

## 1)FACTORS THAT CHANGE EQUILIBRIUM: CONCENTRATION

We know that changing the concentration will also change an equilibrium.

*Here's Why:*

The rate of any chemical reaction actually depends on a factor called the activity of the reacting chemicals. In reasonably dilute solutions the activity is equal to the concentration. In other words, the rate depends on the concentration of the reacting chemicals. The reaction rate depends on the concentration of the reacting chemicals because, with a higher concentration, there will be more collisions. It also depends on a reaction rate constant, and so can be represented by the equation:

$$\text{rate} = k[\text{substance}]$$

In an equilibrium we have two processes going on at the same time:

- $\text{rate}_f = k_f[R]$
- $\text{rate}_r = k_r[P]$

where  $\text{rate}_f$  is the rate in the forward, and  $\text{rate}_r$  the rate in the reverse directions. At equilibrium we know that  $\text{rate}_f = \text{rate}_r$  since the forward and reverse rates are equal at equilibrium.

What would happen to our reaction at equilibrium if we were to increase the concentration of the reactants, R? We would expect the forward rate to increase. So, for a while at least, the rate would go faster in the forward direction. This is no longer an equilibrium, since the rates aren't equal any longer. Of course as the reaction goes forward faster it will make more products, P. More P will increase the rate in the reverse direction. Eventually, we'll reach an equilibrium, but it won't be the same one we started with. Similarly, if we increase the concentration of P, then the reaction would initially go faster in the reverse direction. Again though, it would eventually reach a new equilibrium with equal rates.

**SO, IN GENERAL, WE EXPECT A CHANGE IN CONCENTRATION TO HAVE AN EFFECT ON EQUILIBRIUM.**

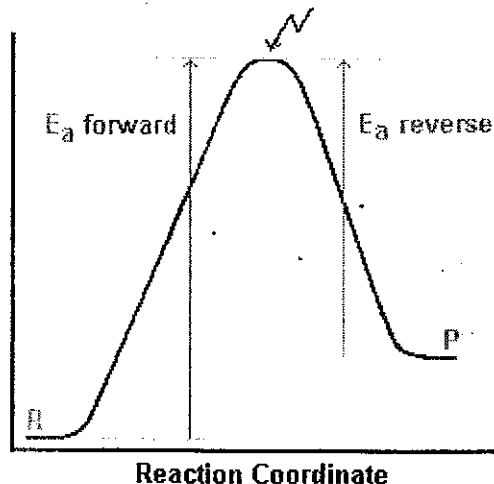
## 2)FACTORS THAT CHANGE EQUILIBRIUM: TEMPERATURE

We know that changing temperature will change an equilibrium.

*Here's Why:*

The rate of a chemical reaction depends on the temperature. In order for molecules to react they must collide, and the kinetic energy of the collision must be great enough to change the molecule's potential energy and allow the atoms to rearrange into new substances. The potential energy holding the atoms to each other in the original molecule is a potential energy barrier to change and is called the activation energy. The reaction rate depends on the temperature because, with a higher temperature, more molecules will be traveling faster. More will have enough kinetic energy to make it over the activation energy barrier as they collide. Notice however that as shown in the diagram below, the activation energy in the forward and reverse directions are not the same. Because of this, the reaction rate in the forward and reverse directions will not be affected equally by changing temperature.

Graph:



When the activation energy in the forward direction is larger (as shown here for an endothermic reaction), an increase in temperature will make the forward reaction increase more rapidly than the reverse. So, for a while, the rate will go faster in the forward direction. This is no longer an equilibrium, since the rates aren't equal any longer. Of course, as the reaction goes forward faster it makes more products, P. More P will increase the rate in the reverse direction. Eventually, we'll get back to an equilibrium, but it won't be the same one as we started with. Temperature change has caused a change to a new equilibrium.

Exactly the opposite would happen if the reaction was exothermic, so that the activation energy in the reverse direction would be greater. A change in temperature would result in the rate initially going faster in the reverse direction until enough products had decomposed that the rate would slow down to the point where the forward and reverse rates were once again equal. This would once again be a new equilibrium.

**SO, IN GENERAL, WE EXPECT A CHANGE IN TEMPERATURE TO HAVE AN EFFECT ON AN EQUILIBRIUM.**

### **3) FACTORS THAT CHANGE EQUILIBRIUM: GAS PRESSURE**

The effect of pressure on solids and liquids is so small that we will ignore it. However, there is a very real and important effect when we increase the pressure of reactions that contain gases. Here's why:

It is very important to clear up some confusion that students have about gas phase reactions. Although we write a chemical equation with two sides — the reactants and the products — in reality when the reaction is carried out, both reactants and products will invariably be in a single container. This means that it is inappropriate to speak of "increasing the pressure on the products (or reactants)".

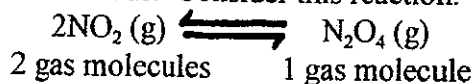
In fact, when we refer to changing the pressure in a reaction, it is usually referring to the pressure change caused by changing the volume of the reaction container. Changing the volume doesn't change the number of particles in a container directly, but it does mean that the number in each unit of volume will be different. Therefore, it changes the pressure.

When the volume increases, there are less molecules per unit volume. This means the number of collisions per unit of surface area decreases, so the pressure is lower.

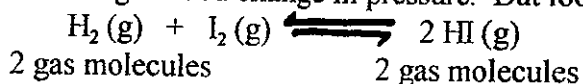
When the volume decreases, there are more molecules per unit volume. This means the number of collisions per unit of surface area increases, so the pressure is higher.

Effectively, increasing the pressure by decreasing the volume increases the concentration. Remember though that it increases the concentration of everything that is in the gas phase, both reactants and products.

We already know that changing the concentration has an effect on an equilibrium, and so we would expect it to do so here. However, we have changed both reactant and product molecule concentrations, so we need to be cautious. Consider this reaction:



There are two molecules of gaseous reactants, but only 1 molecule of gaseous products. Therefore, we expect the effect of an increase in concentration to have a greater effect on the forward reaction. An unbalanced effect on the reaction rate will effect the equilibrium. We would expect this reaction to change with a change in pressure. But look at this reaction:



Here there are two gaseous reactant molecules, but also two gaseous product molecules. The rate of the forward reaction should increase if the pressure increased, but there should be just as great an effect on the reverse reaction. If both rates are effected equally, then the equilibrium is not shifted. Remember that this is like running one step forward, and running one step back, as compared to walking one step forward, and walking one step back. Your actual rate is different in the two cases, but the net result is exactly the same — you remain at a standstill.

In reactions where the number of gaseous reactant molecules are the same as the gaseous product molecules, changing pressure should have no effect on the equilibrium. The above shows us what to expect if we changed the pressure by changing the volume. There are two other ways to change the pressure of gases:

- change the temperature (since temperature effects other reactions as well)
- add an inert gas (overall pressure is increased — more molecules per unit volume so the total number of collisions increases, so the total pressure increases, the concentration of the original molecules is no different than it was before). Since the inert gas does not change the concentration of reactant and product molecules, it will not effect the rate, so it should have no effect on the equilibrium.

**IN GENERAL, WE EXPECT PRESSURE TO HAVE AN EFFECT ON AN EQUILIBRIUM WHEN THERE ARE DIFFERENT NUMBERS OF MOLECULES OF GAS IN THE PRODUCTS AND REACTANTS. WHEN THE NUMBER OF GAS MOLECULES IN THE PRODUCTS AND REACTANTS ARE IDENTICAL, PRESSURE WILL NOT HAVE ANY EFFECT. AN INERT GAS WILL HAVE NO EFFECT ON THE EQUILIBRIUM.**

#### 4) FACTORS THAT CHANGE EQUILIBRIUM: CATALYSTS

A catalyst has no effect on the final equilibrium condition. If a catalyst exists, then it will cause the reaction to reach an equilibrium more quickly, but the final position reached is the same with, or without the catalyst.

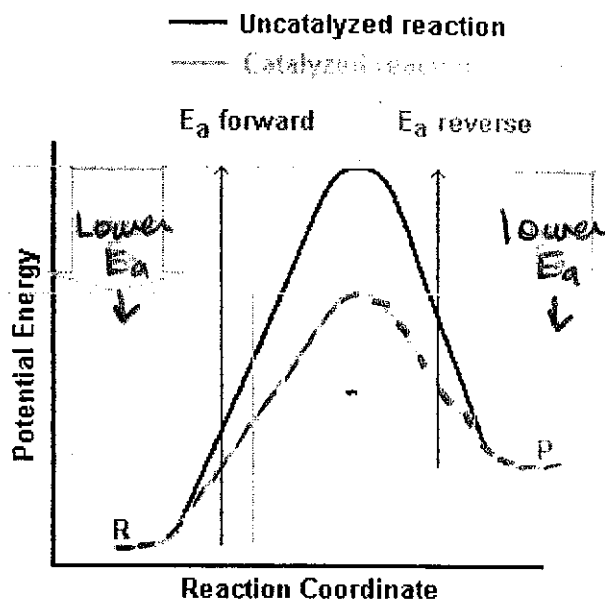
*Here's why:*

An equilibrium must react in both the forward and reverse directions. There is an activation energy barrier for each of these two reactions — a forward and activation energy and a reverse

activation energy. The higher this activation energy barrier, the slower the reaction rate.

A catalyst creates a new reaction pathway, with different reaction steps, with a lower activation energy. Notice though that as shown in the diagram below, the effect on the activation energy in the forward and reverse direction is exactly the same. Because of this, the reaction rates in the forward and reverse directions will be affected equally.

Graph:



The reaction will go faster in the forward direction because of the catalyst. It will go just as fast in the reverse direction. Since both the forward and reverse reaction rates are affected equally, there is no net change to the equilibrium once it has been achieved. What about before you reach equilibrium? Then the rates are not equal, so the catalyst will increase the reaction rate, and an equilibrium will be reached sooner. However, the final equilibrium achieved is exactly the same with or without the catalyst.

**SO, IN GENERAL, WE EXPECT A CATALYST TO HAVE NO EFFECT ON AN EQUILIBRIUM, ONCE EQUILIBRIUM IS ESTABLISHED.**

### 5) FACTORS THAT CHANGE EQUILIBRIUM: SURFACE AREA

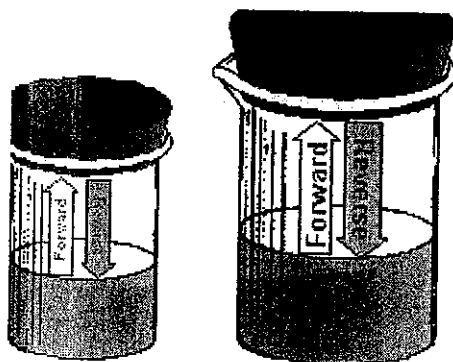
If the surface area is larger, then a reaction will reach an equilibrium more quickly, but the final position reached is the same as with a smaller surface area.

*Here's Why:*

Increasing the surface area in a heterogeneous reaction will normally increase the reaction rate. It does so because with more surface area exposed between the two reacting states, there will be more collisions and therefore a greater chance for a reaction. For example, if we crush a solid before trying to dissolve it in water, it will have more surfaces exposed. Since it can only dissolve from the outside edge, the larger number of surfaces will dissolve more quickly. At the same time, with more surfaces exposed there will also be more sites available for the molecules in the dissolved state to re-crystallize. Similarly, a large beaker of water has more surface area than a small beaker. The water can evaporate faster from a larger surface. However, the water can also condense faster from the vapor state since there is more surface area available for the reverse reaction as well.

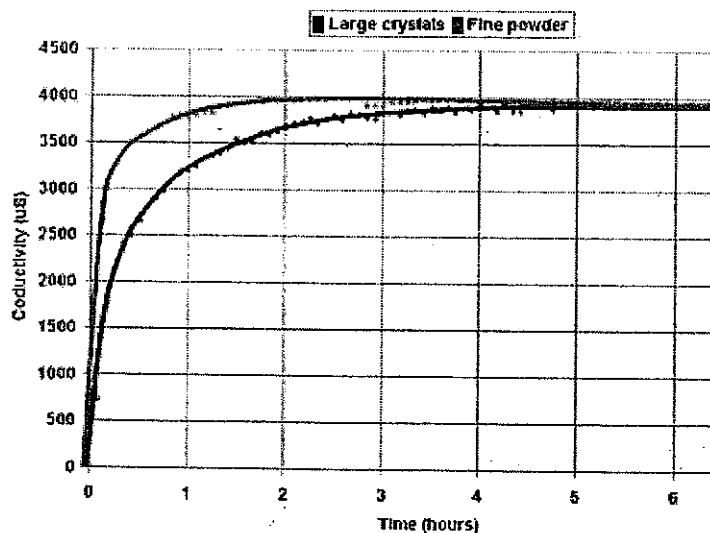
Because of this, the reaction rates in the forward and reverse directions will be affected equally by changing the surface area. The reaction will go faster in the forward direction because of an increase in surface area. It will go just as much faster in the reverse direction. Since both forward and reverse reaction rates are effected the same, there is no net change to the equilibrium once it has been achieved. The net result is that surface area has no effect on equilibrium.

Diagram:



What about before you reach equilibrium? Then the rates are not equal. Increasing the surface area means that you get to equilibrium more quickly. However, eventually you reach a point where the rates in the forward and reverse directions are equal. The approach to equilibrium is different but the final equilibrium achieved is the same with and without the change in surface area.

Graph:



As shown by the red curve, finely crushed crystals dissolve more quickly than do large crystals (the blue graph). However, the final equilibrium concentration reacted is the same for both.

**SO, IN GENERAL, WE EXPECT SURFACE AREA TO HAVE NO EFFECT ON AN EQUILIBRIUM, ONCE EQUILIBRIUM IS ESTABLISHED.**