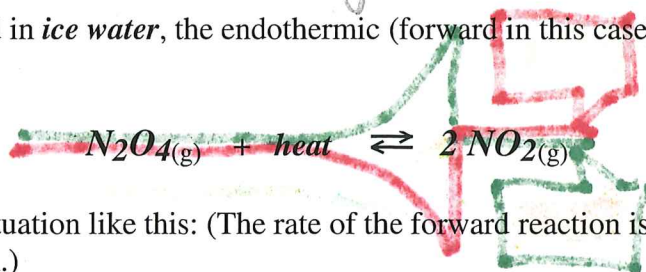
(the stuff on the right has increased and the stuff on the left has decreased)

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

into boiling water and heated? _____

It gets darker

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.)

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



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.

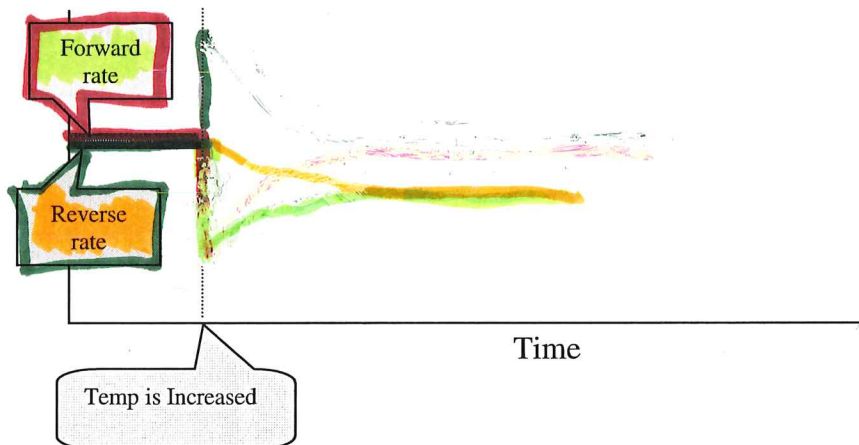
While the reverse reaction is faster than the forward, the $[\text{N}_2\text{O}_4]$ will build up and the $[\text{NO}_2]$ will decrease...



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!**

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





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)



↑
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

Partial Pressure of CO₂ = 60 kPa

Total Pressure = 50 + 60 = 110 kPa

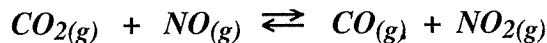
Since a **higher partial pressure** results from putting **more** of a certain gas in the same volume, it is really just another way of saying **concentration**.

^{They} ~~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.

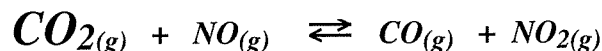
Consider the following system at equilibrium:



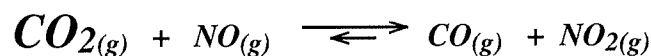
Of course, at equilibrium:

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

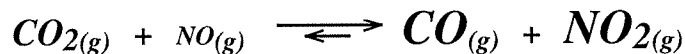
Let's, all of a sudden, **add** some CO_2 to the container that contains all of these. (What we are doing is **increasing the $[\text{CO}_2]$ or the partial pressure of CO_2 .**)



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.

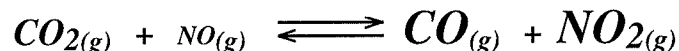


This will cause the $[\text{CO}]$ and the $[\text{NO}_2]$ to *increase* and the $[\text{CO}_2]$ and $[\text{NO}]$ to *decrease*



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!**)



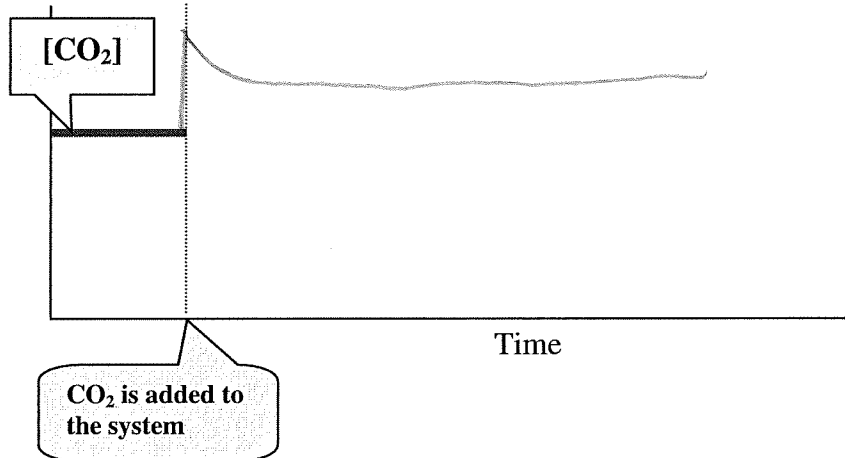
In this new equilibrium, $[\text{CO}]$ and $[\text{NO}_2]$ will be higher than they were originally and $[\text{CO}_2]$ and $[\text{NO}]$ will be lower than they were after we added the CO_2 .

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.

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 equilibrium: $CO_{2(g)} + NO_{(g)} \rightleftharpoons CO_{(g)} + NO_{2(g)}$

Some NO_2 is added to the system.

The reverse reaction will speed up.

This will cause the $[CO_2]$ and the $[NO]$ to increase.

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

Because the rate of the reverse reaction was higher for

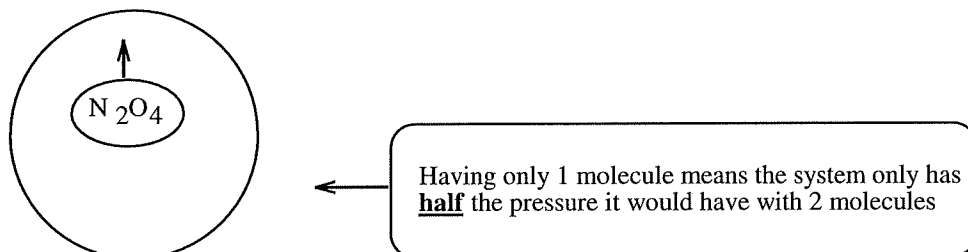
awhile, in the *new* equilibrium mixture, the $[CO_2]$ and the $[NO]$ will be higher

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

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

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

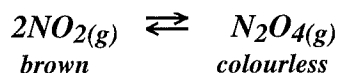
The pressure will be only half of what it was with the 2 molecules of NO₂:



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.

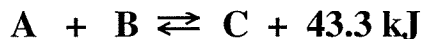
(For example, when you squish a balloon in one place, the air will be forced to another place and the balloon will bulge somewhere else, or the balloon will pop to decrease the pressure!)

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 end 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 in crease and the [C] will de crease.
 - c) Because [A] and [B] are in creasing, the rate of the forward reaction will increase.



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

equal.

At this point a new equilibrium is established.

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

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

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

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 de crease and the [C] will in crease.

- c) Because [C] is in creasing, the rate of the reverse reaction will increase.

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

At this point a new equilibrium is established.

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

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

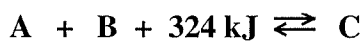
- f) In this example, we say that the equilibrium has shifted to the right

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

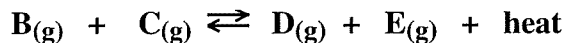
- a) When the temperature is increased the (forward/reverse) reaction speeds up more.

- b) During this time, the [A] and [B] will de crease and the [C] will in crease.

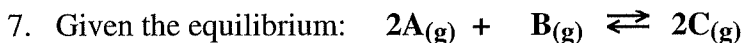
- c) Because [C] is in creasing, the rate of the reverse reaction will increase.



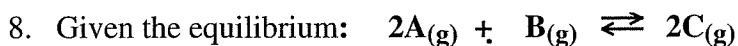
- d) Sooner or later, the forward rate and the reverse rate will again become equal.
At this point a new equilibrium is established.
- e) In the new equilibrium, [A] and [B] will be lower than they were before the temperature is increased.
In the new equilibrium, [C] will be higher than it was before.
- f) In this example, we say that the equilibrium has shifted to the right.
5. Given the equilibrium: $B_{(g)} + C_{(g)} \rightleftharpoons D_{(g)} + E_{(g)} + \text{heat}$
- a) Some B is added to the mixture at equilibrium. The rate of the forward reaction will increase due to the increase in the [B].
- b) While this is happening, the [D] and [E] will gradually increase.
- c) The increase in the [D] and [E] will cause the rate of the reverse reaction to increase.
- d) When the rates of the forward and reverse reactions are equal, we have a new equilibrium.
- e) Due to the addition of B, the equilibrium will shift to the right.
[B] and [C] will decrease and [D] and [E] will increase.
6. Given the equilibrium: $B_{(g)} + C_{(g)} \rightleftharpoons D_{(g)} + E_{(g)} + \text{heat}$
- a) Some D is added to the mixture at equilibrium. The rate of the reverse reaction will increase due to the increase in the [D].
- b) While this is happening, the [B] and [C] will gradually increase.
- c) The increase in the [B] and [C] will cause the rate of the forward reaction to increase.
- d) When the rates of the forward and reverse reactions are equal, we have a new equilibrium.



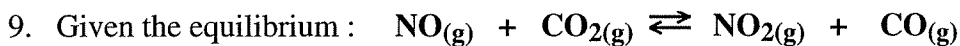
- e) Due to the addition of D, the equilibrium will shift to the left
 [B] and [C] will increase and [D] and [E] will decrease.



- a) If the total pressure on the system is increased, the forward reaction will speed up the most.
- b) While this is happening, the [C] will increase.
- c) This increase in [C] will cause the reverse reaction to speed up.
- d) When the new equilibrium is reached, the [A] and [B] will be lower than before and the [C] will be higher than before.
- e) We say that the increase in total pressure has caused the equilibrium to shift to the right.



- a) If the total pressure on the system is decreased, the reverse reaction will be the faster one.
- b) While this is happening, the [A] and the [B] will increase.
- c) This increase in [A] and the [B] will cause the forward reaction to speed up.
- d) When the new equilibrium is reached, the [A] and [B] will be higher than before and the [C] will be lower than before.
- e) We say that the decrease in total pressure has caused the equilibrium to shift to the left.



- a) Will an increase in total pressure have an effect on the equilibrium? No.
- b) Explain your answer to question (a) The moles of gas on either side are equal.

10. Given the equilibrium: $2A(g) + B(g) \rightleftharpoons 2C(g)$

- a) If the total **volume** of the system is decreased, the pressure will increase, and the forward reaction will be the faster one.
- b) While this is happening, the [C] will increase.
- c) This increase in [C] will cause the reverse reaction to speed up.
- d) When the new equilibrium is reached, the [A] and [B] will be lower than before and the [C] will be higher than before.
- e) We say that the decrease in total **volume** has caused the equilibrium to shift to the right

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? _____

The equilibrium concentrations are not affected.

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

Both the forward and reverse reaction rates are positively and equally affected by the presence of a catalyst.

