**2.5 Chemical equilibrium**

Initially chemists believed that all reactions were irreversible. This means that reactants turn into products only – products are not able to return to the form of the reactants.

**Irreversible reactions**

Chemical equations for irreversible reactions are written as follows:

A + B → C + D

A and B represent reactants and C and D represent products. The reaction direction (shown by the arrow) goes only in one direction from reactants to products.

Many reactions are of this type. For example:

* When you bake a cake, several ingredients are combined together and heated to produce something new and delicious. But you cannot get back to the original ingredients again.
* Burning fuel is not reversible. These kinds of reactions are called combustion reactions. An organic compound reacts with oxygen to produce carbon dioxide and water.

**Reversible reactions**

In 1803, a French chemist called Claude Louis Berthollet realized that some reactions are in fact able to return from products to reactants. These are called reversible reactions. Most reactions are not reversible (they are irreversible). However, there are several reversible reactions that are very important industrially.

Chemical equations for reversible reactions are written as follows:

A + B ⇌ C + D

Again, A and B represent reactants and C and D represent products. The reaction direction (shown by the arrow) goes in both directions, from reactants to products or from products to reactants.

Got it: A reversible reaction is shown by the sign, ⇌

* + a half-arrow to the right shows the direction of the **forward reaction.** The forward reaction is always the reaction going from left to right.
  + a half-arrow to the left shows the direction of the **backward reaction.** The backward reaction is always the reaction going from right to left.

**Dynamic equilibrium**

When a reversible reaction is allowed to continue uninterrupted, there will come a time when the rate at which the forward reaction is taking place equals the rate at which the reverse reaction is taking place. When this happens no further overall change can be measured. In fact, it looks as though the reaction has stopped altogether. This is not actually the case. No overall change is measurable, but the forward and back reactions are continuing all the time, at the same rate.

The important thing to remember is that both the forward and the reverse reactions are continually happening, but the **concentrations (amounts) of each reactant and each product remain constant.**

**Closed systems**

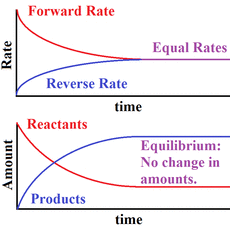
It is only possible to measure a reaction in dynamic equilibrium in a closed system, In a closed system the reactants are placed into a container that can be shut off from the air. In such a system no reactants or products can escape from the container or be added to the container.

If the reaction is a reversible one, as you now know, two possible reactions can take place here, one where A + B is converted to C + D and a second where C + D is converted to A + B. What happens if these are taking place at the same time in a closed system?

Actually, neither the reactants nor the products are ever used up completely because they are both constantly and simultaneously (at the same time) being produced.

If a reversible reaction takes place in a closed system it will eventually reach a state of dynamic **equilibrium**.

At equilibrium the rates of the forward and reverse reactions are the same. In addition, the amounts of reactants and products in the container remain the same as well.



Got it: A **reversible** reaction is a chemical reaction in which the products can be converted back to the original reactants under suitable conditions.

When a reversible reaction reaches equilibrium, the forward and reverse reaction rates are the same and the amounts of reactants and products remain the same.

**le Chatelier’s Principle**

This principle was established in 1884 by the French chemist and engineer Henry-Louis Le Chatelier. The principle states:

**If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to reestablish an equilibrium**

Le Chatelier's principle describes what happens when something disturbs a system that is in equlilibrium. Here you will consider three ways in which you can change the conditions of a chemical reaction at equilibrium:

* changing the concentration of one of the components of the reaction
* changing the pressure on the system
* changing the temperature at which the reaction is run.

By making changes such as these it is possible to force a reversible reaction to favour one direction or the other.

### Concentration Changes

### Consider the following reversible equation:

### A + 2B ⇌ C + D

What do you think happens the concentration of A is increased?

According to Le Châtelier, the position of equilibrium will move to counteract the change. In order to decrease the raised concentration of A, the A will react with B to produce more C and D.  The equilibrium moves to the right.

This kind of intervention would be valuable if B was relatively expensive reactant in the formation of the products C and D. So, in order to maximize the amount of B converted into product one could raise the concentration of A.

What do you think happens the concentration of A is decreased?

In order to make more of A, the reverse reaction would be favoured using up more of C and D in the process.

Usually the concentration of a product is decreased. So, if C is removed from the system the reaction will move to the right to re-establish the equilibrium. In this way more of A and B are converted into product.

### Pressure Changes

### Pressure changes only apply to reaction involving gases (or at least one gas).

### Increasing the pressure

Consider the following reversible reaction:

A(g) + 22B(g) ⇌ C(g) + D(g)

Top of Form

Top of Form

According to Le Châtelier, if the pressure is increased, the position of equilibrium will move to reduce the pressure again. Pressure is caused by gas molecules hitting the sides of their container. The more molecules (moles of gas) in the container, the higher the pressure will be. The system can reduce the pressure by reacting in such a way as to produce fewer molecules.

In this case, there are three moles of reactants, but only two moles of products. So, by forming more C and D, the system causes the pressure to reduce. Increasing the pressure on a gas reaction shifts the position of equilibrium towards the side with fewer moles of gas molecules.

#### Decreasing the pressure

The equilibrium will move to increase the pressure again. This happens when more gas molecules are produced. In this example that means the reaction would have to move to the left.

What do you think would happen if the pressure were changed in a reaction like the following?

2A(g) + 3B(g) ⇌ 4C(g) + D(g)

Since the number of molecules (moles) is the same on both sides of the equation (5) a pressure change will have no effect on the position of the equilibrium.

#### Summary of Pressure Effects

* By adding or removing a gaseous reactant or product the equilibrium will move in the direction of the smaller number of molecules (moles) present.
* By increasing the pressure in the system (usually by decreasing the volume of the container) the equilibrium will move towards the side with the lower number of molecules (moles)
* By decreasing the pressure in the system (usually by increasing the volume of the container) the equilibrium will move towards the side with the higher number of molecules (moles)

**Temperature changes**

Increasing the temperature

 When the volume of a mixture is reduced, a net change occurs in the direction that produces fewer moles of gas. When volume is increased the change occurs in the direction that produces **more** moles of gas. Bottom of Form

If the temperature is increased, then the position of equilibrium will move so that the temperature is reduced again. You already know about exothermic and endothermic reactions. If the forward reaction is exothermic (releasing heat energy), then the reverse reaction will be endothermic (using up heat energy).

Consider the following:

A + 2B ⇌ C + D ∆H = -250 kJ mol-1

(A negative ∆H value tells you that the forward reaction is exothermic and heat is give out).

This system is in equilibrium at 350°C, and the temperature is increased 525°C. The forward reaction is exothermic. To reduce the overall temperature, it needs to absorb the extra heat that has been added.

Therefore, in order to absorb heat from the system the reaction will have to favour the endothermic reaction which is the reverse reaction. So at the new equilibrium point there will be more reactants (A and B) present.

Ask yourself: Would you increase the temperature of the reaction if you had a factory producing C and D for sale in the example just discussed?

Decreasing the temperature

If the temperature is decreased, then the position of equilibrium will move so that the temperature is increased again. So, in the example above a decrease in temperature will push the reaction to the left hand side (the reverse reaction) and a new equilibrium will be established.

Summary of the effects of temperature

* Increasing the temperature of a system in dynamic equilibrium favours the endothermic reaction. The system reacts to the change by absorbing the extra heat which it achieves by reversing the direction of the reaction.
* Decreasing the temperature of a system in dynamic equilibrium favours the exothermic reaction. The system reacts to the change by releasing more heat which it achieves by reversing the direction of the reaction.

### Catalysts

### Remember that catalysts do not take part in chemical reactions, they simply change the rate at which the both the forward and reverse reactions take place. So, adding a catalyst to a reaction in dynamic equilibrium will make no difference to the position of that equilibrium.

### What a catalyst can do, however, is to speed up the time it takes for the equilibrium position to be reached.

**Forcing a reversible reaction in one direction or the other**

Sometimes, especially in industry, it is required to make sure that as much of the reactants is converted into products as possible. This is because the product can be sold and money earned.

As you have already learned, this can be achieved by changing the reaction conditions in a number of ways:

* The concentration of the reactants (or products) can be changed. For example, more reactants can be put into the system and products can be removed from the system.
* The pressure in the reaction container can be increased or decreased.
* The temperature at which the reaction takes place can be increased or decreased

A useful example of a reversible reaction is as follows:

The synthesis of ammonia from nitrogen and hydrogen (The Haber Process in industry)

N2(g) + 3H2(g) ⇌ 3NH3(g)

By changing the temperature and pressure of the reacting gases you can make the reaction go one way more than another

* High pressure forces the reaction to go the right (because there are fewer moles of NH3(g) (3) than moles of N2(g) + H2(g) (4).
* Higher temperature forces the reaction to the right as the ammonia decomposes into nitrogen and hydrogen gases again.
* Therefore, in order to maximize the production of ammonia gas the pressure needs to be increased and the temperature lowered.

Some other examples of reversible reactions:

1. Thermal (using heat) decomposition of ammonium chloride  
     
    NH4Cl(s) ⇌ NH3(g) + HCl(g)
2. Dehydration of blue copper sulfate crystals to form white anhydrous copper sulfate  
     
    CuSO4.5H2O(s) ⇌ CuSO4(s) + 5H2O(l)
3. Reaction between sulfur dioxide and oxygen to form sulfur trioxide  
     
    2SO2(g) + O2(g) ⇌ 2SO3(g)

Activity : Understanding Le Chatelier’s Principle and Dynamic Equilibria

1. Consider the given equation of a chemical reaction in dynamic equilibrium and answer the questions that follow, remembering what Le Chatelier’s Principle says about changes in such reactions:  
     
    2A + 3B ⇌ C + 2D -∆H  
   1. What would happen to the equilibrium if one increased the concentration of A in the reaction?   
      Hint: What could the reaction do to decrease the concentration of A again?
   2. What would happen to the equilibrium if one decreased the concentration of A in the reaction?  
      Hint: What could the reaction do to increase the concentration of A again?
   3. If the reaction given above involved gases, what would happen to the equilibrium if the pressure was increased?
   4. If the reaction given above involved gases, what would happen to the equilibrium if the pressure was decreased?
   5. What would happen to the equilibrium in a reaction where both sides of the equation have the same number of gaseous particles (e.g. A + B ⇌ C + D) and the pressure was changed?
   6. What would happen to the equilibrium of the reaction if the temperature was increased?  
      Remember that -∆H indicates that the forward reaction is exothermic i.e. gives out heat, and the reverse reaction is endothermic i.e. takes in heat. The amount of heat given out is exactly equal to the amount of heat taken in.
   7. What would happen to the equilibrium of the reaction if the temperature was decreased?
   8. What effect might a catalyst have of the equilibrium of a reaction?
   9. If you wanted to make more C and D in the present example what changes would you make to the reaction conditions?
2. Consider the following diagram which depicts the reaction for the synthesis of ammonia from nitrogen and hydrogen, then answer the questions that follow:

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* 1. Write a balanced equation for the reaction

1. Study the following three diagrams:

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* 1. Explain what they are showing. If you were interested in the commercial manufacture of ammonia in which direction would you like the equilibrium to be shifted?
  2. Can you suggest what might happen if you increased the temperature of the reaction?
  3. Will more ammonia form if the temperature is raised? Explain your answer. Note: The forward reaction is exothermic
  4. Can you suggest what might happen if you increased the pressure of the reaction? Hint: The greater the number of particles present in gases, the greater the pressure.
  5. What would happen if you removed ammonia from the reaction vessel as it was being formed?
  6. What would happen if a catalyst was added to the system? The commonly used catalyst for this reaction is iron.
  7. Imagine that you have a company that produces ammonia for sale. What conditions would you suggest to maximise your ammonia output and therefore your profit?

Assessment:

1. Explain what is meant by a reaction that is in dynamic equilibrium. (2)
2. State Le Chatelier’s Principle (2)
3. For a reversible reaction between gases, if the forward reaction is exothermic what is the effect of raising the temperature? (2)
4. For a reversible reaction between gases, if the forward reaction is endothermic what is the effect of raising the temperature? (2)
5. Consider the following reaction which describes what happens in a catalytic converter used to reduce carbon monoxide emissions in motor car exhausts:  
    2CO(g) + O2(g) ↔ 2CO2(g)  
   Suppose the reaction is taking place in a closed vessel and is at equilibrium.
   1. What would happen to the reaction equilibrium and the concentration of CO if a platinum catalyst were added? (2)
   2. What would happen to the reaction equilibrium and the concentration of CO if the temperature were increased? (2)  
      (Note: this is an exothermic reaction in the forward direction).
   3. What would happen to the reaction equilibrium and the concentration of CO if the pressure were increased? (2)
   4. What would happen to the reaction equilibrium and the concentration of CO if the concentration of oxygen were increased? (2)
6. Name the industrial process for the production of ammonia and write down the complete, balanced equation for its formation. (5)

Answers:

1. A reaction that is in dynamic equilibrium is one in which the rate of the forward reaction and the rate of the reverse reaction are equal, so the concentrations of reactants and products no longer change. (2)
2. Le Chatelier’s Principle states that if a reversible reaction that is in a state of dynamic equilibrium is disturbed by changing the conditions, the reaction will do what it can to oppose that change. (2)
3. For a reversible reaction between gases, if the forward reaction is exothermic raising the temperature? (2)
4. For a reversible reaction between gases, if the forward reaction is endothermic raising the temperature increases the yield. (2)
   1. Equilibrium remains the same and CO concentration does not change   
       (2)
   2. Equilibrium moves to the left and CO concentration increases (2)
   3. Equilibrium moves to the right and CO concentration decreases (2)
   4. Equilibrium moves to the right and CO concentration decreases (2)
5. The Haber Process (1)  
    N2(g) + 3H2(g) ↔ 2NH3(g) (4)

