

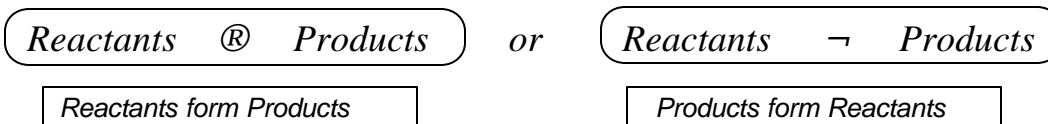
Chemistry 12
Tutorial 1 - Characteristics of Dynamic Equilibrium

Hi there! Tutorial 1 will help you to:

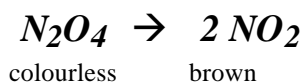
1. Realize that reactions can go both in *forward* and in *reverse*.
2. Define *equilibrium*.
3. Understand the concept of *dynamic equilibrium*.
4. State the *characteristics* of a system at equilibrium

You might remember from the last unit, when we were dealing with *Potential Energy Diagrams*, that the term *Reverse Reaction* came up many times.

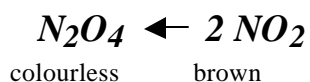
It's important to know that many chemical reactions are *reversible*. That is:



For example, under certain conditions, one mole of the colourless gas N_2O_4 will *decompose* to form two moles of brown NO_2 gas:

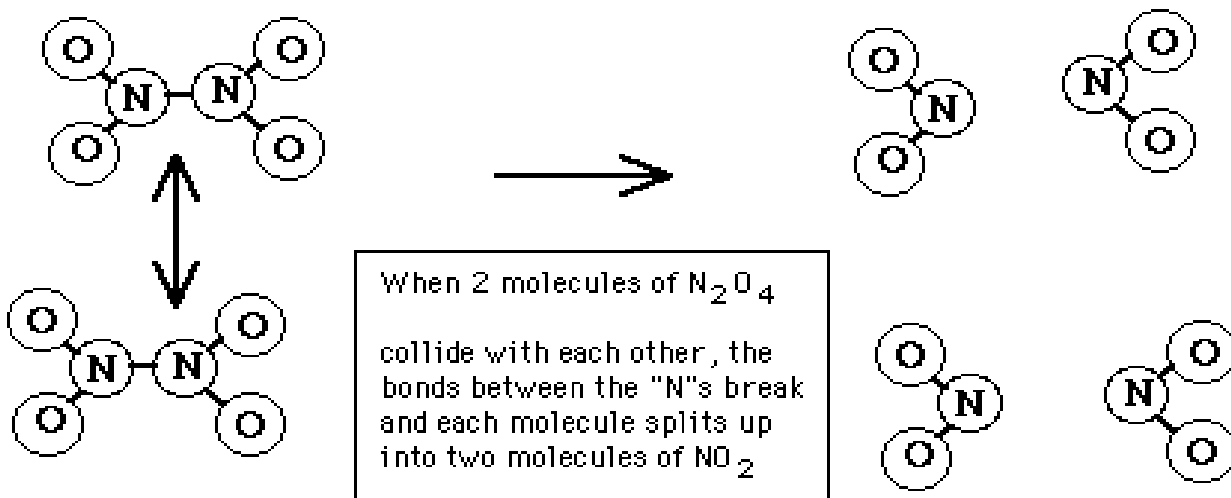


Under other conditions, you can take 2 moles of brown NO_2 gas and change it into one mole of N_2O_4 gas:



In other words, this reaction, as written may go *forward* or in *reverse*, depending on the conditions.

NOW, here's something to think about! If we were to put some N_2O_4 in a flask, the N_2O_4 molecules would collide with each other and some of them would break apart to form NO_2 .



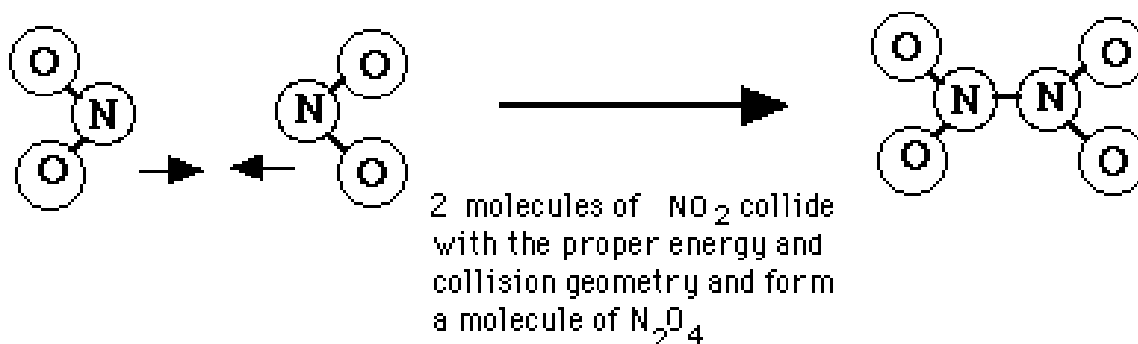
This process, of course is indicated by the *forward reaction*:



Once this has happened for awhile, there is a build up of NO_2 molecules in the same flask. (After all, this is what the reaction is making.)

Now these NO_2 molecules don't just sit there! They are of course moving around and *colliding* with things. Once in awhile, two NO_2 molecules will collide with *each other* and **guess what?**

They **join** to form a molecule of N_2O_4 !



This process, as you might have guessed is indicated by the *reverse reaction*:



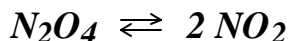
Two things you'll have to realize is that *as long as there is N_2O_4 present, the forward reaction will keep on happening* and *as long as there is NO_2 present, the reverse reaction will keep on happening!*

Also, you must keep in mind that all these molecules are mixed *in the same container!*

At one particular time a molecule of N_2O_4 might be breaking up, and *at the same time* two molecules of NO_2 might be joining to form another molecule of N_2O_4 ! So here's an important thing to understand:

In any reversible reaction, the forward reaction and the reverse reaction are going on at the same time!

This is sometimes shown with a **double arrow**:

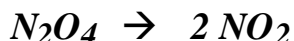


The double arrow means that both the forward and reverse reaction are happening at the same time.

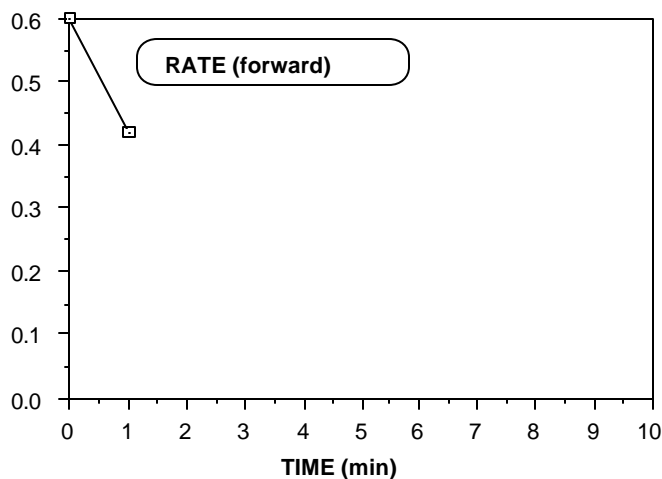
Just a little comment here. The word "*happening*" has a similar meaning to the word "*dynamic*". Just remember that!

Now what we're going to do is look at how the *rate* of the forward reaction changes if we put some pure N_2O_4 in a flask:

If we put some pure N_2O_4 in a flask (No NO_2 yet!), there will be a high *concentration* of N_2O_4 . That is, there will be *lots* of N_2O_4 molecules to collide with each other. So at the beginning of our little experiment, (which we will call "time " 0 ") the *rate* of the *forward* reaction is quite *fast*.



So if we were to make a *graph* of the *rate of the forward reaction* vs. *time*, the graph might start out something like this:



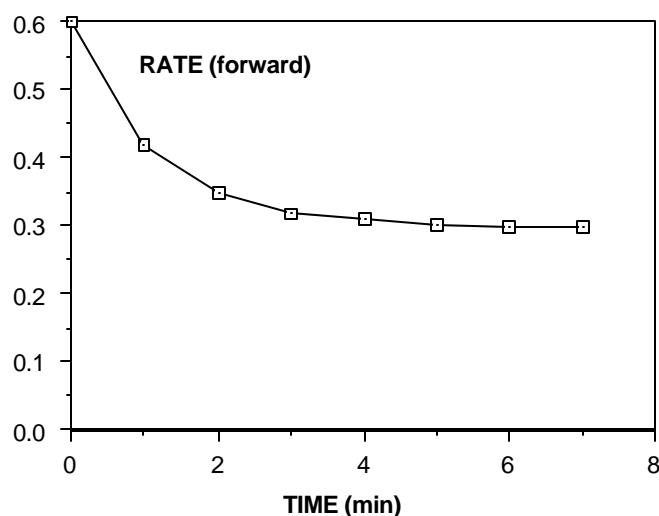
OK, now you might ask: "Why does the rate of the forward reaction go *down* ?

Well, if you recall Unit 1, as the forward reaction proceeds:



the N_2O_4 is used up and so its *concentration goes down*. Also, you must remember that *if the concentration of a reactant goes down, there is less chances of collisions and the rate of the reaction decreases*.

As the reaction continues, the *slower rate* will use up N_2O_4 more slowly, so the $[N_2O_4]$ will not decrease so quickly and therefore the rate will not decrease quite as quickly. (Read the last sentence over a couple of times and make sure it makes sense to you!) For those "graph wise" people, you will probably guess that this means that the *slope of the line* on the graph gets more gradual. The rest of the graph might look something like this:



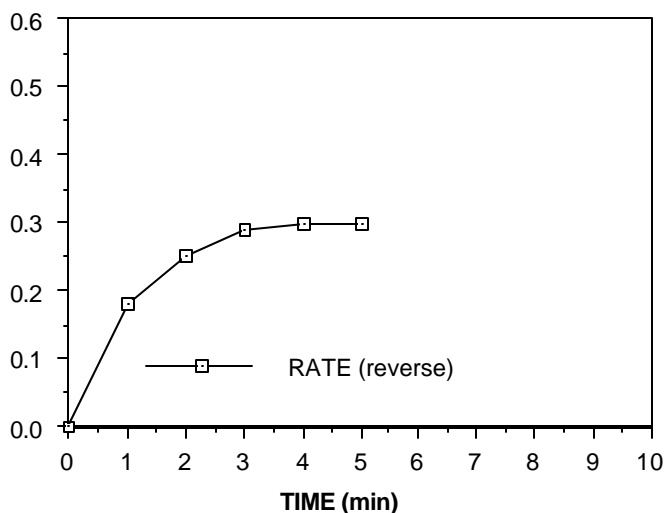
NOW, it's time we consider the rate of the *reverse reaction*.

As you might recall, when we have a container full of pure N_2O_4 , initially there is *no* NO_2 in the container. Since there is *no* NO_2 , there are no NO_2 molecules to collide with each other, and the *rate of the reverse reaction is zero*.

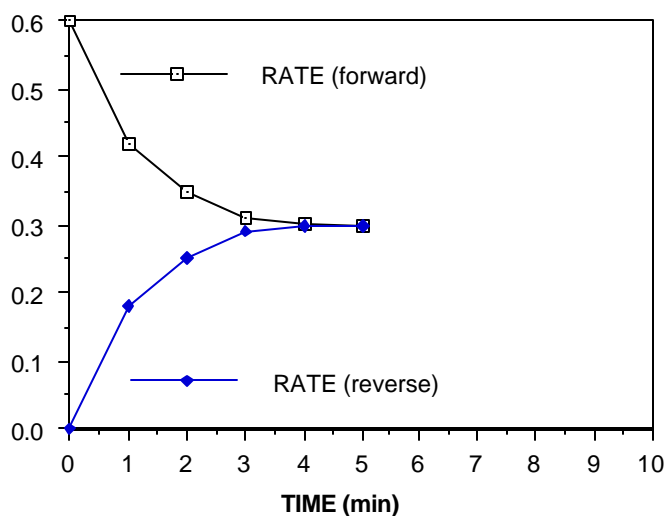
But of course, as time goes on, NO_2 is formed from the *forward reaction* ($N_2O_4 \rightarrow 2 NO_2$) so in a short time, some NO_2 molecules can start colliding and the *reverse reaction* will begin:



As MORE NO_2 is formed by the forward reaction, *the rate of the reverse reaction gradually increases*. Now, for you "graph buffs", the graph of the *Rate of the reverse reaction vs. Time* might look like this:



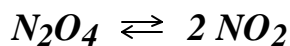
OK. Now, lets look at the graph for the forward rate *and* the reverse rate together:



NOW, focus your attention on the graph at "Time = 4 minutes". You will notice that at this point:

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

At this point, NO_2 is being used up *at the same rate* that it is being formed:

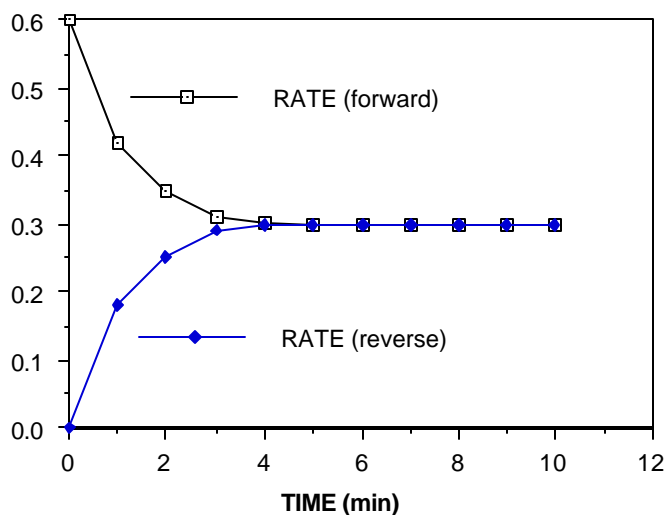


Because this is so, you should be able to convince yourself that *the $[NO_2]$ is no longer changing!*

Because the reverse rate is equal to the forward rate, N_2O_4 is being formed *at the same rate* it is being used up. So, also *the $[N_2O_4]$ is no longer changing either!*

Can you predict what will happen to the graph after 4.0 minutes?

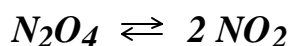
YOU GUESSED IT! The rates of the forward reaction and the reverse reaction, no longer change because the *$[N_2O_4]$ is constant* and the *$[NO_2]$ is also constant*. The graph will look like this:



The situation happening from 4.0 minutes on in this graph has a special name and a special significance. At this point, the system (meaning the container, the N_2O_4 and the NO_2) is said to be ***at equilibrium***. To describe it even more precisely, we can say that *we have reached a state of dynamic equilibrium*..

Here are some things that you must *understand* about ***dynamic equilibrium***:

1. The reaction ***has not stopped!***
2. The forward and the reverse reaction ***continue*** to take place, but their rates are *equal* so there are no changes in concentrations of reactants or products. (The forward and reverse reactions are said to be "balanced") eg. for the reaction:



for each N_2O_4 molecule that breaks up to form two NO_2 molecules, two *other* NO_2 molecules combine to form another N_2O_4 molecule. All this is happening on the ***microscopic level***, so we don't see individual molecules reacting.

3. As far as we can see from the "outside", there *appears to be* nothing happening. All *observable* properties are constant. These include the concentrations of all reactants and products, the total pressure, colour, temperature etc.
4. If no changes were made in conditions and nothing is added or taken away, a system at equilibrium would remain that way forever, the forward and reverse reactions "ticking away", but balanced so that no observable changes happen.

Here are a couple of other things to consider before we summarize everything:

1. Changing the temperature can alter the rates of the reactions at equilibrium. This could "throw off" the balance. So, **for a system at equilibrium, the temperature must remain constant and uniform throughout the system.**
2. Letting material into or out of the system will affect rates so **a system at equilibrium is a closed system.**

3. Again, consider the equilibrium reaction:
$$N_2O_4 \rightleftharpoons 2 NO_2$$

In the example that we did to construct the graphs, we had started with *pure* N_2O_4 and no NO_2 . The forward reaction rate was high at the start, but the reverse reaction rate eventually "caught up", the rates became equal and *equilibrium* was established. Can you guess what would happen if we had started with *pure* NO_2 instead (no N_2O_4)?

To make a long story short, the *reverse* reaction rate would start out high, but the forward rate would eventually "catch up". When the rates became *equal*, again *equilibrium* would be established.

We can summarize all this by saying that **the equilibrium can be approached from the left (starting with reactants) or from the right (starting with products)**

Just a little term before we summarize: The word **macroscopic** means *large scale or visible or observable*. (The opposite is *microscopic*, which means too small to see eg. molecular level). Some **macroscopic** properties are total pressure, colour, concentrations, temperature, density etc.

Alright, let's summarize:

Characteristics of a System at Equilibrium

1. The *rate* of the *forward* reaction = The *rate* of the *reverse* reaction
2. **Microscopic** processes (the forward and reverse reaction) continue in a *balance* which yields **no macroscopic changes**. (so nothing *appears* to be happening.)
3. The system is **closed** and the **temperature** is **constant** and **uniform** throughout.
4. The equilibrium can be approached from the **left** (starting with *reactants*) or from the **right** (starting with *products*).

In our previous examples you will recall that when we started with N_2O_4 or with NO_2 , things happened and equilibrium was eventually established. In general:

If sufficient activation energy is available, systems not at equilibrium will tend to move toward a position of equilibrium.

Self Test on Tutorial 1 - Characteristics of Dynamic Equilibrium

This may be done right on this sheet.

1. Given the reaction: $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{NO}(\text{g}) + \text{CO}_2(\text{g})$

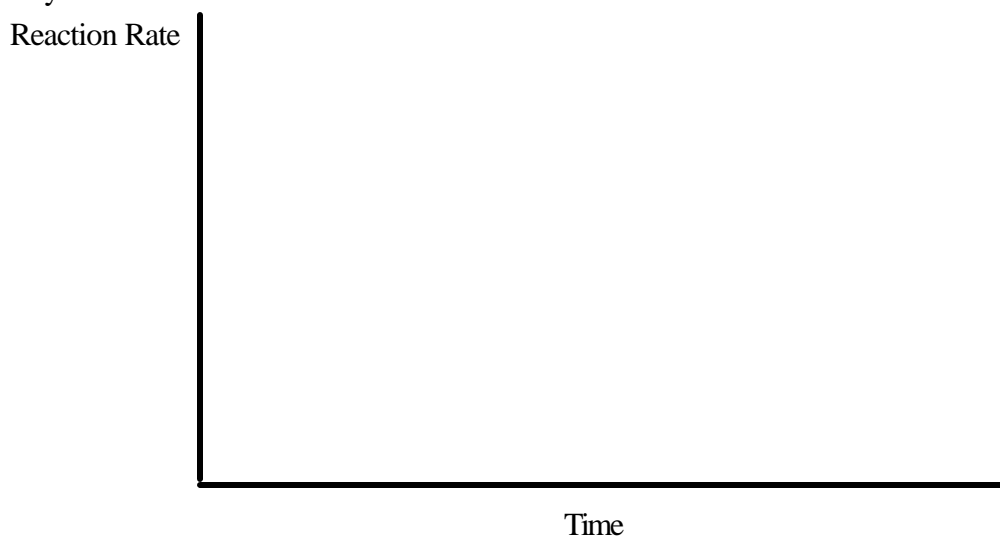
- a) If one mole of NO_2 and one mole of CO are mixed in a 1.0 litre container, the *rate* of the forward reaction will initially be (fast / slow) _____
- b) Immediately after mixing, the rate of the reverse reaction will be _____
- c) While the forward rate $>$ the reverse rate, the $[\text{NO}]$ and the $[\text{CO}_2]$ will be (increasing / decreasing) _____
- d) After the initial mixing, the rate of the *forward reaction* will be _____ing.
The rate of the *reverse reaction* will be _____ing.
- e) Once equilibrium is established, what can be said about the rates of the forward and reverse reaction? _____
- f) Once equilibrium is established, what is happening to the $[\text{NO}]$? _____
- g) Once equilibrium is established, what is happening to the $[\text{CO}_2]$? _____
- h) Once equilibrium is established, what is happening to the $[\text{NO}_2]$? _____
- i) Once equilibrium is established, what is happening to the $[\text{CO}]$? _____

- j) NO_2 is a dark brown colour. All of the other gases are colourless. Describe what will happen to the colour of the gas mixture from when the NO_2 and the CO are mixed until equilibrium is established.
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- k) One mole of NO and one mole of CO_2 are mixed. If left alone at a constant temperature _____ will be established. Once this equilibrium is reached, will be colour be different than the equilibrium in question "j" ?

2. Given the reaction: $\text{CO}_{(g)} + \text{Cl}_{2(g)} \rightleftharpoons \text{COCl}_{2(g)}$

One mole of CO and one mole of Cl_2 are mixed at a certain temperature. On the axes below, draw graphs which show how the rates of the *forward* reaction and the *reverse* reaction vary with time.



3. Give *four* characteristics of a system at *equilibrium*.

1. _____
2. _____
3. _____
4. _____

After you have completed this Self-Test, check answers on "**Tutorial 1 Solutions**" - page 1.
This is the end of Tutorial 1 - See your teacher if there is something you don't understand.