Topic 4.2
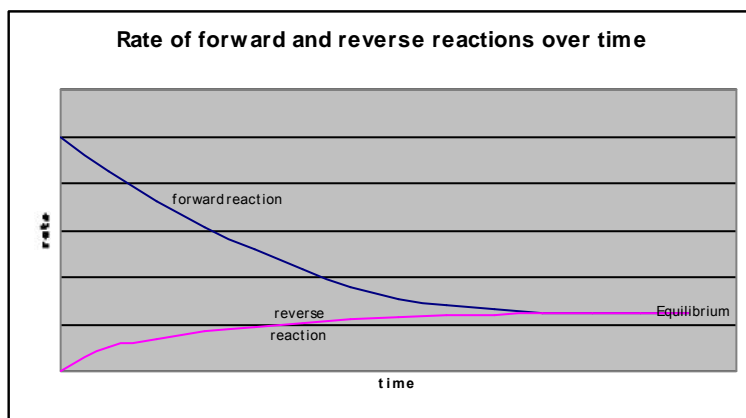
EQUILIBRIA

Dynamic equilibria
Equilibrium constants
Changing the position of equilibrium

REVERSIBLE REACTIONS

Consider a reversible reaction A + B $\rightleftharpoons$ 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:

Rate of forward and reverse reactions over time

rate

forward reaction

reverse reaction

Equilibrium

time

At this stage, a **dynamic equilibrium** has been reached. The reaction has not stopped; it is simply **moving in both directions at the same rate**. 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 reactions, the reverse reaction is not allowed to take place. Many reactions take place in an open system, where the products, often gases, are allowed to escape as they are formed. The reverse reaction is therefore not possible and equilibrium is never reached. The evaporation of water is an example of this:

Eg $H_2O(l) \rightarrow H_2O(g)$
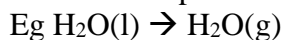
This reaction would not be expected to proceed significantly under normal conditions, since water is more stable than steam at normal temperatures. However puddles will disappear completely if left for long enough. This is because the water vapour is removed by wind currents as soon as it is produced, and so the reverse reaction is not allowed to take place.

In other reactions, even where the system is closed, the reverse reaction is insignificant:

Eg $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

As the reverse reaction is not significant, the reaction is represented by single arrow.

Reactions are therefore only represented by equilibrium signs if
- the system is closed
- the reverse reaction is significant

Eg $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, closed system, reverse reaction significant; reaction represented by equilibrium sign.

EQUILIBRIUM CONSTANTS

1. Expressions for equilibrium constant (K_c)

Consider the reversible reaction $A + 3B \rightleftharpoons C + 2D$

The rate expression for the forward reaction can be written:
Rate = $k_f[A][B]^3$, where k_f is the rate constant for the forward reaction.

The rate expression for the reverse reaction can be written:
Rate = $k_r[C][D]^2$, where k_r is the rate constant for the reverse reaction.

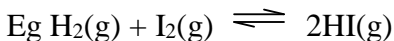At equilibrium, the rates of the forward and reverse reactions are equal:
$k_f[A][B]^3 = k_r[C][D]^2$

This can be rearranged to give $k_f/ k_r = \dfrac{[C][D]^2}{[A][B]^3}$

Since the rate constants are constant at a given temperature, it follows that the term k_f/ k_r is also constant at a given temperature. It is therefore normally regarded as a single constant K_c and is known as the **equilibrium constant** of the reaction.
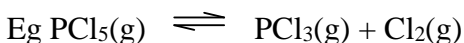
$K_c = \dfrac{[C][D]^2}{[A][B]^3}$

2.   Units for equilibrium constants (K_c)

The units of the equilibrium constant vary, depending on the number of species involved. The units can be deduced by multiplying out the units of concentration and cancelling as appropriate. The units of the above equilibrium constant are $mol^{-1}dm^3$.

Eg $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
$K_c = \dfrac{[HI]^2}{[H_2][I_2]}$ It has no units.

Eg $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
$K_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]}$ It has units of $moldm^{-3}$.

Extension – equilibrium constants

The value and units of equilibrium constant depends on the way the reaction is written.

Eg consider the equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
$K^1_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$ units $mol^{-1}dm^3$.

If written in the following way, however: $SO_2(g) + 1/2O_2(g) \rightleftharpoons SO_3(g)$

$K^2_c = \dfrac{[SO_3]}{[SO_2][O_2]^{1/2}}$ units $mol^{-1/2}dm^{3/2}$.

K^1_c and K^2_c do not have the same units or the same numerical value; in fact $K^1_c = (K^2_c)^2$.

The equilibrium constants of the forward and reverse reactions are not the same, but are related by a simple relationship:

Eg for the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
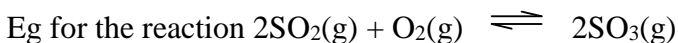
$K_c(f) = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$ $K_c(r) = \dfrac{[SO_2]^2[O_2]}{[SO_3]^2}$

The two equilibrium constants can be related by the relationship $K_c(f) = 1/K_c(r)$

---

3.   Calculations of equilibrium constants (K_c)

If the concentrations of all the reacting species are known, the equilibrium constant can be calculated by putting the values into the expression for the equilibrium constant and computing the value.

Often, however, the concentration of only one of the species at equilibrium is given, and the others must be deduced. This is done by considering the way in which the species react:

Eg Consider the equilibrium $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

If the initial amounts of hydrogen and iodine are a and b, and x moles of hydrogen react with x moles of iodine to give 2x moles of hydrogen iodide, then the amounts of hydrogen and iodine in the mixture at equilibrium are (a-x) and (b-x) respectively.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
Initially: a   b   0
At equilibrium: (a-x)   (b-x)   2x
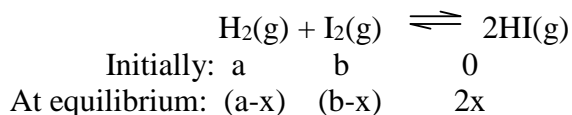
If a, b and the amount of one of the species present at equilibrium is known, then the value of x can be deduced and the amounts of all the other species at equilibrium can also be deduced.

Eg If 1.5 mol of hydrogen and 1.2 mole of iodine are mixed together and allowed to reach equilibrium, the amount of hydogen iodide present at equilibrium is found to be 1.6 mol.

2x = 1.6, so x = 0.8, (a-x) = 0.7 and (b-x) = 0.4
Therefore at equilibrium there are 0.7 moles of hydrogen, 0.4 moles of iodine and 1.6 moles of hydrogen iodide.

These amounts can be converted into concentrations, and then inserted into the expression for equilibrium constant.

CHANGING THE POSITION OF EQUILIBRIUM

If the conditions are changed after equilibrium has been established, the system may no longer be at equilbrium and may 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.

Changing the concentrations of reactants and products has no effect on the rate constants of the forward or reverse reactions. Therefore it **has no effect on the equilibrium constant**.
Given that K_c is unchanged, the effect of changing the concentration of one of the species can be shown with reference to K_c:

Consider the reaction: $aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c [D]^d}{[A]^b [B]^b}$$
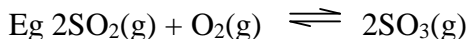
If the concentration of A or B is increased, then [C] and [D] must increase to maintain K_c. Similarly if the concentration of C or D is increased, then [A] and [B] must increase to maintain K_c.
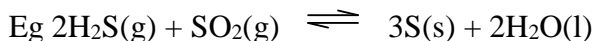
2. Pressure

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.
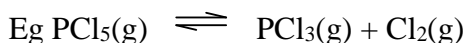
Eg $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
If the pressure is increased, the system will move to the left. If the pressure is decreased, the system will move to the right.

Eg $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
If the pressure is increased, the system will move to the right. If the pressure is decreased, the system will move to the left.

Eg $2H_2S(g) + SO_2(g) \rightleftharpoons 3S(s) + 2H_2O(l)$
If the pressure is increased, the system will move to the right. If the pressure is decreased, the system will move to the left.
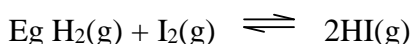
Eg $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
Changing the pressure will have no effect on the position of this equilibrium.

Since changes in pressure affect the reactant concentrations and not the rate constants, it follows that **the equilibrium constant is not affected by changes in 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.
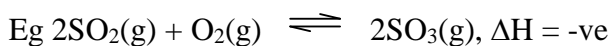
Eg $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, ΔH = -ve
The forward reaction is exothermic so is favoured by decreasing the temperature. The reverse reaction is endothermic so is favoured by increasing the temperature.

Eg $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, ΔH = +ve
The forward reaction is endothermic so is favoured by increasing the temperature. The reverse reaction is exothermic so is favoured by decreasing the temperature.

A change in temperature changes the rate constants for both forward and reverse reactions and is therefore likely to change the value of the equilibrium constant. **If the reaction is exothermic, then an increase in temperature will cause the value of K_c to decrease, and if the reaction is endothermic, then an increase in temperature will cause the value of K_c to increase**.

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.

As the position of equilibrium is unchanged, it follows that **adding a catalyst has no effect on the equilibrium constant**.

5. Summary

Effect of changing conditions on a system at equilibrium

Change	Type of change	Effect on equilibrium position	Effect on equilibrium constant
Concentration	Add reactant or remove product	Moves to right	No effect
	Add product or remove reactant	Moves to left	No effect
Pressure (or volume)	Increase pressure or decrease volume	Moves towards side with fewer gas moles (right if Δn = -ve, left if Δn = +ve)	No effect
	Decrease pressure or increase volume	Moves towards side with more gas moles (left if Δn = -ve, right if Δn = +ve)	No effect
Temperature	Increase temperature	Moves in endothermic direction (right if ΔH = +ve, left if ΔH = -ve)	Increases (if ΔH = +ve) Decreases (if ΔH = -ve)
	Decrease temperature	Moves in exothermic direction (left if ΔH = +ve, right if ΔH = -ve)	Decreases (if ΔH = +ve) Increases (if ΔH = -ve)
Catalyst	Add or remove catalyst	No effect	No effect