Chemistry 12
Notes on Graphs Involving LeChatelier's Principle

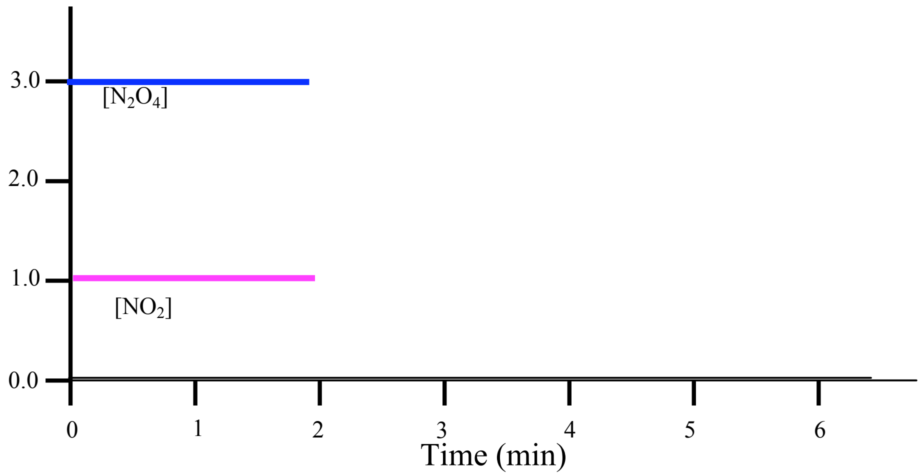
1. Temperature Changes

When a system adjusts due to a temperature change, there are no sudden changes in concentration of any species, so there are no vertical lines on the graph.

Look at the following example:

Given the equilibrium: $N_2O_{4\,(g)}$ + heat $\rightarrow$ 2 $NO_{2\,(g)}$

Let's say that the system is at equilibrium at a certain temperature. We'll just pretend that the $[N_2O_4]$ = 3.0M and the $[NO_2]$ = 1.0M at this temperature.



At Time = 2 minutes, **the temperature is increased**.

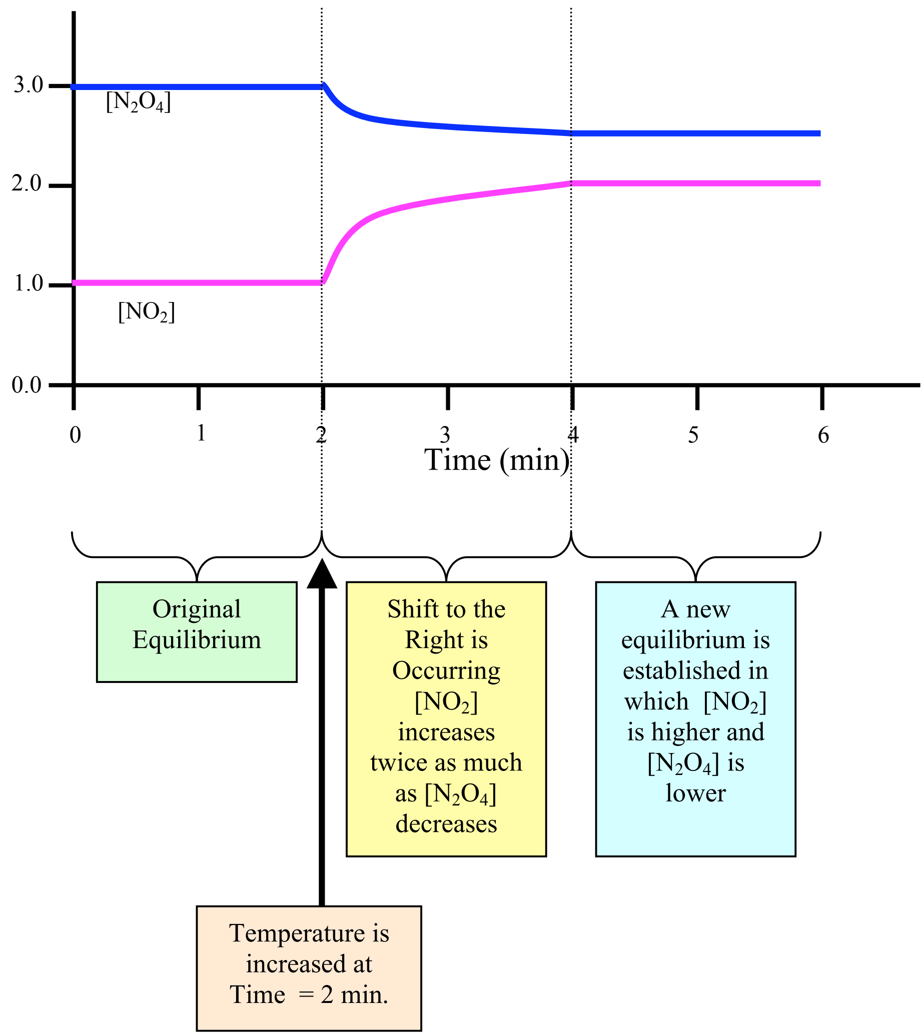
We know by LCP that the equilibrium: $N_2O_{4\,(g)}$ + heat $\rightarrow$ 2 $NO_{2\,(g)}$ will shift to the **RIGHT**, away from the heat term in order to counteract the imposed change.

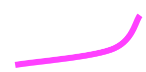
During this shift to the right, the $[N_2O_4]$ will **decrease** and the $[NO_2]$ will **increase**. This is not instant, but takes place gradually, until a NEW equilibrium is established.

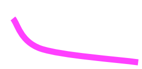
It is also VERY important to note that for every mole of N_2O_4 that is consumed in the shift that 2 moles of NO_2 will be formed (coefficients in balanced equation). So $[NO_2]$ will increase TWICE as much as the $[N_2O_4]$ decreases.

The graph on the next page shows what happens before, during and after this temperature increase and resulting shift. Study it carefully!

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

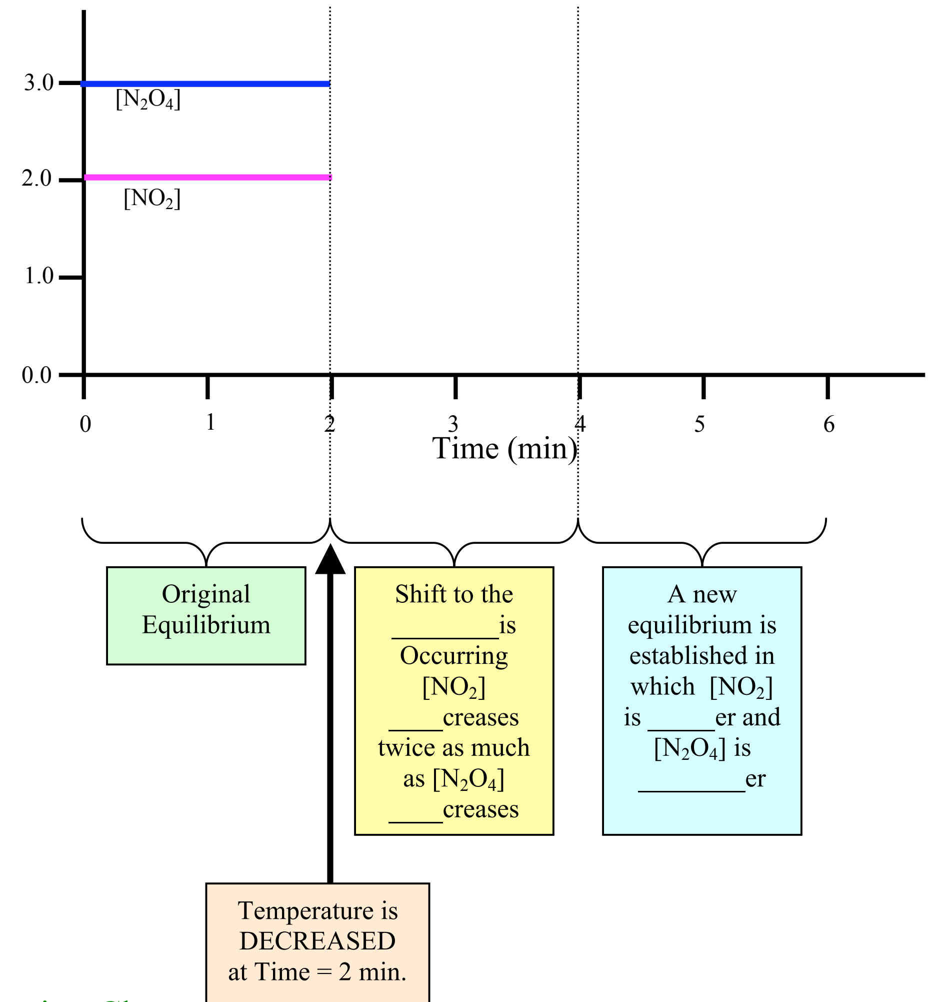


Notice that an increase in a concentration looks like  and **not** like 

Also, a decrease in concentration looks like  and **not** like 

Now it's your turn. On the next page, complete the graph showing the changes that would take place if originally $[N_2O_4] = 3.0M$ and the $[NO_2] = 2.0M$ and the temperature is suddenly DECREASED at Time = 2.0 min. Draw it so that the new equilibrium is achieved at Time = 4 min. Compare yours with the one your teacher does.

$N_2O_4\,(g) + \text{heat} \rightarrow 2\,NO_2\,(g)$

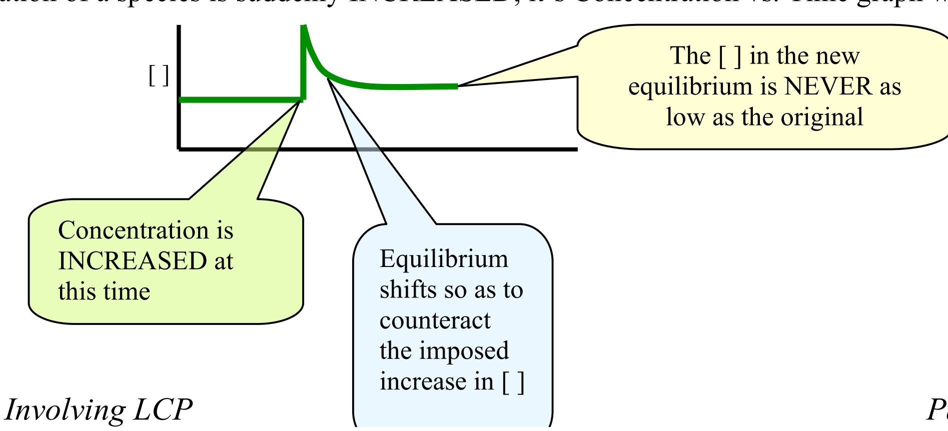


2. Concentration Changes

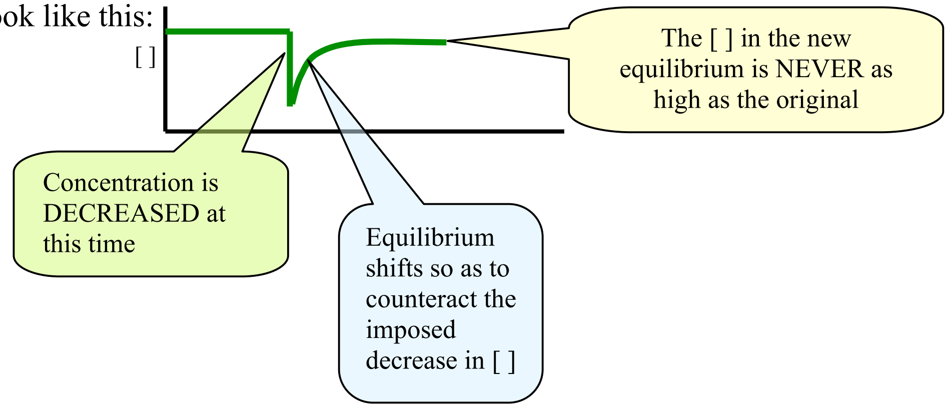
When a concentration is changed (or a substance is added or taken away), there will be a vertical line on the graph because there is a sudden change in concentration.

However, as soon as the change is imposed, the equilibrium will shift so as to counteract the change and eventually establish a new equilibrium.

It is important to note that in a shift, the concentration of any species only PARTIALLY compensates for the imposed change. THE CONCENTRATION NEVER RETURNS TO WHAT IS ORIGINALLY WAS.
If the concentration of a species is suddenly INCREASED, it's Concentration vs. Time graph will look like this:



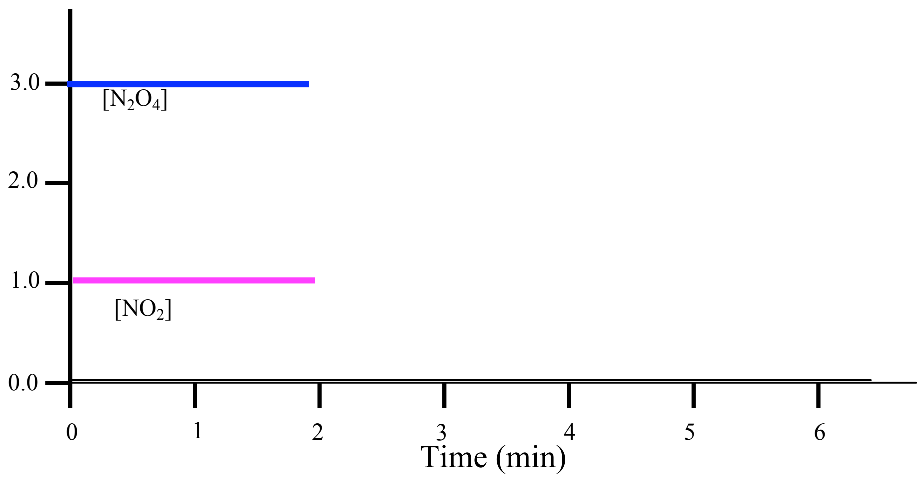
If the concentration of a species is suddenly DECREASED, it's Concentration vs. Time graph will look like this:



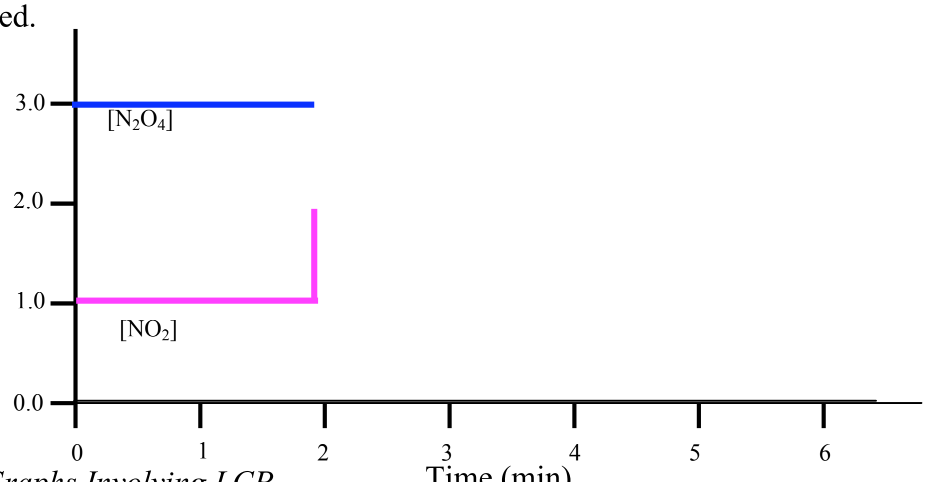
Again, the **extent** of increase or decrease in concentration of a substance during a shift is proportional to the **coefficient of that substance** in the balanced equation. Also, the ONLY substance with the "vertical line" is the one that the experimenter actually increased or decreased. Consider the situation …

Given the equilibrium: $N_2O_{4\,(g)} + \text{heat} \rightarrow 2\,NO_{2\,(g)}$

Let's say that the system is at equilibrium in a closed container. We'll just pretend that the $[N_2O_4]$ = 3.0M and the $[NO_2]$ = 1.0M . The temperature will be kept constant.

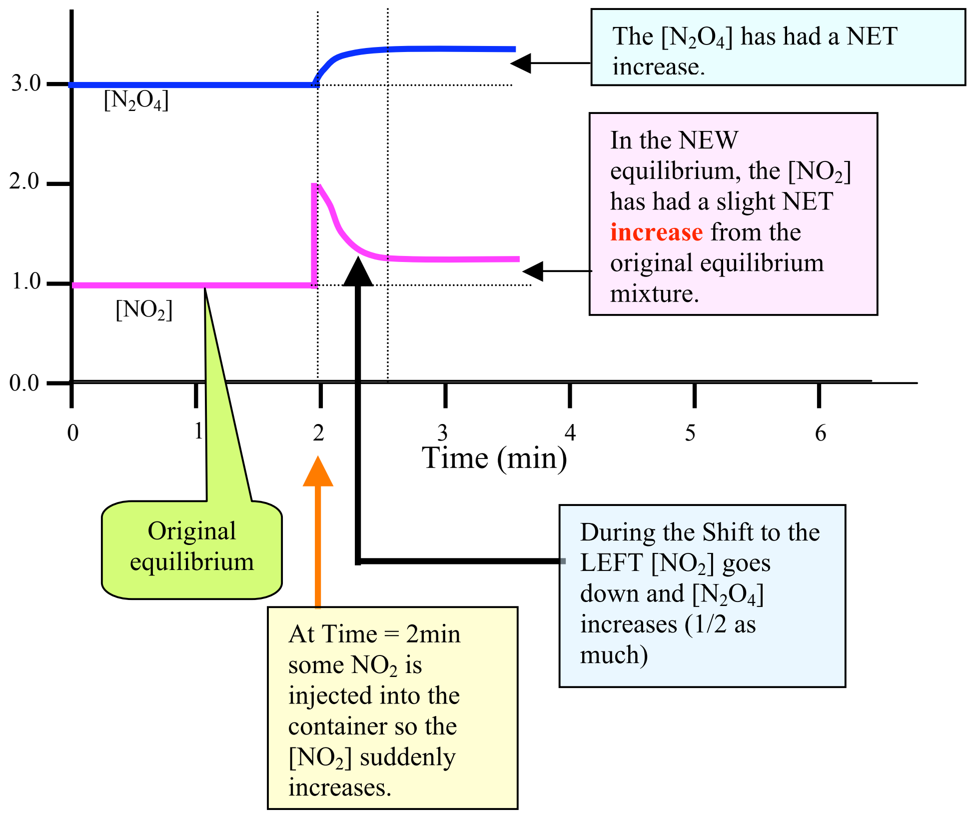


At Time = 2 minutes, more NO_2 is injected into the container. Thus the $[NO_2]$ is suddenly increased.



Now, of course the equilibrium $N_2O_4\ _{(g)}$ + heat → $2\ NO_2\ _{(g)}$ will shift to the **LEFT** in order to counteract the sudden increase in the $[NO_2]$. Thus $[NO_2]$ will **decrease** and the $[N_2O_4]$ will **increase** (but only **half as much** as the $[NO_2]$ decreases due to the 1:2 coefficient ratio!)

$N_2O_4\ _{(g)}$ + heat → $2\ NO_2\ _{(g)}$



3. Changes in Total Pressure (caused by changing the volume of a closed container). Applies to Gaseous Systems.

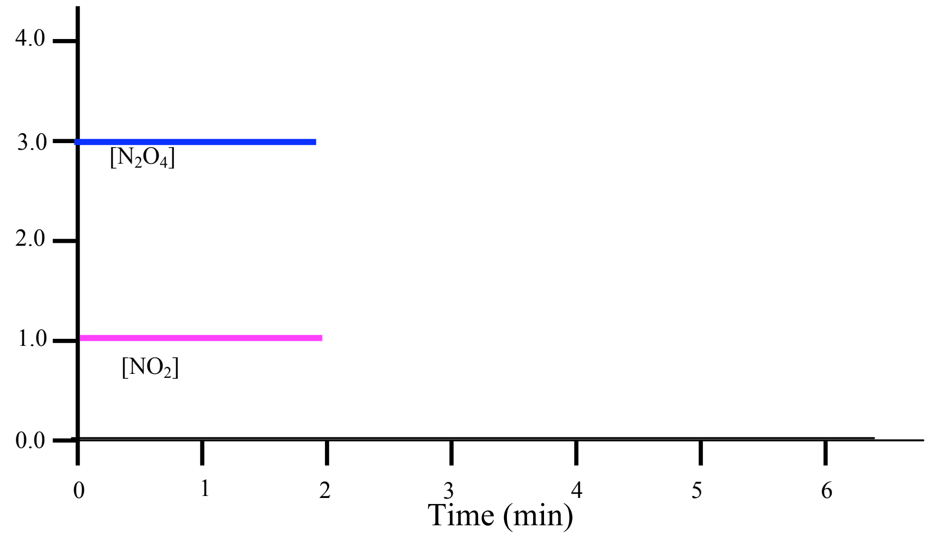
Recall, when the volume of a closed container is DECREASED, the TOTAL PRESSURE increases. When this happens THE CONCENTRATION OF EVERY GAS IN THE CONTAINER **INITIALLY** INCREASES. (# of moles per unit volume).

However, at this point LCP kicks in and the equilibrium will shift whichever way it needs to partially counteract the imposed stress.

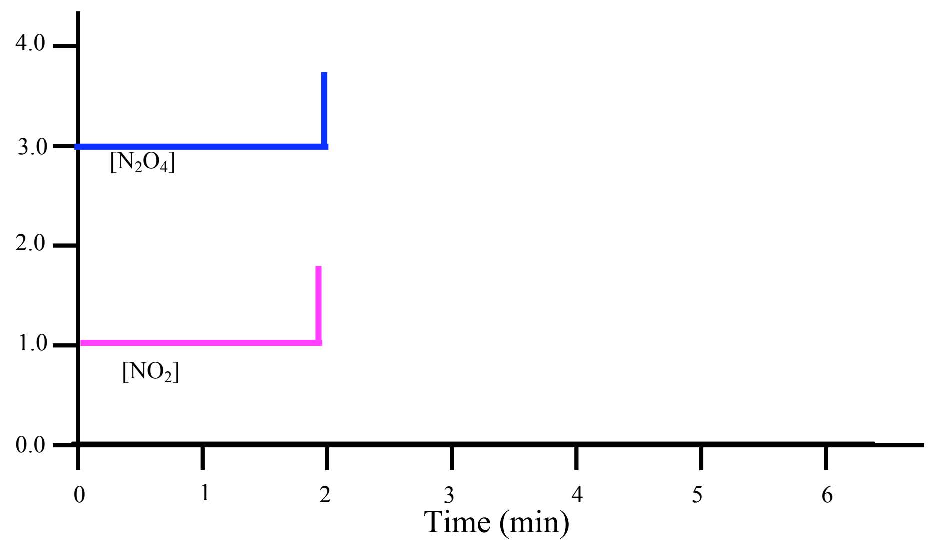
With PRESSURE (or VOLUME) changes **ALL substances** will have vertical lines on the graph at the time the imposed change takes place.

See the example on the next page…

Given the equilibrium: $N_2O_{4\,(g)}$ + heat → $2\ NO_{2\,(g)}$
Let's say that the system is at equilibrium in a **closed container**. We'll just pretend that the $[N_2O_4]$ = 3.0M and the $[NO_2]$ = 1.0M . The temperature will be kept constant.

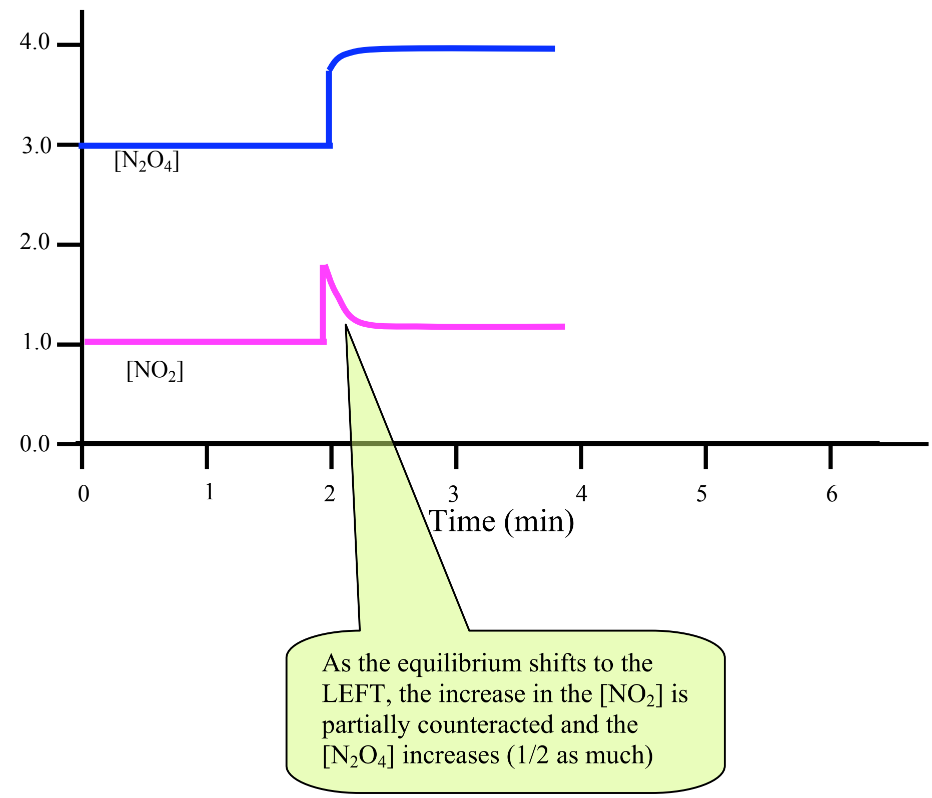


At Time = 2 minutes, the **volume** of the container is suddenly DECREASED. Thus the **concentrations of BOTH gases initially increase**.



Now, in order to counteract the imposed pressure increase, the equilibrium will shift to the side with LESS moles of gas: $N_2O_{4\,(g)}$ + heat → $2\ NO_{2\,(g)}$
In this case, this would be a shift to the LEFT where $[NO_2]$ will decrease and the $[N_2O_4]$ will increase. See the graph on the next page…

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



Now, lets say you were given the equilibrium: $NO_{2(g)} + CO_{(g)} \rightarrow CO_{2(g)} + NO_{(g)}$ in a closed system.

Initially $[NO_2] = 2.0M$, $[CO] = 3.0M$, $[CO_2] = 4.0M$ and $[NO] = 5.0M$

At Time = 2 minutes, the volume of the container is suddenly decreased.
Draw and label a graph showing all that would happen in this case. Compare your answer with that of the teacher.

4. Catalysts

When you add a catalyst to a system at equilibrium, both the forward and the reverse reactions speed up, so there is no change in the concentrations of any of the species in the mixture. Adding a catalyst would have no effect on a graph of Concentration vs. Time!