Applications of the equilibrium law

FACTORS AFFECTING THE POSITION OF EQUILIBRIUM

Change in concentration

$$C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

If more ethanoic acid is added the concentration of ethanoic acid increases so that at the point of addition:

$$K_c \neq \frac{[\text{ester}] \times [\text{water}]}{[\text{acid}] \times [\text{alcohol}]}$$

To restore the system so that the equilibrium law is obeyed the equilibrium will move to the right, so that the concentration of ester and water increases and the concentration of the acid and alcohol decreases.

Change in pressure

If there is an overall volume change in a gaseous reaction then increasing the pressure will move the equilibrium towards the side with less volume. This shift reduces the total number of molecules in the equilibrium system and so tends to minimize the pressure.

$2NO_2(g)$	$\rightleftharpoons$	$N_2O_4(g)$
brown		colourless
(2 vols)		(1 vol)

If the pressure is increased the mixture will initially go darker as the concentration of NO_2 increases then become lighter as the position of equilibrium is re-established with a greater proportion of N_2O_4.

Change in temperature

In exothermic reactions heat is also a product. Taking the heat away will move the equilibrium towards the right, so more products are formed. The forward reaction in exothermic reactions is therefore increased by lowering the temperature

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H^\ominus = -24 \text{ kJ mol}^{-1}$$

brown — colourless

Lowering the temperature will cause the mixture to become lighter as the equilibrium shifts to the right.

For an endothermic reaction the opposite will be true.

Unlike changing the concentration or pressure, a change in temperature will also change the value of K_c. For an exothermic reaction the concentration of the products in the equilibrium mixture decreases as the temperature increases, so the value of K_c will decrease. The opposite will be true for endothermic reactions.

e.g. $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ $\Delta H^\ominus = +41 \text{ kJ mol}^{-1}$

T / K	K_c
298	1.00×10^{-5}
500	7.76×10^{-3}
700	1.23×10^{-1}
900	6.01×10^{-1}

↓ increase

Adding a catalyst

A catalyst will increase the rate at which equilibrium is reached, as it will speed up both the forward and reverse reactions equally, but it will have no effect on the position of equilibrium and hence on the value of K_c.

APPLICATION OF EQUILIBRIUM AND KINETICS TO INDUSTRIAL PROCESSES

The aim in industry is to produce the highest possible yield of the required product in the shortest time for the least cost (both financial and to the environment) in order to maximize profits.

Haber process

Ammonia is used in the manufacture of fertilizers and in the production of nitric acid.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H^\ominus = -92 \text{ kJ mol}^{-1}$$

The hydrogen is obtained from natural gas and the nitrogen from the fractional distillation of liquid air.

Conditions Four volumes of reactants produce two volumes of product, so a high pressure will be required. Increasing the pressure will also increase the number of particles per unit volume. This increases the rate at which equilibrium is reached. In practice a pressure of about 250 atm is used. Since it is an exothermic reaction a low temperature is required to give a high yield of ammonia. However, lowering the temperature will decrease the rate of reaction and it will take longer to reach equilibrium. What is required is the **optimum temperature** where the best compromise between yield and rate is reached. A temperature of about 450 °C is usually used.

In order to increase the rate at which equilibrium is reached (but not the yield) an iron catalyst is used. It is used in a finely divided form (small pieces) so that the surface area is maximized to increase its efficiency. Even when all these conditions are in place the yield is only about 15%.

Contact process

Sulfuric acid is manufactured by the Contact process. It is the most industrially produced chemical, with over 150 million tonnes being produced world-wide every year. It is used for fertilizers, paints, detergents, and fibres, and as a feedstock for other chemicals.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H^\ominus = -197 \text{ kJ mol}^{-1}$$

The sulfur dioxide is obtained from burning sulfur or sulfide ores, and the oxygen is obtained from the fractional distillation of liquid air.

Conditions Three volumes are converted into two volumes, so a high pressure will favour the production of sulfur trioxide. The reaction is exothermic so an optimum temperature, which is a compromise between yield and rate, is required. In practice a yield of more than 99% is obtained when the pressure is 2 atm at a temperature of 450 °C. The catalyst used is vanadium(V) oxide. Since the yield is so high at 2 atm pressure it is uneconomical and unnecessary to build the converter to withstand higher pressures.