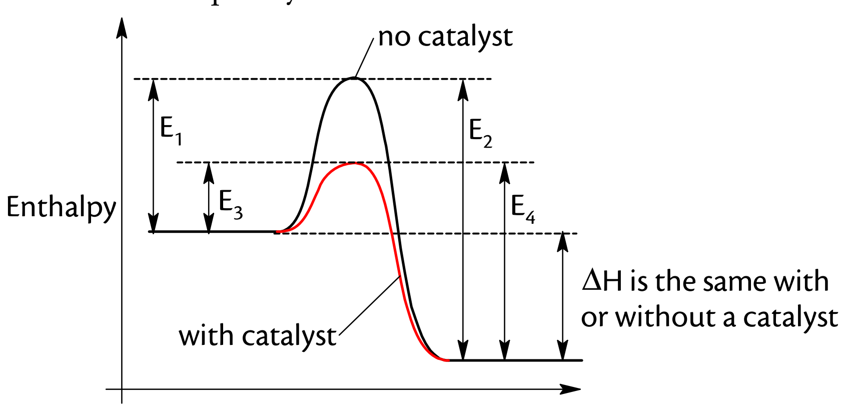
# FACTORS THAT AFFECT THE POSITION OF EQUILIBRIUM

Many reactions in the chemical industry (eg Haber Process) are equilibria. It is important to understand what factors control the position of equilibria since this clearly affects the conversion of reactants to products. Equilibrium is reached when the rates of two opposing reactions become equal, so it seems reasonable to study the factors that we already know affect reaction rates:

a) catalysts
b) concentration
c) pressure (of gases)
d) temperature

**Effect of Catalysts on Equilibrium**
A catalyst has the effect of lowering the energy barrier between reactants and products by providing an alternative reaction path. From the graph we can see that if the barrier is lowered for the forward reaction it is also lowered for the back reaction by the same amount. The net effect is that a catalyst does not alter the position of equilibrium. However, a catalyst speeds up both the forward and back reactions so the same equilibrium is reached more quickly.




$E_1$ Forward activation energy, no catalyst
$E_2$ Back activation energy, no catalyst
$E_3$ Forward activation energy, with catalyst
$E_4$ Back activation energy, with catalyst

**Effect of Concentration on Position of Equilibrium**
Consider the following equilibrium:

$$A + B \rightleftharpoons C + D$$

Increasing the concentration of A or B will speed up the forward reaction so producing more C and D until a new equilibrium position further to the right is established. Decreasing the concentration of C or D will slow down the back reaction which converts C and D into A and B. This means the concentration of C and D will increase again moving the equilibrium position to the right.

By a similar argument either increasing the concentration of C and D or decreasing the concentration of A and B moves the equilibrium to the left.

The two following reactions illustrate these points:

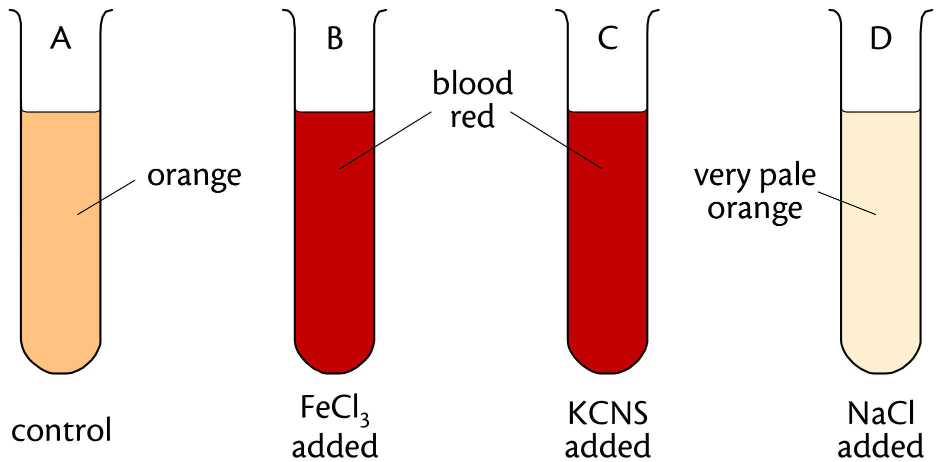
$$\underset{\text{brown liquid}}{ICl_{(l)}} + Cl_{2(g)} \rightleftharpoons \underset{\text{yellow crystals}}{ICl_{3(s)}}$$

When chlorine is added we see an increase in the amount of yellow crystals and a decrease in brown liquid. This is because the increase in the concentration of chlorine has speeded up the forward reaction and moved the equilibrium to the right. Removing chlorine has the opposite effect and the equilibrium moves to the left.

$$\underset{\text{colourless}}{Fe^{3+}_{(aq)}} + CNS^{-}_{(aq)} \rightleftharpoons \underset{\text{red}}{FeCNS^{2+}_{(aq)}}$$

The intensity of the colour indicates the position of the equilibrium i.e. the more red the colour the further right the equilibrium lies.

Some of the equilibrium mixture is put in 4 test tubes and A is kept as a control. The diagram shows what was added to the others and the resulting change in appearance.




The addition of either $Fe^{3+}$ ions or $CNS^{-}$ ions shifts the equilibrium to the right and results in the formation of more of the red complex ion.

When NaCl is added the $Cl^{-}$ ions form a complex with $Fe^{3+}$ so the concentration of $Fe^{3+}_{(aq)}$ falls. This moves the equilibrium to the left and the colour pales.

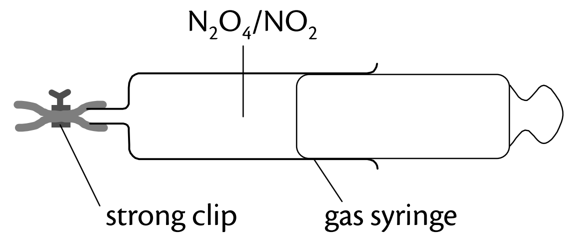
**Effect of Pressure on the Position of Equilibrium**

A change in pressure can only affect equilibria in which gases are involved.

The pressure exerted by a gas is caused by the freely moving gas molecules colliding with the walls of the containing vessel. An increase in the number of molecules in the vessel will cause an increase in pressure, the size of the container being kept constant. Similarly a decrease in the number of molecules causes a decrease in pressure. The effect of changes in pressure on an equilibrium involving gases is equivalent to changes in concentration on a system involving solutions. Increasing the pressure favours whichever reaction brings about a reduction in the total number of gas molecules. Decreasing the pressure favours the reaction that increases the total number of gas molecules.

We can observe the effect of pressure using the brown gas nitrogen dioxide. Nitrogen dioxide ($NO_2$) exists as an equilibrium mixture with its colourless dimer, dinitrogen tetroxide ($N_2O_4$).

$$\underset{\substack{\text{1 mole} \\ \text{colourless}}}{N_2O_4} \rightleftharpoons \underset{\substack{\text{2 moles} \\ \text{brown}}}{2NO_2}$$




When the plunger is pushed in the pressure is increased so the equilibrium shifts to the left to reduce the number of molecules and so reduce the pressure. The full results of this experiment are in the table:

| Applied pressure change | Initial colour change | Final colour change |
|---|---|---|
| Increase (plunger in) | Darkens due to compression | Lightens as equilibrium shifts to the left |
| Decrease (plunger out) | Lightens due to expansion | Darkens as equilibrium shifts to the right |

If an equilibrium system has the same number of gas molecules on both sides of the arrow, a change in pressure will have no effect on the position of equilibrium. However an increase in pressure (i.e. concentration) will increase the rates of both forward and back reactions and so reduce the time for equilibrium to be established.

**Industrial Preparation of Methanol**

We met this reaction in Unit 2

$$\underset{\text{3 moles of gas}}{CO_{(g)} + 2H_{2(g)}} \rightleftharpoons \underset{\text{1 mole of gas}}{CH_3OH_{(g)}}$$

High pressure favours the forward reaction because it gives a reduction in the number of gas molecules. So high pressure increases the yield of methanol. In the original industrial process (1923) the mixture was compressed to 300 atmospheres. In 1966, development of a more efficient catalyst allowed the process to be run at 50 to 100 atmospheres. As we saw earlier a catalyst has no effect on equilibrium position so the more efficient catalyst did not increase the yield of methanol and the lower pressure actually gives a lower yield of methanol. The advantage is that the lower pressure plant is cheaper to build and safer to run. The carbon monoxide/hydrogen mixture (called synthesis gas or syngas) in the above process is generated as follows:

$$\underset{\text{2 moles of gas}}{CH_{4(g)} + H_2O_{(g)}} \rightleftharpoons \underset{\text{4 moles of gas}}{CO_{(g)} + 3H_{2(g)}}$$

In this reaction raising the pressure would favour the back reaction so reducing the yield of syngas. As a result this process is run at normal pressure.

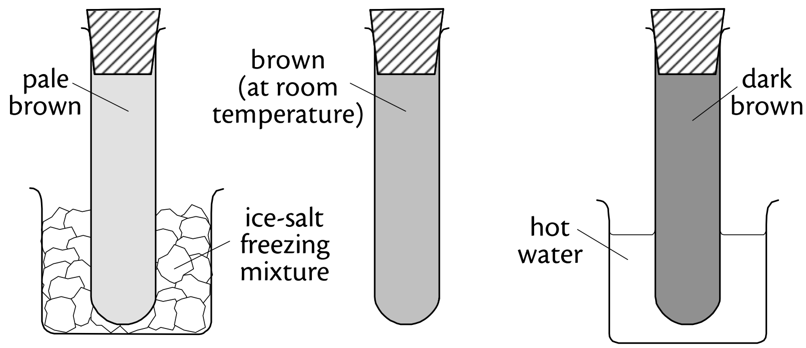
**Effect of Temperature on the Position of Equilibrium**
In a system at equilibrium, if the forward reaction is exothermic the back reaction must be endothermic, and vice versa.

If the temperature is raised, then the rate of both reactions increases but not equally. A rise in temperature favours the reaction that needs to have heat supplied, i.e. the endothermic reaction. A decrease in temperature has the opposite effect and favours the exothermic reaction.

We can observe the effects of temperature using again the $N_2O_4$ / $NO_2$ system

$$\underset{\text{colourless}}{N_2O_4} \rightleftharpoons \underset{\text{brown}}{2NO_2} \qquad \Delta H = +ve$$

Samples of this mixture in 3 test tubes at different temperatures are shown:




When the temperature is raised the forward reaction, which is endothermic, is favoured so the equilibrium shifts to the right. The concentration of $NO_2$ increases and so the colour darkens. Lowering the temperature favours the exothermic reaction which is the back reaction. The equilibrium shifts to the left and the colour lightens as the concentration of $N_2O_4$ increases.

**Industrial preparation of Methanol**
This is an exothermic reaction:

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)} \qquad \Delta H = -91\ \text{kJ mol}^{-1}$$

(The ΔH value is given for the forward reaction)

An increase in temperature favours the back reaction and so decreases the equilibrium concentration of methanol. This suggests that to get a high yield of methanol we should carry out the reaction at low temperature. However, low temperature means a low rate and a long time to establish equilibrium. A compromise is reached at a moderately high temperature (200 to 300°C) which gives a worthwhile rate but a reduced yield of methanol.

The carbon monoxide/hydrogen mixture called syngas is produced in an endothermic reaction.

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)} \qquad \Delta H = +206\ \text{kJ mol}^{-1}$$

This reaction is carried out at 800°C which both gives a high rate and favours the forward endothermic reaction. This shifts the equilibrium to the right and increases the yield of syngas.