Topic 2.3

EQUILIBRIA
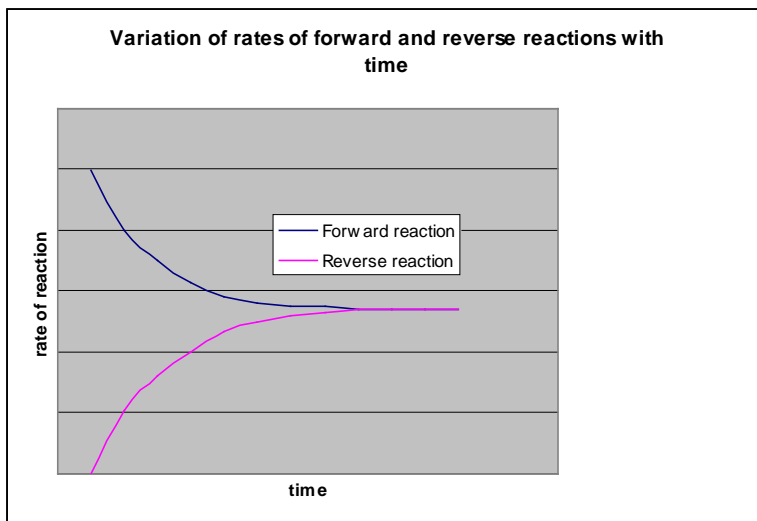
Dynamic Equilbria
Le Chatelier's Principle
Industrial Equilibria

REVERSIBLE REACTIONS

1.   Dynamic equilibria

Consider a reversible reaction A + B == C + D

As the reaction proceeds, the rate of the forward reaction decreases and the rate of the reverse reaction increases. Eventually, the reaction will reach a stage where both forward and backward reactions are proceeding at the same rate:

At this stage, a **dynamic equilibrium** has been reached. "Dynamic" means that the reaction has not stopped; it is simply moving in both directions at the same rate. "Equilibrium" means that the amount of reactants and products in the system is staying the same.This is in contrast to a static equilibrium, in which there is no movement in either direction. Chemical equilibria are in general dynamic rather than static.
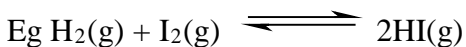
All reactions are reversible in theory; although in practice many are not considered to be so. In some cases the reverse reaction is insignificant; in others, it is not allowed to take place.

2.   Open and closed systems

A **closed system** is one from which reactants and products cannot escape. In closed systems the forward and reverse reactions continue until dynamic equilibrium is reached. All reactions in a closed system are thus reversible in theory, although they are only considered as such if both forward and reverse reactions occur to a significant extent.

Eg $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
In this case the reverse reaction is not significant so the reaction is represented by single arrow.
Eg $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
In this case the reverse reaction is significant, so the reaction is represented by an equilibrium sign: $\rightleftharpoons$

An **open system** is one from which reactants and products can escape. The open air or a fume cupboard is an example of an open system. In an open system, the products are removed as soon as they are formed, so the reverse reaction is not allowed to take place. Such reactions clearly never reach equilibrium, but proceed until all the reactions have been converted into products. Reactions which proceed under these conditions are clearly irreversible.
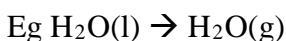
Eg $H_2O(l) \rightarrow H_2O(g)$
This reaction would not be expected to proceed significantly under normal conditions, since water is more stable than steam at normal temperatures. However puddles will disappear completely if left for long enough. This is because the water vapour is removed by wind currents as soon as it is produced, and so the reverse reaction is not allowed to take place. Thus the system never reaches equilibrium and the reaction is irreversible.

Thus if a reaction is represented by an equilibrium sign, it is often assumed that:
-   **the system is closed**
-   **the reverse reaction is significant**

LE CHATELIER'S PRINCIPLE

If the conditions are changed after equilibrium has been established, the rates of the forward and reverse reactions may be affected by different amounts and the system may no longer be at equilibrium. If this is the case, it will move in one direction or another to re-establish equilibrium. The direction in which the system will move to re-establish equilibrium can be predicted by **Le Chatelier's principle**:

"**If a constraint is imposed on a system at equilibrium, then the system will respond in such a way as to counteract the effect of that constraint**."

Such constraints can be the **addition or removal of one of the reactants or products**, **a change in pressure**, **a change in temperature** or **the addition of a catalyst**.

Each must be treated separately:

1. Concentration

Le Chatelier's principle predicts that if a reactant's concentration in a system is increased, the system will move to the right in order to decrease the concentration of that reactant. If the reactant's concentration is decreased, the system will move to the left in order to replace that reactant. Similarly, if a product's concentration is increased then the system will move to the left and if a product's concentration is decreased then the system will move to the right.

This fact can be explained by considering the effect of changing the concentration of one of the species on the rates of the forward and backward reactions.
Consider the reaction $A + B == C + D$
If the concentration of A or B is increased, the rate of the forward reaction, but not the reverse reaction, is increased. Therefore the equilibrium will move to the right. If the concentration of A or B is decreased, the rate of the forward reaction, but not the reverse reaction decreases. Therefore the equilibrium will move to the left.

Example: $H_2(g) + I_2(g) == 2HI(g)$
    If more hydrogen (or iodine) is added, the system will move to the right in order to remove the extra hydrogen (or iodine)
    If iodine is removed, the system will move to the left to replace the lost iodine.
    If hydrogen iodide is added, the system will move to the left to remove the hydrogen iodide.
    If hydrogen iodide is removed, the system will move to the right to replace the lost hydrogen iodide

In summary: **When the concentration of one of the species is increased, the system will move to remove that species. When the concentration of one of the species is decreased, the system will move to replace that species**.
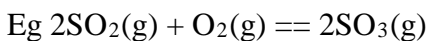
2. Pressure

The pressure in a system depends on the number of gas molecules in the system. Le Chatelier's principle therefore predicts that if the pressure of the system is increased, the system will move towards the side which has fewer gas moles. If the pressure of the system is decreased, the system will move towards the side which has more gas moles. If the number of gas moles on both sides in the same, then pressure has no effect on the equilibrium position.
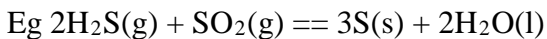
Eg $PCl_5(g) == PCl_3(g) + Cl_2(g)$
If the pressure is increased, the system will move to the left, where there are fewer moles. If the pressure is decreased, the system will move to the right, where there are more moles.
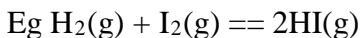
Eg $2SO_2(g) + O_2(g) == 2SO_3(g)$
If the pressure is increased, the system will move to the right, where there are fewer moles. If the pressure is decreased, the system will move to the left, where there are more moles.

Eg $2H_2S(g) + SO_2(g) == 3S(s) + 2H_2O(l)$
If the pressure is increased, the system will move to the right, where there are fewer moles. If the pressure is decreased, the system will move to the left, where there are more moles

Eg $H_2(g) + I_2(g) == 2HI(g)$
Changing the pressure will have no effect on the position of this equilibrium, as there is the same number of moles on both sides.

In summary: **When the pressure is increased, the system will move to the side with fewer moles in order to decrease the pressure. When the pressure is decreased, the system will move to the side with more moles in order to increase the pressure**.

3. Temperature

If the forward reaction is exothermic, then the temperature of the system will rise if the forward reaction takes place. The reverse reaction will therefore be endothermic, and the temperature of the system will fall if the reverse reaction takes place.

Le Chatelier's principle therefore predicts that an increase in temperature will favour the endothermic reaction, and that a decrease in temperature will favour the exothermic reaction. If the forward reaction is exothermic, then an increase in temperature will cause the system to shift to the left, and a decrease in temperature will cause the system to shift to the right. If the forward reaction is endothermic, than an increase in temperature will cause the system to shift to the right, and a decrease in temperature will cause the system to shift to the left. If $\Delta H = 0$, then a change in temperature will have no effect on the position of equilibrium.
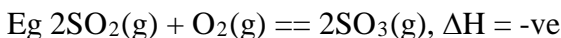
Eg $2SO_2(g) + O_2(g) == 2SO_3(g)$, ΔH = -ve
An increase in temperature will favour the direction which decreases the temperature, ie the endothermic direction. As the forward reaction is exothermic, the reverse reaction must be endothermic and so the reaction will proceed to the left.
A decrease in temperature will favour the exothermic direction, so it can increase the temperature. This is the forward reaction so the reaction will proceed to the right.

Eg $CaCO_3(s) == CaO(s) + CO_2(g)$, $\Delta H = +ve$

An increase in temperature will favour the endothermic direction in order to decrease the temperature, so the reaction will proceed to the right. A decrease in temperature will favour the exothermic direction in order to increase the temperature, so the reaction will proceed to the left.

In summary: **When the temperature is increased, the system will move in the endothermic direction in order to decrease the temperature. When the temperature is decreased, the system will move in the exothermic direction in order to increase the temperature**.

4. Catalysts

The addition of a catalyst will have no effect on the position of equilibrium. It will increase the rate of the forward and reverse reactions, but by the same amount. The position of equilibrium will thus be unchanged.
It increases the rate of reaction by lowering the activation energy. However it decreases the activation energy of the forward and reverse reactions by the same amount:

reaction pathway
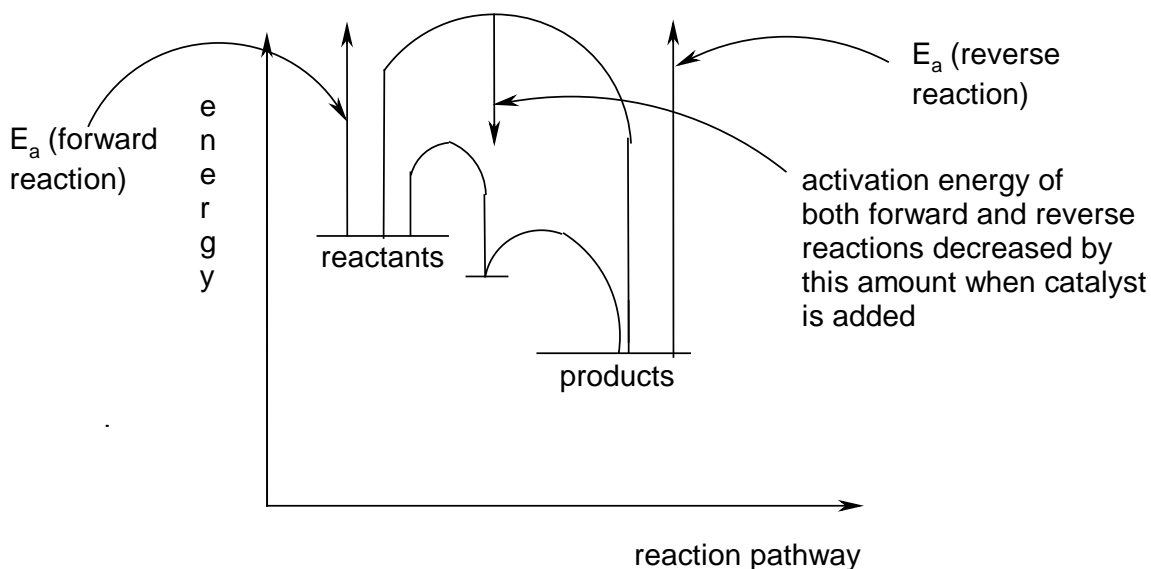
In summary: **When a catalyst is added, the rates of the forward and reverse reactions are increased by the same amount and the position of equilibrium is thus unaffected**.

INDUSTRIAL EQUILIBRIA

Many large-scale industrial processes involve reversible reactions. These reactions do not go to completion but reach an equilibrium. The position of this equilibrium depends on the conditions employed, and Le Chatelier's principle can be used to predict the conditions which will maximise the amount of product formed.

The position of equilibrium, however, is not the only factor which must be considered when choosing the best conditions for an industrial reaction. Other important economic factors which must be considered are the rate of reaction and the cost of maintaining the reaction conditions. Each must be considered in turn and a set of conditions which maximises the amount of product formed at reasonable cost is chosen.

In industrial equilibria, there are three key factors which must be considered:

- The yield of product
- The rate of reaction
- The cost of maintaining the reaction conditions

There are a number of important industrial processes involving equilibrium reactions. A few examples will be considered:

a)   The Contact Process

The Contact process is important in the manufacture of sulphuric acid. The process involves a number of steps, but the most important one is the conversion of sulphur dioxide to sulphur trioxide:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
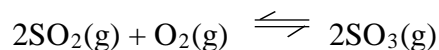
This reaction is exothermic, and so an increase in temperature will decrease the yield of sulphur trioxide. The position of equilibrium is thus favoured by low temperature.

If the temperature is too low, however, the rate of reaction will be so slow that the sulphur trioxide is not produced quickly enough for the reaction to be commercially viable. It is therefore necessary to choose a compromise temperature; high enough for the reaction to proceed at a reasonable rate, but low enough for the yield to be reasonable.

The reaction involves a reduction in the number of gas moles, and so an increase in pressure will increase the yield of sulphur trioxide. The position of equilibrium is thus favoured by high pressure.

High pressure also favours the rate of reaction. However the cost of maintaining conditions of high pressure is significant, and this limits the maximum pressure that can be applied.

Catalysts increase the rate of reaction without affecting the position of equilibrium. This reaction therefore takes place in the presence of a catalyst, V_2O_5. The catalyst ceases to become effective at very low temperatures, and this places a further constraint on the minimum temperature which can be used in the reaction.

The optimum conditions for this reaction are 400°C and a little above atmospheric pressure. Under these conditions 98% yield is achieved.

The reaction should not be carried out above 400°C because:
- the yield of sulphur trioxide is poor
- the cost of maintaining the temperature is high

The reaction should not be carried out below 400°C because:
- the rate of reaction is slow
- the catalyst is not effective at low temperatures

The reaction should not be carried out above atmospheric pressure because:
- the cost of maintaining the pressure is high

The reaction should not be carried out below atmospheric pressure because
- the yield of sulphur trioxide is poor
- the reaction is too slow

(b)   The Haber Process

The Haber process involves the manufacture of ammonia by the following reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
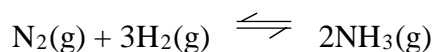
This reaction is also exothermic, and so an increase in temperature will decrease the yield of ammonia. The position of equilibrium is thus favoured by low temperature.

If the temperature is too low, however, the rate of reaction will be so slow that the ammonia is not produced quickly enough for the reaction to be commercially viable. It is therefore necessary to choose a compromise temperature; high enough for the reaction to proceed at a reasonable rate, but low enough for the yield to be reasonable.

The reaction involves a reduction in the number of gas moles, and so an increase in pressure will increase the yield of ammonia. The position of equilibrium is thus favoured by high pressure.

High pressure also favours the rate of reaction. However the cost of maintaining conditions of high pressure is significant, and this limits the maximum pressure that can be applied.

Catalysts increase the rate of reaction without affecting the position of equilibrium. This reaction therefore takes place in the presence of a catalyst, iron.

The optimum conditions for this reaction are 450°C and a pressure of 200 atm. Under these conditions a 15% yield is achieved. The unreacted nitrogen and hydrogen are recycled.

(c)   The production of ethanol

Most ethanol produced for industrial purposes is manufactured by the reaction of ethene with steam:

$$H_2C=CH_2(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$$
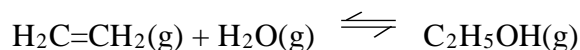
This reaction is also exothermic.
Like the Haber Process and the Contact process, the best yield is obtained by using a low temperature and a high pressure.

Excess steam is also used to push the equilibrium to the right and ensure that all of the ethene is used up.

However a number of other factors must be considered:
- a low temperature slows down the reaction rate
- a high temperature can cause the ethene to polymerise
- high pressure increases the cost of equipment
- too much steam dilutes the catalyst

The chosen temperature is 300 °C and the chosen temperature is 65 atm.
The catalyst used is concentrated phosphoric acid.

The yield achieved under these conditions is only 5% but, like in the Haber process, the unreacted ethene and steam can be recycled.

(d)   The production of methanol

Most methanol is made industrially be reacting carbon monoxide with hydrogen in a reversible reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$
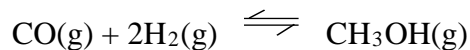
This reaction is also exothermic and the best yield is obtained by using a low temperature and a high pressure.

Compromise conditions of 230 °C and 100 atm are used.
A copper catalyst is used.

The yield achieved under these conditions is only 5% but, like in the Haber process, the unreacted carbon monoxide and hydrogen can be recycled.

CARBON NEUTRALITY

A **carbon-neutral** process is one which has no net carbon dioxide emissions into the atmosphere.

The alcohols methanol and ethanol can both be burnt to release energy.
They are very useful fuels as they generally release less polluting gases than hydrocarbon fuels.

It is also possible, under certain circumstances, to use these fuels in a carbon-neutral and renewable way.

Ethene is made from crude oil. So ethanol produced from ethene is non-renewable. As the combustion of ethanol releases carbon dioxide, this process is therefore not carbon neutral.

Most carbon monoxide is made by reacting methane or propane with steam. So methanol produced in this way is non-renewable. As the combustion of methanol releases carbon dioxide, this process is therefore not carbon-neutral.

However it is also possible to make ethanol by the fermentation of glucose.
Glucose can be made quickly by planting sugar and so the ethanol made in this way can be considered a renewable fuel.
The overall process of growing sugar, fermenting it and burning the ethanol is also a carbon-neutral process:
1)   production of glucose $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 3O_2$
         (six molecules of carbon dioxide absorbed)
2)   fermentation of glucose $C_6H_{12}O_6 \rightarrow 2 C_2H_5OH + 2CO_2$
         (two molecules of carbon dioxide released)
3)   combustion of ethanol $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$
         (two molecules of carbon dioxide released per molecule of ethanol, so two
         molecules of ethanol release four molecules of carbon dioxide)
Total carbon dioxide emissions = -6 +2 +4 = 0, so the process is carbon-neutral.