Edexcel

A - Level

Chemistry

CODE: (WCH11)

Topic 13

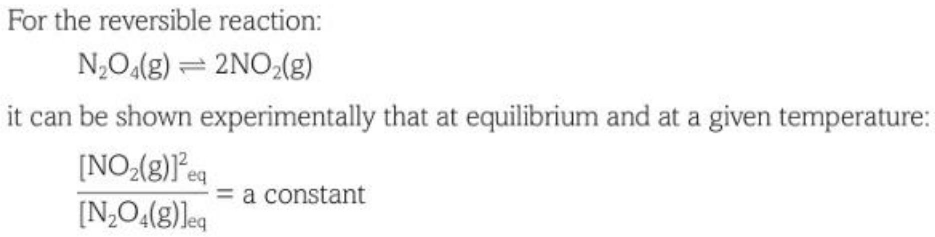
Chemical equilibria

13A 1 Equilibrium constant, K_C

HOMOGENEOUS REACTIONS

A homogeneous reaction is one in which all reactants and products are in the same phase. For example, all are gases or all are in aqueous solution.

In this section, we will study quantitatively how changes in concentration affect the equilibrium position.
For the reversible reaction:



For the reversible reaction:

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

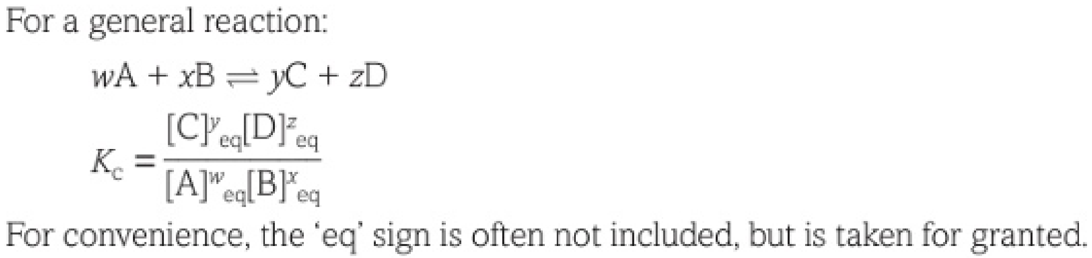
it can be shown experimentally that at equilibrium and at a given temperature:

$$\frac{[NO_2(g)]^2_{eq}}{[N_2O_4(g)]_{eq}} = \text{a constant}$$

This value is called the equilibrium constant and is given the symbol K_c.

There are two ways of obtaining a value for the equilibrium constant:

- the first is by experimentation, and this is the method we will look at in this section
- the second is by calculation using thermodynamic equations, and this will be covered in Section 13A.5. For a general reaction:



For a general reaction:

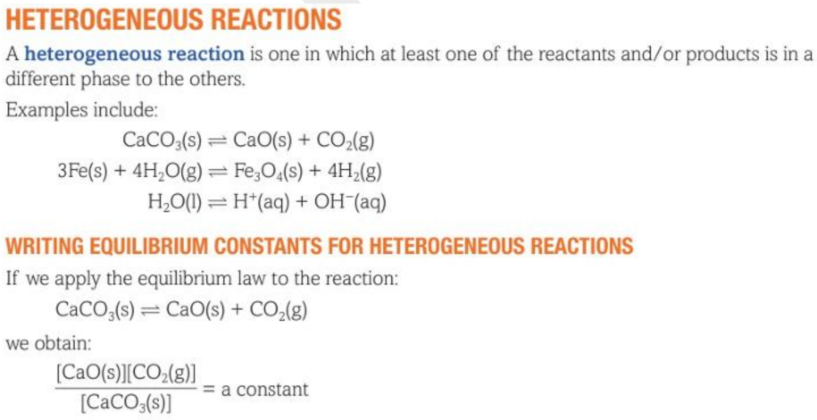
$$wA + xB \rightleftharpoons yC + zD$$

$$K_c = \frac{[C]^y_{eq}[D]^z_{eq}}{[A]^w_{eq}[B]^x_{eq}}$$

For convenience, the 'eq' sign is often not included, but is taken for granted.

DETERMINATION OF THE EQUILIBRIUM CONSTANT

To determine the value of the equilibrium constant for a reaction, known amounts of reactants are allowed to reach equilibrium with their products. At equilibrium, the amount of one of the substances is measured and the amounts of the others can be calculated using the stoichiometry of the equation.



HETEROGENEOUS REACTIONS

A **heterogeneous reaction** is one in which at least one of the reactants and/or products is in a different phase to the others.

Examples include:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

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

WRITING EQUILIBRIUM CONSTANTS FOR HETEROGENEOUS REACTIONS

If we apply the equilibrium law to the reaction:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

we obtain:

$$\frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]} = \text{a constant}$$

However, the concentration of a solid at a given temperature is determined by its density, which has a constant value. Hence, the expression can be simplified to:

$$[CO_2(g)] = \text{a constant}$$

This constant is given the symbol K_c.

So, $K_c = [CO_2(g)]$ for the above equilibrium.

Similarly, for the equilibrium:

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

$$K_c = \frac{[H_2(g)]^4}{[H_2O(g)]^4}$$

13A 2 Equilibrium constant, K_p

HOMOGENEOUS REACTIONS

For reversible reactions involving gases we can express the concentrations of the reactants and products in terms of their partial pressures. The partial pressure of an individual gas in a mixture of gases is defined as the pressure that the gas would exert if it alone occupied the volume of the mixture. The total pressure of the mixture is then equal to the sum of the partial pressures of all the gases present in the mixture.

If we have a mixture of two gases, A and B, then the total pressure, p, of the mixture is related to the partial pressures of A and B by the following equation:

$$p = p_A + p_B$$

where p_A = partial pressure of A and p_B = partial pressure of B.

For the general reaction:

$$wA(g) + xB(g) \rightleftharpoons yC(g) + zD(g)$$

we can define another equilibrium constant, K_p, in terms of partial pressures:

$$K_p = \frac{(p_C)^y(p_D)^z}{(p_A)^w(p_B)^x}$$

CALCULATING PARTIAL PRESSURES

The partial pressure of an individual gas in a mixture of gases is calculated by multiplying its mole fraction by the total pressure, for example:

$$p_A = x_A p$$

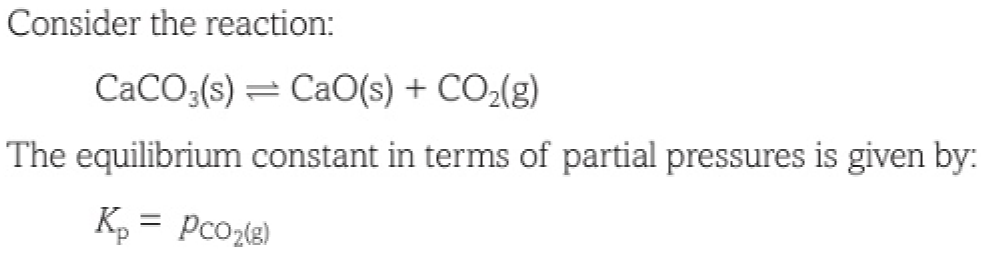
where x_A = the mole fraction of gas A in the mixture.

$$\text{mole fraction of A} = \frac{\text{number of moles of A}}{\text{total number of moles of gas}}$$

HETEROGENEOUS REACTIONS

SOLIDS AND GASES

For solids that are in equilibrium with gases, the partial pressure terms of any solids are not included in the expression for Kp. You will recall that Kc has a similar rule.

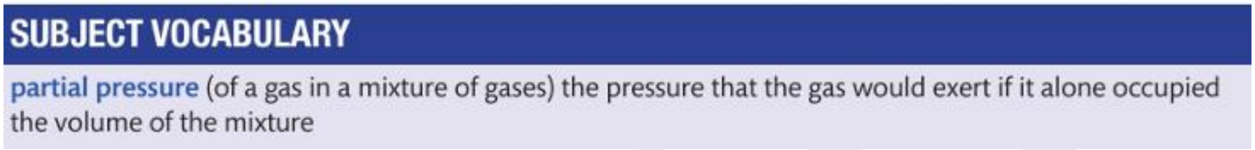


Consider the reaction:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The equilibrium constant in terms of partial pressures is given by:

$$K_p = p_{CO_2(g)}$$



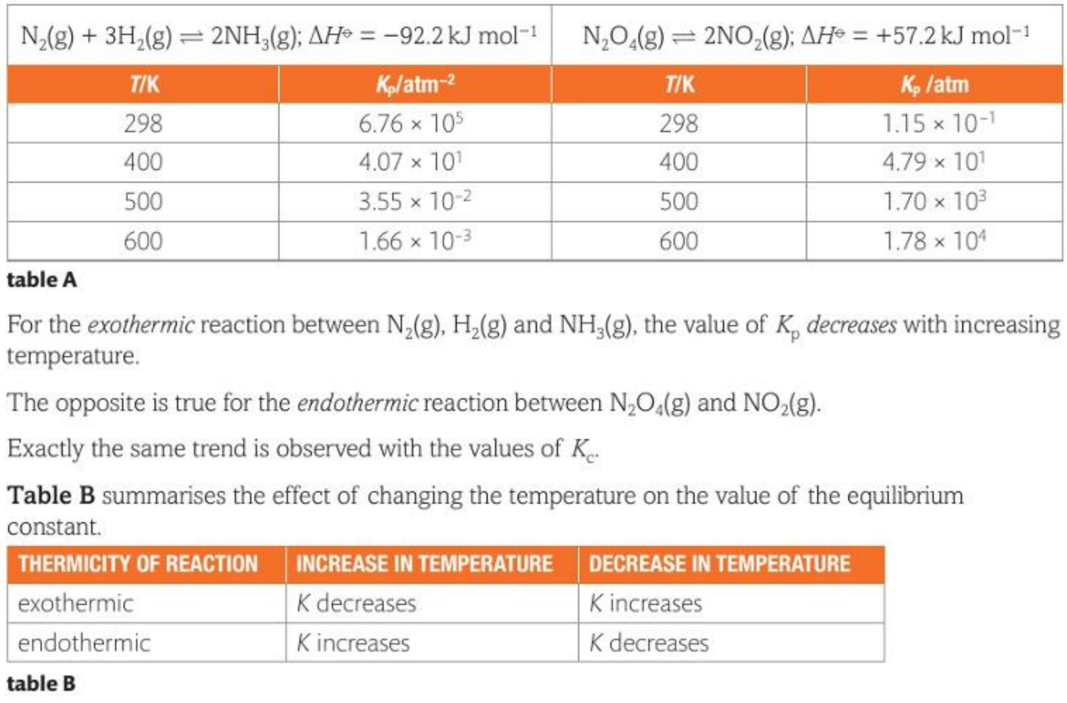
SUBJECT VOCABULARY

partial pressure (of a gas in a mixture of gases) the pressure that the gas would exert if it alone occupied the volume of the mixture

13A 3 Factors affecting equilibrium constant 1

EFFECT OF TEMPERATURE ON K_p, AND K_c

In this section we will discuss the effects of temperature on equilibrium constants. Table A gives the values of the equilibrium constant, K_p, at different temperatures for two gaseous reactions.



$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta H^{\ominus} = -92.2$ kJ mol^{-1}		$N_2O_4(g) \rightleftharpoons 2NO_2(g)$; $\Delta H^{\ominus} = +57.2$ kJ mol^{-1}	
T/K	K_p/atm^{-2}	T/K	K_p /atm
298	6.76×10^5	298	1.15×10^{-1}
400	4.07×10^1	400	4.79×10^1
500	3.55×10^{-2}	500	1.70×10^3
600	1.66×10^{-3}	600	1.78×10^4

table A

For the *exothermic* reaction between $N_2(g)$, $H_2(g)$ and $NH_3(g)$, the value of K_p *decreases* with increasing temperature.

The opposite is true for the *endothermic* reaction between $N_2O_4(g)$ and $NO_2(g)$.

Exactly the same trend is observed with the values of K_c.

Table B summarises the effect of changing the temperature on the value of the equilibrium constant.

THERMICITY OF REACTION	INCREASE IN TEMPERATURE	DECREASE IN TEMPERATURE
exothermic	*K* decreases	*K* increases
endothermic	*K* increases	*K* decreases

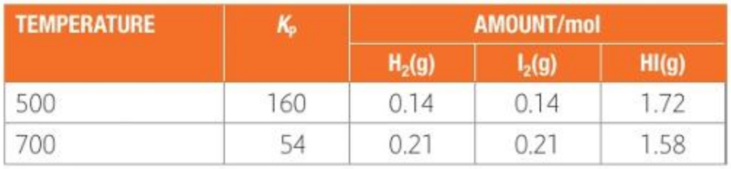
table B

CHANGE IN TEMPERATURE ALTERS THE EQUILIBRIUM POSITION

If the equilibrium constant for a reaction changes with a change in temperature, then it follows that the equilibrium position also changes. This is illustrated by the data in table C, which shows the value of K_c, and the amounts of reactants and products at equilibrium for the reaction between hydrogen and iodine to form hydrogen iodide:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad \Delta H^{\circ} = -9\,\text{kJ mol}^{-1}$$

In each case, one mole of hydrogen is mixed with one mole of iodine and equilibrium is allowed to establish, at the given temperature, in a vessel of volume 1 dm^3.



TEMPERATURE	K_p	AMOUNT/mol		
		$H_2(g)$	$I_2(g)$	$HI(g)$
500	160	0.14	0.14	1.72
700	54	0.21	0.21	1.58

table C

13A 4 Factors affecting equilibrium constant 2

EFFECT OF CONCENTRATION

The most important thing to appreciate is that the only factor that can change the value of K_c, is a change in temperature. That is, K_c, is constant at a given temperature.

When the concentration of one of the components of an equilibrium mixture is altered, there is an immediate change in the reaction quotient, Q_c, which is the mathematical relationship between the concentrations of the components.

At this point, the reaction quotient is no longer equal to the equilibrium constant, K_c. Therefore, the equilibrium composition changes until the reaction quotient and equilibrium constant become equal. The following examples illustrate this process.

REACTION QUOTIENT, Qc

For a general reaction:

$$wA + xB \rightleftharpoons yC + zD$$

the reaction quotient, Q_c, is given by the expression:

$$Q_c = \frac{[C]^y[D]^z}{[A]^w[B]^x}$$

where the concentration terms are not necessarily those at equilibrium.

At equilibrium $Q_c = K_c$.

QUALITATIVE PREDICTIONS

In Topic 9 (Book 1: IAS) we said that qualitative predictions do not always give us the correct result. The worked example below shows this.

WORKED EXAMPLE 2

The amounts of N_2, H_2 and NH_3 in an equilibrium mixture are 0.510 mol, 0.197 mol and 0.204 mol, respectively:

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

The total volume of the gaseous mixture is 1.00 dm^3.

Work out the direction of the shift in equilibrium position if 0.140 mol of N_2 gas is suddenly added to the equilibrium system at constant temperature and pressure.

Show your calculations.

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{(n_{NH_3}/V)^2}{(n_{N_2}/V)(n_{H_2}/V)^3}$$

where n is the amount (in mol) and V is the total volume (in dm^3) of the mixture.

(Remember that concentration = amount ÷ volume.)

Step 1: Calculation of K_c.

$$K_c = \frac{(0.204)^2/1^2}{(0.510)/1 \times (0.197)^3/1^3} = 10.7$$

Step 2: Calculation of new total number of moles of gas.

Original total moles of gas = (0.510 + 0.197 + 0.204) = 0.911

New total moles of gas = (0.911 + 0.140) = 1.051

Step 3: Calculation of new volume of gas mixture.

Since the pressure remains constant, the gas mixture will expand. If we assume that the gas mixture behaves like an ideal gas, then the volume of gas is proportional to the number of moles:

$$n_1/V_1 = n_2/V_2$$

So the new volume of the gas mixture =

$$(1.051 \div 0.911) \times 1\ dm^3 = 1.154\ dm^3$$

Step 4: Calculation of Q_c immediately after the addition of nitrogen.

$$Q_c = \frac{(0.204)^2/(1.154)^2}{(0.650)/1.154 \times (0.197)^3/(1.154)^3} = 11.15$$

Step 5: Compare Q_c with K_c.

11.15 > 10.7, therefore $Q_c > K_c$.

For equilibrium to be re-established, Q_c must decrease. This can only happen by the equilibrium shifting to the left, to increase the denominator in the equation.

The addition of more nitrogen, at constant pressure, results in a shift of the equilibrium position to the left. Our prediction told us that the equilibrium would shift to the right, away from the nitrogen added.

The problem with making predictions is that two conflicting changes are occurring here:

1. the increase in the number of moles of nitrogen should result in a shift of equilibrium to the right
2. the increase in volume should result in a shift to the left.

We have no way of knowing which effect is greater unless we perform the calculations shown above.

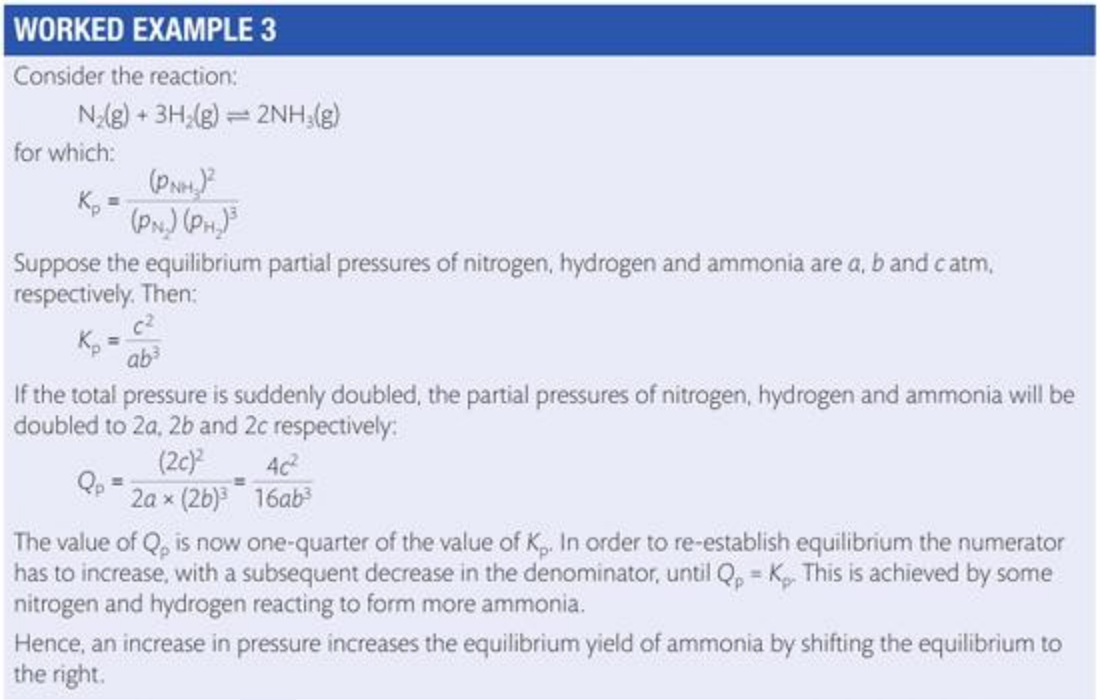
EFFECT OF PRESSURE

As with concentration, a change in pressure, at constant temperature, on an equilibrium system containing gases has no effect on the value of either Kc or Kp.

Once again, any change in the equilibrium position occurs in order to maintain the equilibrium constant at a constant value.

If the partial pressure of only one of the component gases is changed, then the overall effect on Kp, can be predicted in the same way the effects of changes in concentration on Kc, were described in the previous section.

However, if the total pressure of a gaseous system is suddenly increased or decreased, then the partial pressures of all the gases will either increase or decrease. The effect on the position of equilibrium can be explained using the equilibrium law. This is shown in the following worked example.



WORKED EXAMPLE 3

Consider the reaction:

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

for which:

$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3}$$

Suppose the equilibrium partial pressures of nitrogen, hydrogen and ammonia are *a*, *b* and *c* atm, respectively. Then:

$$K_p = \frac{c^2}{ab^3}$$

If the total pressure is suddenly doubled, the partial pressures of nitrogen, hydrogen and ammonia will be doubled to 2*a*, 2*b* and 2*c* respectively:

$$Q_p = \frac{(2c)^2}{2a \times (2b)^3} = \frac{4c^2}{16ab^3}$$

The value of Q_p is now one-quarter of the value of K_p. In order to re-establish equilibrium the numerator has to increase, with a subsequent decrease in the denominator, until $Q_p = K_p$. This is achieved by some nitrogen and hydrogen reacting to form more ammonia.

Hence, an increase in pressure increases the equilibrium yield of ammonia by shifting the equilibrium to the right.

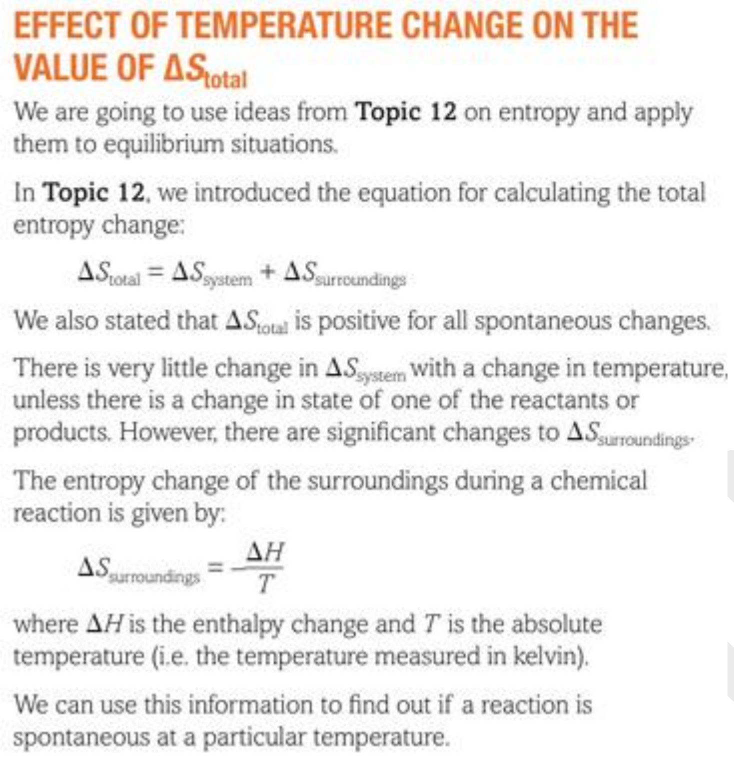
EFFECT OF ADDING A CATALYST

A catalyst does not influence the value of the equilibrium constant or equilibrium position for a reaction. It increases the rate of both forward and backward reactions, but does not affect the final concentrations of reactants and products at equilibrium. Therefore, a catalyst does not affect the equilibrium constant.

SUBJECT VOCABULARY

reaction quotient a measure of the relative amounts of products and reactants present during a reaction at any given time

13A 5 RELATING ENTROPY TO EQUILIBRIUM CONSTANTS



EFFECT OF TEMPERATURE CHANGE ON THE VALUE OF ΔS_{total}

We are going to use ideas from **Topic 12** on entropy and apply them to equilibrium situations.

In **Topic 12**, we introduced the equation for calculating the total entropy change:

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

We also stated that ΔS_{total} is positive for all spontaneous changes.

There is very little change in ΔS_{system} with a change in temperature, unless there is a change in state of one of the reactants or products. However, there are significant changes to $\Delta S_{surroundings}$.

The entropy change of the surroundings during a chemical reaction is given by:

$$\Delta S_{surroundings} = -\frac{\Delta H}{T}$$

where ΔH is the enthalpy change and T is the absolute temperature (i.e. the temperature measured in kelvin).

We can use this information to find out if a reaction is spontaneous at a particular temperature.

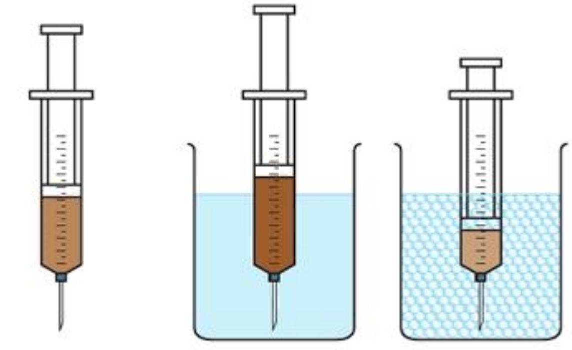
RELATIONSHIP BETWEEN TOTAL ENTROPY CHANGE, ΔS $_{total}$ AND THE EQUILIBRIUM CONSTANT, K

For a reversible reaction that can reach equilibrium, the equilibrium position can be reached from either side of the reaction. This means that both the forward and the backward reactions are spontaneous, so ΔS $_{total}$ must be positive in both directions.

You may think this is impossible. To explain it we can look at the equilibrium reaction

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

colourless brown



(a) room temperature (b) hot water (c) crushed ice

fig B A mixture of N_2O_4 gas and NO_2 gas in a gas syringe: (a) at room temperature; (b) immersed in hot water; (c) immersed in crushed ice.

The differences in colour in fig B show how the position of equilibrium changes as the temperature changes.
In hot water, the mixture becomes darker brown. The equilibrium position has shifted to the right to produce more NO_2.

Note that the volume has become larger because the mixture expands as it gets hotter.

In iced water, the mixture becomes lighter brown. This shows that the equilibrium position has shifted to the left to produce more N_2O_4.

Note that the volume has become smaller because the reaction mixture has cooled.
Fig C shows how it is possible for the reaction to be spontaneous in each direction.

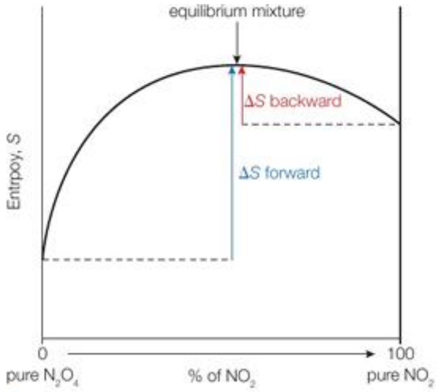


fig C A graph of entropy against percentage NO_2 in a mixture of N_2O_4 and NO_2.

At equilibrium, the total entropy change is zero and

$$\Delta S_{\text{total}}\,[\text{forward reaction}] = \Delta S_{\text{total}}\,[\text{backward reaction}]$$

The relationship between the total entropy of the reaction and the equilibrium constant is given by

$$\Delta S_{\text{total}} = R\ln K$$

where K can be K_c or K_p, and R is the gas constant.

Note that this matches with the conclusion that a high value of K corresponds to a large positive total entropy change.

USING TOTAL ENTROPY CHANGE TO CALCULATE AN EQUILIBRIUM CONSTANT

As mentioned above, $\Delta S_{\text{total}} = R\ln K$.

Rearranging the equation gives us:

$$\ln K = \frac{\Delta S_{\text{total}}}{R}$$

So:

$$K = e^{\Delta S_{\text{total}}/R}$$

RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT AND POSITION OF EQUILIBRIUM

There is no firm rule about the relationship between the equilibrium constant, K, and the position of equilibrium of the reaction. However, as a general rule we can say that a very large value of K suggests that the position of equilibrium is well over to the products side (i.e. the right-hand side of the equation).

Similarly, a very small value of K suggests that the position of equilibrium is well over to the reactants side (i.e. the left-hand side of the equation).