Extension Work

This work is not mandatory. It is to assist you in revision of unit 2.

Watch the following clip.

https://drive.google.com/file/d/1VwDOXNdQLwIcl_yESmyHPBsVtxZqTu1D/view?usp=sharing

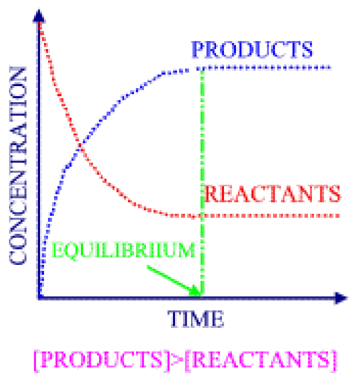
The point when the rates of the forward and reverse reactions in a reversible reaction are equal is known as equilibrium.

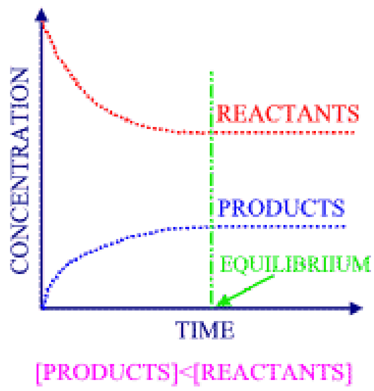
Consider reactants A and B producing C.

$$A + B \rightleftharpoons C$$

At equilibrium, the forward and reverse reactions **still continue**, but at the **same rate**. This is a position of dynamic (or moving) equilibrium. At equilibrium, the composition of the reactants and products **remains constant** indefinitely. **Remember** that equilibrium does not mean that the concentration of reactants and products are equal.

The two graphs below show how the possible concentrations of reactants and products may alter during the course of a reaction.





At equilibrium, there is a greater concentration of products.

At equilibrium, there is a greater concentration of reactants.

Equilibrium Constant (K)

The equilibrium constant (upper case K) characterises the equilibrium composition of the reaction mixture.
*In Advanced Higher Chemistry, the letter k/K is used on several occasions. It is important to note when to use upper case (K) or lower case (k).

Consider the following reaction

$aA + bB \rightleftharpoons cC + dD$ (a, b, c and d are the stoichiometric coefficients, i.e. the numbers of the balanced equation)

The equilibrium constant, $K = \frac{[\text{Products}]}{[\text{Reactants}]}$ ← square brackets mean concentration

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

This can be found on page 4 of the data booklet.

[A], [B], [C] and [D] are the equilibrium concentrations of substances A, B, C and D.

Homogeneous Equilibria

The Haber process is considered to be an example of a homogeneous equilibrium as all reactants are in the same physical state.

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

The expression for the equilibrium constant is given by

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

Heterogeneous Equilibria

In a heterogeneous equilibrium the substances are in more than one physical state.

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

$$K = \frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]}$$

$K = [CO_2]$

In heterogeneous equilibria, the concentration of solids and pure liquids e.g. H_2O are taken as 1.

Calculating equilibrium constant K from concentration

An equilibrium exists in the reaction between nitrogen monoxide and oxygen to form nitrogen dioxide.

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

Calculate the equilibrium constant given the following information for the mixture of gaseous O_2, NO and NO_2 at **500 Kelvin.**

(The concentrations of substances are normally quoted at a specific temperature. The unit of temperature in Kelvins is often used in such examples).

0 degrees Celsius = 273 Kelvin.

$O_2 = 1.0 \times 10^{-3}$ mol l^{-1} / $NO = 1.9 \times 10^{-3}$ mol l^{-1} / $NO_2 = 5.0 \times 10^{-2}$ mol l^{-1}

The equilibrium constant, $K = \frac{[\text{Products}]}{[\text{Reactants}]}$ $\quad K = \frac{[NO_2]^2}{[O_2][NO]^2}$ $\quad K = \frac{[5.0 \times 10^{-2}]^2}{[1.0\times10^{-3}][1.9\times10^{-3}]^2}$

$K = \underline{6.9 \times 10^5}$

The equilibrium constant, K, has NO UNITS.

The value of the equilibrium constant can indicate the position of equilibrium.

K>1 equilibrium lies to the right (i.e. indicating more products)

K<1 equilibrium lies to the left (i.e. indicating more reactants)

In the example above, as K is much greater than 1, then it can be concluded that equilibrium lies to the right, i.e. there will be a larger composition of products than reactants at equilibrium.

Factors Affecting Equilibrium Constant

The equilibrium constant, K, is independent of changes in concentration, pressure and the addition of a catalyst. These changes may result in equilibrium being achieved faster or slower but they DO NOT alter the actual value of the equilibrium constant K.

The equilibrium constant, K, is affected by changes in TEMPERATURE, i.e. it is temperature dependent (due to this most questions involving equilibrium constant will be quoted at a specific temperature). We can consider the effect of temperature in more detail by looking at an exothermic reaction and an endothermic reaction.

Exothermic

$A + B \rightleftharpoons C + D \quad \Delta H = -ve$

A rise in temperature will shift the equilibrium to the left (knowledge from Higher Chemistry), decreasing the CONCENTRATIONS of products and increasing the CONCENTRATIONS of reactants. This will cause a **decrease in K.**

A decrease in temperature would have the opposite effect.

Endothermic

$E + F \rightleftharpoons G + H \quad \Delta H = +ve$

A rise in temperature will shift the equilibrium to the right (knowledge from Higher Chemistry), increasing the CONCENTRATIONS of products and decreasing the CONCENTRATIONS of reactants. This will cause an **increase in K.**

A decrease in temperature would have the opposite effect.

Revision 2a - Questions

1. Write an expression for K for the following equilibrium reactions:

(a) $CO_2(g) + NO(g) \rightleftharpoons CO(g) + NO_2(g)$

(b) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

2. Consider the equilibrium:

$2HI(g) \rightleftharpoons H_2(g) + I_2(g) \quad \Delta H = -52 \text{ kJ mol}^{-1}$

(a) Write an expression for the equilibrium constant, K.
(b) What would be the effect on the equilibrium constant of
 (i) Increasing the temperature
 (ii) Increasing the pressure
 (iii) Adding more hydrogen iodide

3. The reaction below is known as the Contact process and is carried out in industry.

$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \quad \Delta H = +ve$

(a) Write an expression for *K*, the equilibrium constant for this reaction.

(b) (i) Predict how an increase in temperature would affect the position of equilibrium.
 (ii) Explain the effect this increase in temperature would have on the value of *K*.

4. The following reaction exists in equilibrium:

$2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$

Calculate the value of the equilibrium constant, K, for the decomposition of nitrosyl bromide at 350 Kelvin, given that the equilibrium mixture contains:

NOBr: 0.60 mol l^{-1}

NO: 0.20 mol l^{-1}

Br_2: 0.30 mol l^{-1}

5. Consider the following reaction.

$$CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g)$$

At 900 °C the equilibrium concentrations are:

$[CS_2] = 0{\cdot}012\ mol\ l^{-1}$ $[H_2] = 0{\cdot}0020\ mol\ l^{-1}$

$[H_2S] = 0{\cdot}00010\ mol\ l^{-1}$ $[CH_4] = 0{\cdot}0054\ mol\ l^{-1}$

(*a*) Write down the expression for the equilibrium constant, K, for this reaction.

(*b*) Calculate the value of the equilibrium constant, K, at 900 °C.

6. The value for the equilibrium constant, *K*, for a specific example of the following reaction is equal to 1:

$$\text{acid} + \text{alcohol} \rightleftharpoons \text{ester} + \text{water}$$

(a) (i) Predict the maximum yield of ester, given this value of *K*. 1

(ii) Give **one** reason why this yield might not be achieved in practice. 1

(b) A student suggested that a careful choice of catalyst could increase the yield of ester. Comment on this suggestion. 2

(c) Another pupil suggested that increasing the concentration of the alcohol in the reaction mixture would increase the yield of ester by altering the value of *K*. Comment on this suggestion. 2

7. The reaction

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

has an equilibrium constant of 3·9 at 950 °C.

The equilibrium concentrations of $CO(g)$, $H_2(g)$ and $H_2O(g)$ at 950 °C are given in the table.

Substance	Equilibrium concentration ($mol\ l^{-1}$)
$CO(g)$	$5{\cdot}0 \times 10^{-2}$
$H_2(g)$	$1{\cdot}0 \times 10^{-2}$
$H_2O(g)$	$4{\cdot}0 \times 10^{-3}$

What is the equilibrium concentration of $CH_4(g)$, in $mol\ l^{-1}$, at 950 °C?

Answers

1.a) $$K = \frac{[CO][NO_2]}{[CO_2][NO]}$$

b) $$K = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$$

2.a) $$K = \frac{[H_2][I_2]}{[HI]^2}$$

b) i) Decrease ii) No effect iii) No effect

3.a) $$K = \frac{[O_2][SO_2]^2}{[SO_3]^2}$$

b) i) The forward reaction is endothermic, therefore an increase in temperature would shift the equilibrium to the right.

ii) As the equilibrium would shift to the right, there would be a greater composition of products. This would increase the equlibrium constant.

4. 0.033

5. (a) $$\frac{[CH_4(g)][H_2S(g)]^2}{[CS_2(g)][H_2(g)]^4}$$ K State symbols not required

(b) $$\frac{0.0054 \times 0.00010^2}{0.012 \times 0.0020^4}$$ K

$$\frac{5.4 \times 10^{-11}}{1.92 \times 10^{-13}}$$

= 281/281.25/281.3

6. (a) (i) Yield = 50%

(ii) side reactions *or* impurities

(b) The suggestion is wrong.
A catalyst only brings the reaction to the **same** equilibrium more quickly.

(c) *K* is a constant at a fixed temperature and altering the alcohol concentration will not change the value of *K*.
It will, however, increase the yield of the ester as the forward reaction will be increased.

7. 4.875×10^{-5} mol l^{-1}