Chemical Equilibria

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Please note that these guides are a collation of my personal notes, teachers' notes, chemistry books, and websites such as chemguide, chemsheets, chemwiki and wikipedia.

Equilibriums

Many reactions are equilibria - their reactants and products exist together rather than going to completion with all the reactant turning readily to products. A dynamic equilibrium involves 2 opposing processes that occur at equal rates. In dynamic equilibriums, constant macroscopic properties can be observed while microscopic processes continue to occur.

Factors Affecting Dynamic Equilibrium

The position of equilibrium is not fixed for a reaction, but changes as you change the reaction conditions.

When a system in dynamic equilibrium is upset, it responds in such a way as to return it to equilibrium again. The tendency of systems to behave in this way was noted by the French chemist Henri Le Chatelier, who in 1888 proposed that:

- Whenever a system which is in dynamic equilibrium is disturbed, it tends to respond in such a way as to oppose the disturbance and so restore equilibrium.

This is known as **Le Chatelier's principle**.

This is pg 204 from the Edexcel Chemistry Textbook

The main factors affecting the position of the equilibrium are:

- Temperature
- Pressure
- Concentration

Temperature

Using the Haber Process as an example

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$ Forward ΔH negative

If we want to increase the yield of ammonia (NH_3), we will decrease the temperature so the forward reaction will be favoured. The forward reaction is exothermic and will release energy to make up for the temperature we decreased.

If we increased the temperature, the backward reaction will be favoured as it is endothermic and will absorb the extra energy we added.

However you have to remember, even though a decrease in temperature will increase the yield of the products, it will on the other hand decrease the rate of the reaction. Hence a compromise is reached, 450°C.

Pressure

A change in the pressure will shift the position of the equilibrium more in gaseous reactions (both the reactants and the products are gases). Increasing the pressure means more particles are present in a specific volume. In effect, the side with smaller number of moles will be favoured to counteract the pressure we increased. In the case of the Haber process, there are 4 moles on the reactant side and 2 on the product side. Hence increasing the pressure will favour the side with less moles. While decreasing the pressure will favour the reactant side. Note: if there are the same number of moles on both sides the equilibrium will not shift. So why don't we increase pressure to the maximum possible level in the Haber process?

Well, even though increasing the pressure increases the yield of the product, it will also cost a lot and will be too dangerous. As for cost, increasing pressure will need a lot of energy which will cost a lot of money. Also we will need a chamber capable of accommodating such pressures which will be quite expensive. Finally these pressure pose a threat to workers around as it comes with the risk of explosions. Hence a compromise pressure is used in the Haber process (250 atmospheric pressure).

Concentration

This applies more for reactions taking place in aqueous solution. Increasing the concentration of reactants will cause a shift to the products side and vice versa. Nothing more really :P

Catalyst

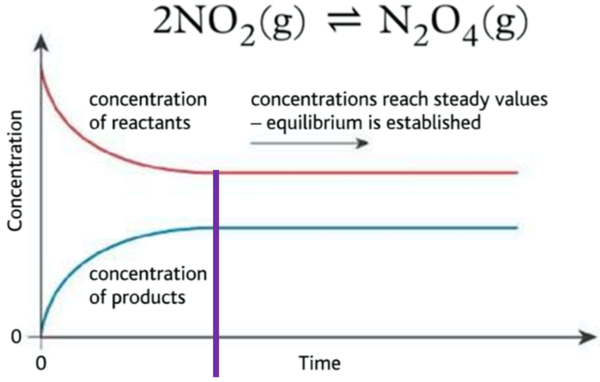
A catalyst doesn't change the position of the equilibrium however it makes the reaction reach equilibrium faster. For example decreasing the temperature will favour the Ammonia side, but it will shift slowly, hence a catalyst will make this shift take place quicker.

Examples of Equilibriums

NO_2 & N_2O_4 Equilibrium

Nitrogen dioxide (NO_2, a brown gas) is formed by the oxidation of nitrogen monoxide (NO) released by car engines. Nitrogen dioxide is in equilibrium with dinitrogen tetraoxide, N_2O_4 which is colourless. The double headed arrow is used to represent equilibrium.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$



As equilibrium is reached the concentrations of reactants and products in a chemical process reach steady valued. They reach a steady state after the vertical line I added to the graph.

ICl and Cl_2 Equilibrium

Iodine(I) chloride and iodine(III) chloride

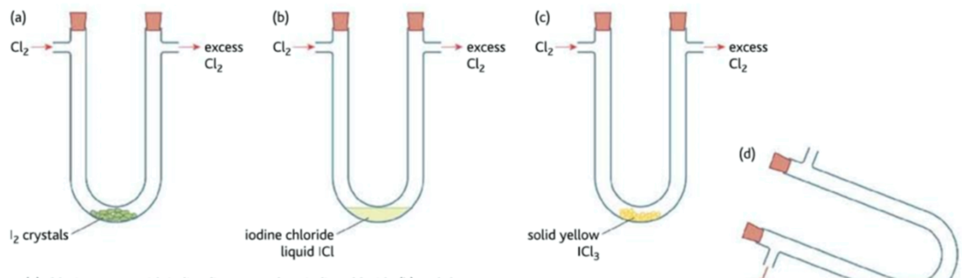
If chlorine gas is passed through a U-tube containing solid iodine, a brown liquid, iodine(I) chloride, ICl is formed with a brown vapour above it. The bottom of the U-tube gets hot – the reaction is exothermic. If more chlorine gas is passed though the U-tube a yellow solid, iodine(III) chloride, ICl_3 is formed:

$$I_2(s) + Cl_2(g) \rightarrow 2ICl(l)$$

$$ICl(l) + Cl_2(g) \rightleftharpoons ICl_3(s)$$

If the chlorine supply is removed, and the U-tube is tipped horizontal, the yellow crystals disappear and a brown gas is seen. The equilibrium is moving back to the left to reform the iodine(I) chloride and chlorine. These were separated from the reaction mixture when the U-tube was tipped. If the chlorine supply is attached again the yellow solid forms as the equilibrium moves to the right, opposing the increase in chlorine concentration and producing iodine(III) chloride again.

This is pg 205 from the Edexcel Chemistry Textbook



In (a) chlorine reacts with iodine first to produce iodine chloride (b) and then iodine(III) chloride (c). When the U tube is tilted, the iodine(III) chloride decomposes to reform iodine chloride. The equilibrium moves to the left.

fig. 2.7.5 Investigating the equilibrium between iodine(I) chloride, iodine(III) chloride and chlorine.

Methane From Methane Hydrate

There are huge amounts of methane trapped as solid methane hydrate in ice structures deep in the oceans (see **fig. 2.7.7(a)**). Methane hydrate is in equilibrium with gaseous methane and water:

$$\text{methane hydrate(s)} \rightleftharpoons \text{methane(g)} + \text{water(l)}$$

The forward reaction is endothermic. According to Le Chatelier's principle, if the Earth's temperature rises, the equilibrium will move to the right to oppose this change, releasing more methane into the atmosphere.

If there is an increase in pressure, since methane is a gas, the equilibrium will move to the left. Moving to the left turns the methane gas back into solid methane hydrate, which does not exert a pressure, so this change in the equilibrium reduces the pressure.

It has been suggested that the sudden release of large amounts of methane gas from methane hydrate deposits could be a cause of past and future climate change.

This is pg 207 from the Edexcel Chemistry Textbook