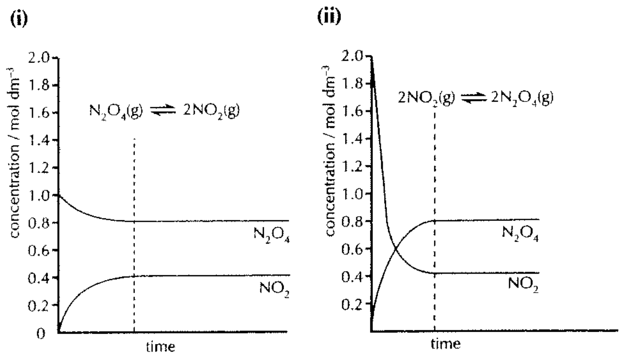
The equilibrium law

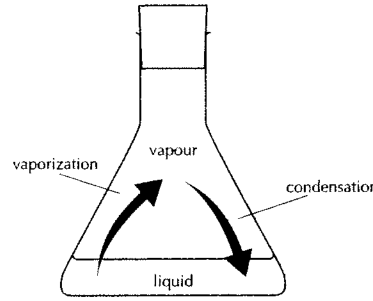
DYNAMIC EQUILIBRIUM

$$A + B \underset{\text{reverse reaction}}{\overset{\text{forward reaction}}{\rightleftharpoons}} C + D$$

Most chemical reactions do not go to completion. Once some products are formed the reverse reaction can take place to reform the reactants. In a closed system the concentrations of all the reactants and products will eventually become constant. Such a system is said to be in a state of **dynamic equilibrium**. The forward and reverse reactions continue to occur, but at equilibrium the rate of the forward reaction is equal to the rate of the reverse reaction.



Graph **(i)** shows the decomposition of N_2O_4. Graph **(ii)** shows the reverse reaction starting with NO_2. Once equilibrium is reached (shown by the dotted line), the composition of the mixture remains constant and is independent of the starting materials.



Dynamic equilibrium also occurs when physical changes take place. In a closed flask, containing some water, equilibrium will be reached between the liquid water and the water vapour. The faster moving molecules in the liquid will escape from the surface to become vapour and the slower moving molecules in the vapour will condense back into liquid. Equilibrium will be established when the rate of vaporization equals the rate of condensation.

$$H_2O(l) \rightleftharpoons H_2O(g)$$

CLOSED SYSTEM

A closed system is one in which neither matter nor energy can be lost or gained from the system, that is, the macroscopic properties remain constant. If the system is open some of the products from the reaction could escape and equilibrium would never be reached.

THE EQUILIBRIUM CONSTANT

Consider the following general reversible reaction in which w moles of A react with x moles of B to form y moles of C and z moles of D.

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

At equilibrium the concentrations of A, B, C, and D can be written as $[A]_{eqm}$, $[B]_{eqm}$, $[C]_{eqm}$, and $[D]_{eqm}$ respectively. The equilibrium law states that for this reaction at a particular temperature

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

where K_c is known as the equilibrium constant.

Examples Formation of sulfur trioxide in the Contact process

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$$K_c = \frac{[SO_3]^2_{eqm}}{[SO_2]^2_{eqm} \times [O_2]_{eqm}}$$

Formation of an ester from ethanol and ethanoic acid

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

$$K_c = \frac{[CH_3COOC_2H_5]_{eqm} \times [H_2O]_{eqm}}{[C_2H_5OH]_{eqm} \times [CH_3COOH]_{eqm}}$$

In both of these examples all the reactants and products are in the same phase. In the first example they are all in the gaseous phase and in the second example they are all in the liquid phase. Such reactions are known as **homogeneous reactions**. Another example of a homogeneous system would be where all the reactants and products are in the aqueous phase.

MAGNITUDE OF THE EQUILIBRIUM CONSTANT

Since the equilibrium expression has the concentration of products on the top and the concentration of reactants on the bottom it follows that the magnitude of the equilibrium constant is related to the position of equilibrium. When the reaction goes nearly to completion $K_c >> 1$. If the reaction hardly proceeds then $K_c << 1$. If the value for K_c lies between about 10^{-2} and 10^2 then both reactants and products will be present in the system in noticeable amounts. The value for K_c in the esterification reaction above is 4 at 100 °C. From this it can be inferred that the concentration of the products present in the equilibrium mixture is roughly twice that of the reactants.

LE CHATELIER'S PRINCIPLE

Provided the temperature remains constant the value for K_c must remain constant. If the concentration of the reactants is increased, or one of the products is removed from the equilibrium mixture then more of the reactants must react in order to keep K_c constant, i.e the position of equilibrium will shift to the right (towards more products). This is the explanation for Le Chatelier's principle, which states that if a system at equilibrium is subjected to a small change the equilibrium tends to shift so as to minimize the effect of the change.

2. equilibrium shifts to minimize effect

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

1. remove product

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

$2NO_2(g)$	$\rightleftharpoons$	$N_2O_4(g)$	$\Delta H^{\ominus} = -24 \text{ kJ mol}^{-1}$
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}	increase ↓
500	7.76×10^{-3}	
700	1.23×10^{-1}	
900	6.01×10^{-1}	

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.

Equilibrium calculations and phase equilibrium

UNITS OF THE EQUILIBRIUM CONSTANT

The units of K_c depend on the powers of the concentrations in the equilibrium expression.
Haber process: units of K_c: $dm^6\ mol^{-2}$

$$K_c = \frac{[NH_3]^2}{[H_2]^3 \times [N_2]} = \frac{\text{concentration}^2}{\text{concentration}^4} = \text{concentration}^{-2} = dm^6\ mol^{-2}$$

If they are the same on the top and bottom then K_c has no units.
Esterification: K_c: no units

$$K_c = \frac{[\text{acid}] \times [\text{alcohol}]}{[\text{ester}] \times [\text{water}]} = \frac{\text{concentration}^2}{\text{concentration}^2}$$

EQUILIBRIUM CALCULATIONS

The equilibrium law can be used either to find the value for the equilibrium constant, or to find the value of an unknown equilibrium concentration.

(a) 23.0 g (0.50 mol) of ethanol was reacted with 60.0 g (1.0 mol) of ethanoic acid and the reaction allowed to reach equilibrium at 373 K. 37.0 g (0.42 mol) of ethyl ethanoate was found to be present in the equilibrium mixture. Calculate K_c to the nearest integer at 373 K.

	$C_2H_5OH(l)$	+	$CH_3COOH(l)$	$\rightleftharpoons$	$CH_3COOC_2H_5(l)$	+	$H_2O(l)$
Initial amount / mol	0.50		1.00		–		–
Equilibrium amount / mol	(0.50 – 0.42)		(1.00 – 0.42)		0.42		0.42
Equilibrium concentration / mol dm^{-3} (where V = total volume)	$\frac{(0.50-0.42)}{V}$		$\frac{(1.00-0.42)}{V}$		$\frac{0.42}{V}$		$\frac{0.42}{V}$

$$K_c = \frac{[\text{ester}] \times [\text{water}]}{[\text{alcohol}] \times [\text{acid}]} = \frac{(0.42/V) \times (0.42/V)}{(0.08/V) \times (0.58/V)} = 4 \text{ (to the nearest integer)}$$

(b) What mass of ester will be formed at equilibrium if 2.0 moles of ethanoic acid and 1.0 moles of ethanol are reacted under the same conditions?

Let x moles of ester be formed and let the total volume be V dm^3.

$$K_c = 4 = \frac{[\text{ester}] \times [\text{water}]}{[\text{alcohol}] \times [\text{ester}]} = \frac{x^2/V^2}{(1.0-x)/V \times (2.0-x)/V} = \frac{x^2}{(x^2 - 3x + 2)}$$

$\Rightarrow 3x^2 - 12x + 8 = 0$

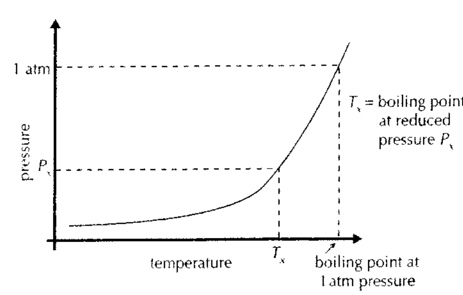
solve by substituting into the quadratic expression $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a} \Rightarrow x = \dfrac{12 \pm \sqrt{144 - 96}}{6}$

$x = 0.845$ or ~~3.15~~ (it cannot be 3.15 as only 1.0 mol of ethanol was taken)
Mass of ester = 0.845 × 88.08 = 74.4 g (Note: IB Diploma Programme chemistry does not examine the use of the quadratic expression.)

PHASE EQUILIBRIUM

Dynamic equilibrium between a liquid and its vapour occurs when the rate of vaporization is equal to the rate of condensation. The vapour pressure of a liquid is the pressure exerted by the particles in the vapour phase. It is independent of the surface area of the liquid or of the size of the container, although in a bigger container it may take longer for the equilibrium to become established. The vapour pressure of any liquid does depend both on the strength of the molecular forces holding the liquid particles together and on the temperature.

The stronger the intermolecular forces the lower the vapour pressure at a particular temperature. Vaporization is an endothermic process, as energy is absorbed to break these intermolecular forces. The enthalpy change required to overcome these forces is known as the enthalpy of vaporization. Water is a covalent substance with a low molar mass, but it has strong hydrogen bonding between its molecules. This explains why water has a relatively low vapour pressure and a relatively high enthalpy of vaporization.



As the temperature increases so does the number of particles with sufficient energy to overcome the attractive forces, and the vapour pressure also increases. A liquid boils when its vapour pressure is equal to the external pressure, as this allows bubbles of vapour to form in the body of the liquid. The boiling point of a liquid can be lowered simply by lowering the external pressure. This principle is useful to purify substances which decompose at or near their normal boiling point, by distilling them under reduced pressure. In mountainous regions where the external pressure is low the boiling point of water can be increased by using a pressure cooker.

IB QUESTIONS – EQUILIBRIUM

1. Which statement is true about chemical reactions at equilibrium?

   A. The forward and backward reactions proceed at equal rates
   B. The forward and backward reactions have stopped
   C. The concentrations of the reactants and products are equal
   D. The forward reaction is exothermic

2. Chemical equilibrium is referred to as **dynamic** because, at equilibrium, the

   A. equilibrium constant changes.
   B. reactants and products keep reacting.
   C. rates of the forward and backward reactions change.
   D. concentrations of the reactants and products continue to change.

3. What is the equilibrium expression for the reaction: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$?

   A. $K_c = \frac{[NH_3]}{[N_2][H_2]}$ **C.** $K_c = \frac{2[NH_3]}{3[N_2][H_2]}$

   B. $K_c = \frac{2[NH_3]}{[N_2][H_2]}$ **D.** $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

4. For a reaction which goes to completion, the equilibrium constant, K_c, is:

   A. >>1 **B.** <<1 **C.** = 1 **D.** = 0

5. The equilibrium constant for the reaction below is 1.0×10^{-14} at 25 °C and 2.1×10^{-14} at 35 °C. What can be concluded from this information?

   $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

   A. $[H_3O^+]$ decreases as the temperature is raised.
   B. $[H_3O^+]$ is greater than $[OH^-]$ at 35 °C.
   C. Water is a stronger electrolyte at 25 °C.
   D. The ionization of water is endothermic.

6. Ethanol is manufactured from ethene using the reaction below:

   $C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g) \quad \Delta H = -46$ kJ

   Which conditions favour the highest yield of ethanol?

   A. High pressure and low temperature
   B. High pressure and high temperature
   C. Low pressure and low temperature
   D. Low pressure and high temperature

7. N_2O_4 and NO_2 produce an equilibrium mixture according to the equation below:

   $N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = 57.2$ kJ mol^{-1}

   An increase in the equilibrium concentration of NO_2 can be produced by increasing which of the factors below?

   I. Pressure II. Temperature

   A. I only **C.** Both I and II
   B. II only **D.** Neither I nor II

8. Which change(s) will increase the amount of $SO_3(g)$ at equilibrium?

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

   I. Increasing the temperature
   II. Decreasing the volume
   III. Adding a catalyst

   A. I only **C.** I and III only
   B. II only **D.** I, II and III

9. For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92$ kJ

   What conditions will produce the highest percentage of NH_3 at equilibrium?

   A. High pressure and high temperature
   B. High pressure and low temperature
   C. Low pressure and high temperature
   D. Low pressure and low temperature

HL

10. The reaction between sulfur dioxide and oxygen occurs according to the equation below:

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

    A higher equilibrium concentration of SO_3 will be produced by all of the following changes in reaction conditions EXCEPT

    A. increasing the pressure. **C.** adding a catalyst.
    B. adding more O_2. **D.** decreasing the temperature.

11. The reaction between methane and hydrogen sulfide is represented by the equation below:

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

    What is the equilibrium expression for this reaction?

    A. $[CS_2][H_2]/[CH_4][H_2S]$
    B. $4[CS_2][H_2]/2[CH_4][H_2S]$
    C. $[CS_2] + 4[H_2]/[CH_4] + 2[H_2S]$
    D. $[CS_2][H_2]^4/[CH_4][H_2S]^2$

12. At 35 °C $K_c = 1.6 \times 10^{-5}$ mol dm^{-3} for the reaction

    $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

    Which relationship must be correct at equilibrium?

    A. [NO] = [NOCl] **C.** $[NOCl]<[Cl_2]$
    B. $2[NO]=[Cl_2]$ **D.** [NO]<[NOCl]

13. Methanol can be produced from carbon monoxide and hydrogen according to the equation:

    $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

    In a certain equilibrium mixture, [CO] = 0.2 mol dm^{-3}, $[H_2]$ = 0.1 mol dm^{-3}, $[CH_3OH]$ = 2 mol dm^{-3}. What is the value of K_c (dm^6 mol^{-2}) for this reaction?

    A. 1×10^{-3} **C.** 1×10^{2}
    B. 1×10^{-2} **D.** 1×10^{3}