

Anglo-Chinese School (Independent)

Year 5 (2022) IBDP Chemistry HL



TOPIC 7 EQUILIBRIUM

(IBDP syllabus Topic 7)

- 7.1 Equilibrium
 - Essential Idea: Many reactions are reversible. These reactions will reach a state of equilibrium when the rates of the forward and reverse reaction are equal. The position of equilibrium can be controlled by changing the conditions.

(IBDP syllabus Topic 17)

- 17.1 The equilibrium law
 - Essential Idea: The position of equilibrium can be quantified by the equilibrium law. The equilibrium constant for a particular reaction only depends on the temperature.

7.1 Equilibrium

Solution Nature of science:

Obtaining evidence for scientific theories—isotopic labelling and its use in defining equilibrium. (1.8) Common language across different disciplines—the term dynamic equilibrium is used in other contexts, but not necessarily with the chemistry definition in mind. (5.5)

Understandings:

- A state of equilibrium is reached in a closed system when the rates of the forward and reverse reactions are equal.
- The equilibrium law describes how the equilibrium constant (*K_c*) can be determined for a particular chemical reaction.
- The magnitude of the equilibrium constant indicates the extent of a reaction at equilibrium and is temperature dependent.
- The reaction quotient (Q) measures the relative amount of products and reactants present during a reaction at a particular point in time. Q is the equilibrium expression with non-equilibrium concentrations. The position of the equilibrium changes with changes in concentration, pressure, and temperature.
- A catalyst has no effect on the position of equilibrium or the equilibrium constant.

Applications and skills:

- The characteristics of chemical and physical systems in a state of equilibrium.
- Deduction of the equilibrium constant expression (K_c) from an equation for a homogeneous reaction.
- Determination of the relationship between different equilibrium constants (*K_c*) for the same reaction at the same temperature.
- Application of Le Châtelier's principle to predict the qualitative effects of changes of temperature, pressure and concentration on the position of equilibrium and on the value of the equilibrium constant.

Guidance:

- Physical and chemical systems should be covered.
- Relationship between K_c values for reactions that are multiples or inverses of one another should be covered.
- Specific details of any industrial process are not required.

17.1 The equilibrium law

ØNature of science:

Employing quantitative reasoning—experimentally determined rate expressions for forward and backward reactions can be deduced directly from the stoichiometric equations and allow Le Châtelier's principle to be applied. (1.8, 1.9)

Understandings:

- Le Châtelier's principle for changes in concentration can be explained by the equilibrium law.
- The position of equilibrium corresponds to a maximum value of entropy and a minimum in the value of the Gibbs free energy.
- The Gibbs free energy change of a reaction and the equilibrium constant can both be used to measure the position of an equilibrium reaction and are related by the equation, $\Delta G = -RT \ln K$

Applications and skills:

- Solution of homogeneous equilibrium problems using the expression for K_c .
- Relationship between ΔG and the equilibrium constant.
- Calculations using the equation $\Delta G = -RT \ln K$

Guidance:

- The expression $\Delta G = -RT \ln K$ is given in the data booklet in section 1.
- Students will not be expected to derive the expression $\Delta G = -RT \ln K$.
- The use of quadratic equations will not be assessed.

7.1 Equilibrium

7.1.1 Reversible Chemical Reaction

• Consider the following example:

When heated strongly in the open, calcium carbonate decomposes to form calcium oxide and carbon dioxide:

$$CaCO_3$$
 (s) \xrightarrow{heat} CaO (s) + CO₂ (g)

As the carbon dioxide, CO_2 escapes, it is impossible for the calcium oxide, CaO to be converted back to calcium carbonate, $CaCO_3$. We say that the above reaction is irreversible. However, if calcium carbonate is heated in a closed evacuated container (closed system), the following reverse reaction becomes possible.

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

In the closed system, both the forward and reverse reactions take place simultaneously, the reaction is known as a reversible reaction. Reversible reactions are chemical reactions that can take place in both directions and they are denoted by the use of a double headed arrow, \rightleftharpoons .

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

- Reversible reactions have the following characteristics:
 - Reversible reactions can only occur in a closed system, where there is no gain or loss of chemicals to or from the surroundings.
 - The reaction that proceeds from left to right is known as the forward reaction.
 - The reaction that proceeds from right to left is known as the reverse reaction.
 - At equilibrium, the rates of the forward and reverse reactions are equal.
 - Equilibrium can be achieved from either direction: you can start with either reactants or products.

7.1.2 Dynamic Equilibrium

- In a reversible reaction, dynamic equilibrium is achieved when the rates of the forward and reverse reaction are equal. At this stage, the concentration of all the reactants and the products remain constant if the temperature is kept constant.
- Consider the following dynamic equilibrium:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

• The dynamic nature of the equilibrium can be demonstrated by adding a small amount of radioactive iodine (I₂*) to the above reaction at a state of equilibrium. Measurements will show that after some time, the mixture contains radioactive hydrogen iodide (HI*), indicating that the reaction is still continuing. After a period of time, the forward reaction rate becomes equal to the reverse reaction rate. A state of dynamic equilibrium is re–established.



• At a microscopic (molecular) scale, reactions continue but both the forward and reverse reaction rates are equal. At dynamic equilibrium, there is no change in macroscopic properties such as colour and density of the reaction mixture.

(TOK: Refer to Pg 313 of chemistry course companion.)

7.1.3 Graph of Concentration vs Time and Rate vs Time

 Consider the decomposition of the colourless gas dinitrogen tetroxide (N₂O₄) to form dark brown nitrogen dioxide (NO₂) gas.

> N_2O_4 (g) $\rightleftharpoons 2NO_2$ (g) Colourless Brown

• The reaction begins with an initial concentration of 0.0400 mol dm⁻³ of N_2O_4 and the formation of NO_2 is indicated by the appearance of a brown colour. The progress of the reaction can be monitored by measuring the intensity of the brown colour with a spectrophotometer.

- According to the chemical equation, 2.0 mol of NO₂ forms for each mole of N₂O₄ that decomposes, so the concentration of N₂O₄ remaining at any time can be computed by subtracting half the concentration of NO₂ formed from the initial concentration of N₂O₄. As time passes, the concentration of N₂O₄ decreases and the concentration of NO₂ increases until both concentrations level off at constant equilibrium values.
- The concentrations of the reactants and products **reach constant values**, not because the reactions stop, but because the **rates of the forward and reverse reactions become equal**. A **dynamic equilibrium is reached**.



 Because reaction rates depend on concentrations, the rate of the forward reaction decreases as the concentration of N₂O₄ decreases, while the rate of the reverse reaction increases as the concentration of NO₂ increases. Eventually, the decreasing rate of the forward reaction and the increasing rate of the reverse reaction become equal.

Therefore, at dynamic equilibrium,

- Rate of forward reaction = Rate of reverse reaction
- The substances are still reacting together although the concentration of the reactants and products remain constant.

- Main features of the equilibrium state:
 - Equilibrium is dynamic
 - The reaction has not stopped but both forward and reverse reactions are still occurring at the same rate.
 - Equilibrium is achieved in a closed system
 - A closed system has no exchange of matter with the surroundings, so equilibrium is achieved where both reactants and products can react and recombine with each other.
 - The concentrations of reactants and products remain constant (but may not be the same) at equilibrium
 - They and being produced and destroyed at an equal rate.
 - There is no change in macroscopic properties
 - Macroscopic properties are observable properties such as colour and density. These do not change as they depend on the concentrations of the components of the mixture.
 - o Equilibrium can be reached from either direction
 - The same equilibrium mixture will result under the same conditions, no matter whether the reaction is started with all reactants, all products or a mixture of both.

Example 1: Chemical System

• Consider the synthesis of ammonia in a closed container which has different concentrations of nitrogen gas and hydrogen gas.

$$N_{2}(g) + 3H_{2}(g) \rightleftharpoons 2NH_{3}(g)$$

• The following two graphs show how the concentration of reactants and products change until the time when equilibrium is reached. Equilibrium can be reached from either direction.



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Example 2: Physical System

• Consider water in a closed flask at constant temperature, as shown in the diagram below.



• Fast moving water molecules at the surface may have enough kinetic energy to escape. As the number of molecules in the vapour phase increases, the pressure of the water vapour increases. As the water vapour becomes more concentrated, the rate of condensation increases. Eventually, the rate of condensation equals the rate of vaporisation when equilibrium is reached.

7.1.4 Activation Energy and Reversibility

- The reversibility of a reaction depends on the relative activation energies of the forward and backward reactions.
- **Irreversible reactions** are those:
 - which have a very high activation energy for the backward reaction ($E_b >> E_f$).
 - in which only the forward reaction takes place.



- **Reversible reactions** are those:
 - those with a smaller difference in their activation energies for the forward and backward reactions.
 - those in which both the forward and backward reactions can take place.

• Case (i): E_f < E_b



- At equilibrium, there is a higher concentration of products than reactants.
- The position of equilibrium lies to the right (products).



- At equilibrium, there is a higher concentration of reactants than products.
- Position of equilibrium lies to the left (reactants).

• Comparison of the Concentration vs Time Graphs for cases (i) and (ii):



Exercise 1

- 1. (a) What are the characteristics of a reversible reaction at dynamic equilibrium?
 - Rate of the forward reaction is equal to the rate of the reverse reaction
 - Forward and reverse reactions must be occurring
 - Concentrations of reactants and products unchanged
 - (b) What condition(s) is / are necessary before dynamic equilibrium can be achieved?
 - Temperature must be constant
 - Closed system
 - Equilibrium is dependent on rates of forward and backward reactions which are temperature dependent
- 2. When the gases sulfur dioxide and oxygen are mixed in a 2:1 ratio by volume, the two gases slowly react to form the sulfur trioxide according to the following equation.

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

Sketch a graph showing how the rates of the forward and reverse reactions change from the time the two gases are mixed to the time the reaction reaches equilibrium. Label the graph clearly.



- 7.1.5 The Reaction Quotient (Q), Equilibrium Constant Expression and Equilibrium constant (K_c)
- **Homogenous** chemical equilibria refer to systems where the reactants and products are in the **same physical states**.
- Consider a reaction at equilibrium,

$$a\mathbf{A} + b\mathbf{B} \rightleftharpoons c\mathbf{C} + d\mathbf{D}$$

• where *a*, *b*, *c*, *d* are the coefficients in the balanced equation, the equilibrium constant expression at a particular temperature is:

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

- \circ [] = concentration of the reactants or products **at equilibrium** in mol dm⁻³.
- Units of $K_c = (\text{mol } dm^{-3})^{c+d-a-b}$
- If the chemical equation is written in the reverse direction, the new equilibrium constant expression, K_c is the reciprocal of the original equilibrium constant expression, K_c .

$$\mathcal{K}_{c}^{\,\prime} = \frac{1}{\mathcal{K}_{c}} = \frac{[\mathsf{A}]^{a}[\mathsf{B}]^{b}}{[\mathsf{C}]^{c}[\mathsf{D}]^{d}}$$

- The value of the new equilibrium constant K_c is the reciprocal of the value of the original equilibrium constant K_c .
- The expression for the reaction quotient, Q, looks like that used to calculate equilibrium constant, K_c but Q can be calculated for any set of conditions, not just for equilibrium.
- The reaction quotient (Q) measures the relative amount of products and reactants present during a reaction at a particular point in time. **Q represents the expression** with non-equilibrium concentrations.

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

- Q can be used to determine which direction a reaction will shift to reach equilibrium.
 - o If $K_c > Q$, a reaction will proceed forward, converting reactants into products.
 - If $K_c < Q$, the reaction will proceed in the reverse direction, converting products into reactants.
 - If $Q = K_c$, the system is at equilibrium.



Consider the neutralisation reaction between aqueous ammonia and dilute ethanoic acid. The balanced chemical equation for the reaction is:

 NH_3 (aq) + CH_3COOH (aq) $\Rightarrow NH_4^+$ (aq) + CH_3COO^- (aq)

Write the equilibrium constant expression for the reaction and state its units.

$$\mathcal{K}_{c} = \frac{\left[\mathsf{NH}_{4}^{+}\right]\left[\mathsf{CH}_{3}\mathsf{COO}^{-}\right]}{\left[\mathsf{NH}_{3}\right]\left[\mathsf{CH}_{3}\mathsf{COOH}\right]}$$

No units.

Example 4

Consider the reaction between iron(III) ions and iodide ions in aqueous solution. The balanced ionic equation is:

$$2Fe^{3+}$$
 (aq) + $3I^{-}$ (aq) $\Rightarrow 2Fe^{2+}$ (aq) + I_{3}^{-} (aq)

Write the equilibrium constant expression for the reaction and state its units.

$$\mathcal{K}_{c} = \frac{\left[\mathsf{Fe}^{2+}\right]^{2} [\mathrm{I}_{3}^{-}]}{\left[\mathsf{Fe}^{3+}\right]^{2} [\mathrm{I}^{-}]^{3}}$$

Units of $K_c = (\text{mol dm}^{-3})^{2+1-2-3} = (\text{mol dm}^{-3})^{-2} = \frac{\text{mol}^{-2} \text{ dm}^6}{1-2}$

In the reaction:

$$CH_{3}COOH(l) + C_{2}H_{5}OH(l) \rightleftharpoons CH_{3}COOC_{2}H_{5}(l) + H_{2}O(l)$$

Write the equilibrium constant expression and state its units.

 $\mathcal{K}_{c} = \frac{[CH_{3}COOC_{2}H_{5}][H_{2}O]}{[CH_{3}COOH][C_{2}H_{5}OH]}$

No units.

Example 6

At a certain temperature the reaction,

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

has an equilibrium constant, $K_c = 13.8$.

If $[CO]_0 = 2.5 \text{ mol } dm^{-3}$; $[Cl_2]_0 = 1.2 \text{ mol } dm^{-3}$; and $[COCl_2]_0 = 5.0 \text{ mol } dm^{-3}$, which direction (forward or reverse) will reaction occur to reach equilibrium? (where []_0 represents the concentration at time = 0 seconds)

 $Q = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = \frac{5.0}{(2.5)(1.2)} = 1.7$

Since $Q < K_c$ the reaction mixture is not an equilibrium mixture. The product concentrations are too low and a net forward reaction will occur until $Q = K_c$.

Enrichment: Heterogeneous Equilibrium

An example of a heterogeneous equilibrium is the thermal decomposition of solid calcium carbonate in a sealed vessel.

$$CaCO_3$$
 (s) \Rightarrow CaO (s) + CO₂ (g)

Other examples of heterogeneous equilibrium include:

- $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(l)$
- $SnO_2(s) + 2CO(g) \rightleftharpoons Sn(s) + 2CO_2(g)$
- $NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$

It has been found that for systems where a pure solid or liquid is in equilibrium with a gas:

- The position of equilibrium is independent of the amount of solid or liquid as long as some is present and the temperature is kept constant
- Concentration terms for pure solids or liquids need not appear in the expression for *K*_c. This is because the concentration of a pure solid or a pure liquid which is similar to its density; which remains almost constant at any temperature.

Exercise 2

Write the equilibrium constant expressions for the reactions below, stating their units.

1. Fe^{3+} (aq) + SCN⁻ (aq) \rightleftharpoons $[Fe(SCN)]^{2+}$ (aq)

$$\mathcal{K}_{c} = \frac{\left[\text{Fe}(\text{SCN})^{2+} \right]}{[\text{Fe}^{3+}][\text{SCN}^{-}]} \quad ; \quad \text{Units} = \text{mol}^{-1} \text{ dm}^{3}$$

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

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$
; Units = mol⁻² dm⁶

3. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$
; Units = mol⁻¹ dm³

4. $4NH_3(g) + 5O_2(g) \Rightarrow 4NO(g) + 6H_2O(g)$

$$K_c = \frac{[NO]^4 [H_2O]^6}{[O_2]^5 [NH_3]^4}$$
; Units = mol dm⁻³

7.1.6 Magnitude of K_c and the Position of Equilibrium

• The equilibrium constant, K_c , is essentially a measure of the extent of a reversible reaction. If the value of K_c is much greater than 1 then the position of equilibrium lies to the products side (or to the right) and the mixture contains mainly the products. An example of this is the oxidation of zinc when it is added to a solution of copper(II) ions.

Zn (s) + Cu²⁺ (aq)
$$\rightleftharpoons$$
 Zn²⁺ (aq) + Cu (s) $K_c = 1 \times 10^{37}$ at 298 K

For this reaction, it has almost gone to completion since K_c is extremely large.

• If the value of *K_c* is lesser than 1 then the position of equilibrium lies to the reactants side (or to the left) and the mixture contains mainly the reactants. An example of this is the dissociation of ethanoic acid in water.

CH₃COOH (aq) \Rightarrow CH₃COO⁻ (aq) + H⁺ (aq) $K_c = 1.8 \times 10^{-5} \text{ mol dm}^{-3} \text{ at } 298 \text{ K}$

From the value of K_c , we can deduce that the acid is mainly in the undissociated molecular form at 298 K and it is a weak acid.

• Relationship between K_c and the extent of a reversible reaction:

Reaction hardly proceeds	Reactants predominate at equilibrium	About equal amounts of products and reactants	Products predominate at equilibrium	Reaction virtually goes to completion
$K_c < 10^{-10}$	$K_c = 10^{-2}$	$K_c = 10^0 = 1$	$K_{c} = 10^{2}$	$K_{c} > 10^{10}$

- The magnitude of K_c only shows the extent of the reaction. It does not indicate the kinetics of the reaction; it does not give any information about the rates of conversion of products into reactants. The value of K_c is only temperature dependent and is not affected by:
 - o changes in the concentrations of the reactants or products,
 - o changes in the pressure of the system for gaseous reactants and products,
 - the use of a catalyst.
- When the stoichiometric coefficient of a reaction has been multiplied by a factor, *n*, the K_c is raised to the power of the factor $(K_c)^n$, so if the reaction has been multiplied by 2, K_c is squared.

Example:

Reaction 1: N₂ (g) + $3H_2$ (g) $\Rightarrow 2NH_3$ (g)

The equilibrium constant for reaction 1, $K_{c1} = \frac{[NH_3]^2}{[N_2][H_2]^3}$

Reaction 2: $2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)$

The equilibrium constant for reaction 2, $K_{c2} = \frac{[NH_3]^4}{[N_2]^2[H_2]^6} = \left(\frac{[NH_3]^2}{[N_2][H_2]^3}\right)^2$

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

The following concentrations were measured for an equilibrium mixture at 500 K:

 $[N_2] = 3.0 \text{ x } 10^{-2} \text{ mol } dm^{-3}$; $[H_2] = 3.7 \text{ x } 10^{-2} \text{ mol } dm^{-3}$; $[NH_3] = 1.6 \text{ x } 10^{-2} \text{ mol } dm^{-3}$

Calculate the value of the equilibrium constant for the forward and backward reactions.

$$\mathcal{K}_{c} = \frac{[\mathrm{NH}_{3}]^{2}}{[\mathrm{N}_{2}][\mathrm{H}_{2}]^{3}} = \frac{\left[1.6 \times 10^{-2}\right]^{2}}{[3.0 \times 10^{-2}]\left[3.7 \times 10^{-2}\right]^{3}} = 1.7 \times 10^{2} \,\mathrm{mol}^{-2} \,\mathrm{dm}^{6}$$

 $K_{\rm c}' = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{K_{\rm c}} = \frac{1}{1.7 \times 10^2} = 5.9 \times 10^{-3} \, {\rm mol}^2 \, {\rm dm}^{-6}$

• In summary, the manipulations of the value of K_c are as such:

	Effect on equilibrium expression	Effect on K_c
Inversing the reaction	Inverts the expression	$\frac{1}{K_c}$
Multiply reaction coefficients by a factor of <i>n</i>	Expression is raised to the power of <i>n</i>	(K _c) ⁿ
Halving the reaction coefficients	Square roots the expression	$\sqrt{K_{c}}$
Adding together 2 reactions	Multiplies the 2 expressions	(K _{c1}) x (K _{c2})

7.2 The Position of Equilibrium

7.2.1 Le Châtelier's Principle

Le Châtelier's principle states that if a change is made to the conditions of a system at dynamic equilibrium, then the position of equilibrium will shift to counteract the change and establish a new equilibrium.

- At equilibrium, if the conditions such as the temperature, concentration and pressure of a closed system are changed, it will cause the system to go into a state to "re-equilibrate". The system will be driven to restore the state of equilibrium by means of changing the composition of the equilibrium mixture. Therefore, the initial composition of the mixture will be different from the final composition of mixture after the state of equilibrium is restored. (The composition of mixture refers to the relative amounts of reactants and products present at equilibrium.)
- However, Le Châtelier's principle is only a generalisation and it cannot be used to explain why the position of equilibrium changes or calculate the exact amount of each of the reactant or product. It is merely used as a prediction of what will happen and it helps to describe qualitatively the position of equilibrium when the system's new dynamic equilibrium is restored.
- On the other hand, the equilibrium expression can be used to calculate quantitatively the percentage composition of the products and reactants of systems in equilibrium.

7.2.2 Changes in Concentration and the Equilibrium Law

• Consider a reaction at equilibrium,

$$\mathsf{A} + \mathsf{B} \rightleftharpoons \mathsf{C} + \mathsf{D}$$

	If some A is added to a reaction at equilibrium	lf s	some A is removed from a reaction at equilibrium
•	The forward reaction works to remove excess A and position of equilibrium shifts from left to right.	•	The reverse reaction works to replace A and the position of equilibrium shifts from right to left.
•	A and B react to produce more C and D.	•	C and D react together to produce more A and B.
•	At the new equilibrium, there will be more C and D but less B compared to the original equilibrium.	•	At the new equilibrium, there will be more B but less C and D compared to the original equilibrium.
•	K _c remains unchanged.	•	K _c remains unchanged.

In the Haber process,

N₂ (g) + 3H₂ (g)
$$\rightleftharpoons$$
 2NH₃ (g)
 $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

- (a) When more nitrogen is added at constant volume, [N₂] increases.
- Using the equilibrium law argument:



- \circ H₂ reacts with the added N₂ to form NH₃.
- \circ [NH₃] increases; [N₂] is increased and [H₂] is decreased since K_c is unchanged.
- The position of equilibrium shifts to the right (favouring products).
- Using the rate argument:



- \circ Adding more N_2 increases its concentration, which causes an increase in the rate of forward reaction.
- \circ This uses up N₂ and H₂, so the rate of the forward reaction slowly decreases.
- \circ \quad As more NH_3 is formed; the rate of the reverse reaction increases.
- The decreasing rate of forward reaction and the increasing rate of backward reaction finally become equal when a new equilibrium is re-established.

- (b) When some ammonia is removed, $[NH_3]$ decreases.
- Using the equilibrium law argument:



- \circ N₂ and H₂ react to make up for the lost NH₃.
- All concentrations of reactants and products decrease since K_c is unchanged.
- The position of equilibrium shifts to the right (favouring products).
- Using the rate argument:



- \circ Removing NH₃ decreases the rate of reverse reaction.
- \circ The rate of forward reaction gradually decreases as the forward reaction uses up N_2 and $H_2.$
- The forward rate slows, while the rate of the reverse reaction increases until they are again equal when a new equilibrium is re–established.

7.2.3 Changes in Pressure and the Equilibrium Law

• Consider a reaction at equilibrium,

4A (a)	+ 3B	$(a) \rightleftharpoons 2C$	(a) +	D (a)
			(9)	

	Pressure of a system in equilibrium is increased		Pressure of a system in equilibrium is decreased
•	Increasing the reaction pressure will cause the position of equilibrium to move in the direction that results in a decrease in the total number of moles of gaseous particles .	•	Decreasing the reaction pressure will cause the position of equilibrium to move in the direction that results in an increase in the total number of moles of gaseous particles.
•	The position of equilibrium shifts from left to right, A and B will react to form C and D.	•	The position of equilibrium shifts from right to left and C and D will react to form A and B.
•	At the new equilibrium, there will be more C and D but less A and B compared to the original equilibrium.	•	At the new equilibrium, there will be more A and B but less C and D compared to the original equilibrium.
•	K_c remains unchanged.	•	<i>K</i> _c remains unchanged.

Note: Pressure changes will only affect reactions in which the number of moles of gaseous reactants is not equal to the number of moles of gaseous products.

Predict what will happen to the equilibrium concentrations when the pressure is increased in the Haber process.

When the pressure is increased in the Haber process,



By Le Châtelier's principle, doubling the pressure doubles all the concentrations, the position of equilibrium shifts to the right (products) to decrease the total number of moles of gases. K_c remains unchanged.

Enrichment: Adding an inert gas – (noble gas or a gas that does not react with those in the reaction).

- If an inert gas is added at constant volume to the equilibrium mixture, the total pressure of the system will increase. However, all concentrations of the different components of the reacting mixture will be unchanged. Hence there is no effect on the position of equilibrium.
- If the gas is added such that the pressure is kept constant, then the total volume must increase. Thus, the concentrations of reactants and products will be reduced. By Le Châtelier's principle, the system will respond by shifting the equation to the side that has the greater number of gaseous molecules.



7.2.4 Changes in Temperature and the Equilibrium Law

• Consider a reaction at equilibrium,

$$A + B \rightleftharpoons C + D$$
 , $\Delta H = +ve \text{ or } -ve$

	Increase in reaction temperature		Decrease in reaction temperature
•	Heat energy is added to the equilibrium mixture.	•	Heat energy is removed from the equilibrium mixture.
•	The position of equilibrium shifts to favour the endothermic reaction to remove some heat energy.	•	The position of equilibrium shifts to favour the exothermic reaction to produce some heat energy.
•	K _c changes.	•	K₀ changes.

- Why K_c changes when temperature changes
- If we assume that the forward and backward reactions are first order in each of the substances and reaction is elementary, then the rate expressions for the forward and backward reactions are:

Forward rate = k_f [A] [B] ; Reverse rate = k_b [C] [D]

where k_f and k_b are the rate constants at a given temperature.

Hence the ratio of these rate constants must also be a constant.

At equilibrium,

Forward rate = Reverse rate

 $k_{f} [A] [B] = k_{b} [C] [D]$

$$\frac{k_{f}}{k_{b}} = \frac{[C][D]}{[A][B]} = K_{c}$$

Therefore, K_c is temperature dependent only.

In the synthesis of ammonia,

 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), \quad \Delta H = -92.4 \text{ kJ mol}^{-1}$

$$K_c = \frac{[\mathsf{NH}_3]^2}{[\mathsf{N}_2][\mathsf{H}_2]^3}$$

- When there is an increase in temperature, it will favour the endothermic reaction as it absorbs heat. Since the backward reaction is endothermic, NH_3 will decompose into N_2 and H_2 .
- The position of equilibrium will shift to the left and [NH₃] decreases while [N₂] and [H₂] increase.
- As there are more reactants than products at the new equilibrium, K_c will decrease.
- The rates of both forward and backward reactions will increase, however, the rate of backward reaction increases more than the rate of forward reaction.

Enrichment Material

The effect of temperature on the solubility of solids in liquids can be explained with the help of Le Châtelier's Principle. If during the dissolving process, heat is absorbed, the solubility increases with increase in temperature. Examples include ammonium chloride and sodium nitrate. In contrast, substances, such as calcium chloride, release heat during dissolving. The solubility of these substances decreases with increase in temperature. The dissolving of gases in liquids is always exothermic and hence the solubility of gases in liquids decreases with an increase in temperature. (This is one reason for chilling carbonated drinks).

7.2.5 Effect of Catalysts on Position of Equilibrium

- A catalyst alters the rate of a chemical reaction without being used up in the reaction. In a reversible reaction, it lowers the activation energies of both the forward and backward reactions.
- Therefore, a catalyst will only change the rate of the reaction but not the position of equilibrium as it increases the reaction rates of the forward and the backward reactions by the same extent.
- Catalysts increases the rate constants of both the forward and backward reactions by the same extent. Adding a catalyst will change the activation of a reaction. The rate constant, k, will in turn be affected. This can be explained by using the Arrhenius $\frac{-E_a}{RT}$.
- Catalysts have no effect on the composition of an equilibrium mixture and *K*_c does not change but equilibrium is reached in a shorter time.

Exercise 3

1. $H_2O(g) + C(s) \rightleftharpoons CO(g) + H_2(g)$ $\Delta H = +131 \text{ kJ mol}^{-1}$

At 1000 °C, the above reaction reaches equilibrium and 1 atmospheric pressure is used.

- (a) What would be the effect on the concentrations of CO and H_2 in the equilibrium mixture if
 - (i) temperature increases to 1500 °C?

When the temperature is increased, the position of equilibrium shifts to the right so as to remove excess heat by favouring the forward endothermic reaction. Therefore, more CO and H_2 will be formed.

(ii) pressure doubles to 2 atm?

When the pressure is increased, the position of equilibrium shifts to the left so as to reduce the pressure by reducing the total number of molecules of gas. Therefore less CO and H_2 will be formed.

(b) If more carbon monoxide was added to the equilibrium mixture, how would this affect the amount of H_2O and H_2 in the equilibrium mixture?

When more CO gas was added, the position of equilibrium shifts to the left so as to remove some of the extra CO and thus more H_2O will be produced in the equilibrium mixture.

When more CO gas was added, the position of equilibrium shifts to the left so as to remove some of the extra CO, which will react with some H_2 and thus less H_2 will be left in the equilibrium.

2. $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$ blood-red complex

In which direction will the equilibrium for the above reaction shift to and hence the predicted observation, when

(a) extra SCN⁻ is added to the equilibrium mixture;

The position of equilibrium will shift to the right to decrease the [SCN⁻].

(b) some Fe^{3+} is removed from the equilibrium mixture.

The position of equilibrium will shift to the left to increase the [Fe³⁺].

- **3.** For the following reversible reactions, in which direction will the position of equilibrium shift to if there is an increase in pressure?
- (a) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

There will be no change in position of equilibrium.

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

The position of equilibrium will shift to the right.

(c) $H_2O(g) + C(s) \rightleftharpoons CO(g) + H_2(g)$

The position of equilibrium will shift to the left.

Summary – Changes of Conditions on Position of Equilibrium and Kc

Consider, $aA + bB \rightleftharpoons cC + dD$ ΔH

	Changes to conditions at equilibrium	Equilibrium position shifts	Equilibrium constant, <i>K</i> c	Rate of reaction
1	Concentration of A and/or B increased	→ right	No change	Increase (forward reaction)
2	Concentration of C and/or D increased	← left	No change	Increase (backward reaction)
3	Pressure is increased (Consider only moles of gaseous products and reactants)	essure is reasedWhen A, B, C and D are gasesonsider only les of gaseous ducts and ctants) \rightarrow right, If $(a + b) > (c + d)$ \leftarrow left, If $(a + b) < (c + d)$		Increase
4	Temperature increased	\rightarrow right, If $\Delta H > 0$ (endothermic)	Increase	Faster for both forward and reverse reactions
		← left, If ∆H < 0 (exothermic)	Decrease	
		No effect If $\Delta H = 0$	No change	
5	Addition of catalyst	No effect	No change	Both forward and backward reactions are speeded up equally



7.2.6 Equilibrium in Industrial Processes

Many important industrial processes are reversible reactions and the physical conditions
affect the position of equilibrium. Industrial manufacturers are concerned with finding the
optimum conditions to maximize the yield of the products. In addition, they must
consider the rate at which the products are being produced or whether it is economically
viable so that the time taken is significant.

The Haber Process

• Ammonia, NH₃, is manufactured by the Haber process which was first patented in 1908. It was a significant achievement as it meant that countries could manufacture artificial fertilisers.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), \Delta H = -92.4 \text{ kJ mol}^{-1}$$

- About 80% of the 140 million tons of ammonia produced each year is used to make fertilisers and the rest used to make nitric acid, polymers such as nylon and other chemicals.
- In the process, nitrogen and hydrogen gases are passed over a finely divided iron catalyst. Only about 15 to 20% of the reactants are converted into ammonia, NH₃, at equilibrium.



Theoretical conditions	Conditions chosen
High pressure gives a higher yield of NH ₃ but requires a higher cost for the expensive chamber to withstand the high pressure.	Moderate pressure is used to keep the cost and maintenance of equipment low.
Low reaction temperature gives a higher yield of NH_3 . However, low reaction temperature slows down the rate of reaction.	Moderate temperature is used to speed up the reaction. Although the percentage yield of ammonia at equilibrium is reduced but the process is faster.
Use of catalyst increases the rate of reaction and allows equilibrium to be reached in a shorter time. Note – the percentage yield of NH_3 is not affected.	Catalyst of finely divided iron is used.

β NOS – The Haber Process and Cause and Effect (refer to page 327 of Chemistry Course Companion)

Exercise 4

1. The equilibrium between nitrogen dioxide (dark brown) and dinitrogen tetroxide (colourless) is represented by the following equation:

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

Given that ΔH is negative and $K_c = 1$ at 328 K

(a) Write the equilibrium constant expression, K_c .

$$K_c = \frac{[N_2O_4]}{[NO_2]^2}$$

(b) State and explain the effect of increasing temperature on the value of K_c .

K_c decreases;

Forward reaction is exothermic / ΔH is negative / position of equilibrium shifts to left

(c) State and explain the visible change that takes place as a result of a decrease in pressure.

The mixture will get darker / darker brown than expected;

Equilibrium position shifts to the left / towards reactants (NO_2) to favour an increase in the number of (moles) molecules of gas.

(d) Two moles of NO₂ and two moles of N₂O₄ were placed in an empty 1 dm³ container and mixture reached equilibrium at 328 K. Predict, with reference to the value of K_c , whether the equilibrium mixture would contain greater or lesser than two moles of NO₂.

Equilibrium mixture contains less than 2 moles of NO₂;

given values gives $\frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{2}$, i.e. $[NO_2]^2$ is too much as K_c stated is 1 at 328 K

forward reaction where NO_2 converts to N_2O_4 is preferred.

(Explanation may include the reaction quotient, $Q < K_c$ to predict)

2. The following equilibrium is established at 1700 °C.

 $CO_2(g) + H_2(g) \rightleftharpoons H_2O(g) + CO(g)$

- (a) Initially, only carbon dioxide gas and hydrogen gas is present, sketch the rate of reaction against time for each reaction and explain the shape of the graph.
 - the forward reaction
 - the reverse reaction until shortly after equilibrium is established.



forward reaction: highest concentration, thus rate is fast at the beginning; as reaction proceeds, concentrations decrease, so the rate slows

reverse reaction: zero rate initially / at t = 0 (no products present); rate increases as concentration of products increases;

dynamic equilibrium happens when rate of forward reaction = rate of backward reaction

(b) K_c for the reversible reaction is determined at two different temperatures. At 850 °C, $K_c = 1.1$ whereas at 1700 °C, $K_c = 4.9$.

Explain whether the forward reaction is exothermic or endothermic.

 K_c increases from 1.1 to 4.9 with (increasing) temperature;

When temperature increases, $[H_2O]$ and [CO] increases and $[H_2]$ and $[CO_2]$ decreases. Hence, forward reaction is favoured / equilibrium position shifts to the right.

By Le Chatelier's Principle, a increase in temperature favours the endothermic reaction to absorb heat (to decrease temperature).

Hence forward reaction is endothermic.

3. $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$ $\Delta H = -92.5 \text{ kJ mol}^{-1}$

Carbon monoxide and hydrogen gases are passed over a Zn / Cr_2O_3 catalyst at 300 °C and 300 atm to manufacture methanol, CH₃OH.

(a) In this reaction, what conditions of temperature and pressure are required to produce a large amount of methanol in the equilibrium mixture?

A low temperature will shift the position of equilibrium to the right so as to produce more methanol by favoring the forward exothermic reaction.

A high pressure will shift the position of equilibrium to the right so as to reduce the increased pressure by favouring the product as there are lesser total number of moles of gas molecules.

- (b) 300 °C is a moderate temperature.
 - (i) State one advantage of using a very high temperature (i.e. over 1000 °C).

Rate of reaction is faster at 1000 °C than at 300 °C.

(ii) State one advantage of using a very low temperature (i.e. below 100 °C).

Higher yield of methanol at below 100 °C.

(iii) Explain the choice of using a moderate temperature

The reaction can be completed quickly without compromising on the product's yield.

(c) Explain the advantage of using excess hydrogen in the reaction.

This will ensure that the position of equilibrium shifts to the right giving a higher yield of methanol.

17.1 The Equilibrium Law

• The equilibrium expression for homogenous reaction can be used to calculate the value for K_c . If the value of K_c is known, it can be used to calculate the concentration of a product.

Example 11

Consider the following data from the synthesis of ammonia at 600 °C.

Trial	[N ₂] / mol dm ⁻³	[H ₂] / mol dm ⁻³	[NH ₃] / mol dm ⁻³
1	0.922	0.763	0.157
2	0.399	1.197	0.203
3	2.590	2.770	1.820

Calculate the K_c value for the three trials. What do you notice about the value of K_c ?

 $N_{2}(g) + 3H_{2}(g) \rightleftharpoons 2NH_{3}(g)$

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

• The value of K_c is the same for all the trials, K_c is 0.0602 mol⁻² dm⁶. The position of equilibrium lies towards the reactants i.e. nitrogen and hydrogen.

Example 12

Two gases P_2 and R_2 react as follows:

$$\mathsf{P}_{2}\left(\mathsf{g}\right)+\mathsf{R}_{2}\left(\mathsf{g}\right)\rightleftharpoons\mathsf{2}\mathsf{P}\mathsf{R}\left(\mathsf{g}\right)$$

A mixture containing 0.50 mol of P_2 and 0.40 mol of R_2 was placed in a closed vessel and allowed to reach equilibrium. The graph below shows how the amount in moles of each gas varies with time. Calculate the value of the equilibrium constant for the forward and reverse reaction.



17.1.1 ICE Method

- Deduce the balanced chemical equation for the reaction.
- Arrange the data according to the ICE method.
 - I: The initial concentration of the reactants and products.
 - C: The change in concentration. This is the amount by which the concentration of reactants decrease and the concentration of products increase. These changes must be consistent with the stoichiometric ratios shown by the coefficients in the balanced chemical equation.
 - E: equilibrium concentration is the concentration of reactants and products when equilibrium is established.
- Substitute the concentration at equilibrium into the equilibrium constant expression and determine the value of the equilibrium constant.

Example 13

Nitrogen(IV) oxide NO₂, dissociates to form nitrogen(II) oxide and oxygen.

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

The following graph shows the variation of concentration of NO₂ until equilibrium is reached.



Calculate the equilibrium concentration of the products and comment whether K_c is greater or lesser than 1.

	2NO ₂	2NO	O ₂
Initial	0.5	0	0
Change	-0.4	+0.4	+0.2
Equilibrium	0.1	0.4	0.2

$$K_{\rm c} = \frac{[O_2][NO]^2}{[NO_2]^2} = \frac{[0.2][0.4]^2}{[0.1]^2} = \frac{3.2 \text{ mol dm}^{-3}}{3.2 \text{ mol dm}^{-3}}$$

K_c is greater than 1.

When 1.0 mole each of CH₃OH and CH₃CO₂H react together according to the equation,

$$CH_{3}OH(l) + CH_{3}CO_{2}H(l) \rightleftharpoons CH_{3}CO_{2}CH_{3}(l) + H_{2}O(l)$$

the equilibrium mixture contains 0.2 mol each of CH₃CO₂CH₃ and H₂O at room temperature.

(a) Calculate K_c at room temperature.

	CH₃OH (l)	CH₃CO₂H (l)	CH ₃ CO ₂ CH ₃ (l)	H ₂ O (l)
Initial	1.0	1.0	0	0
Change	-0.2	-0.2	+0.2	+0.2
Equilibrium	0.8	0.8	0.2	0.2

$$\mathcal{K}_{c} = \frac{[CH_{3}CO_{2}CH_{3}][H_{2}O]}{[CH_{3}OH][CH_{3}CO_{2}H]} = \frac{\left[\frac{0.2}{V}\right]\left[\frac{0.2}{V}\right]}{\left[\frac{0.8}{V}\right]\left[\frac{0.8}{V}\right]} = \frac{\mathbf{0.0625}}{\mathbf{0.0625}} \text{ (no units)}$$

(b) If 3.0 moles each of CH_3OH and CH_3CO_2H were mixed together at room temperature, how much $CH_3CO_2CH_3$ will be produced at equilibrium?

	CH₃OH (l)	CH ₃ CO ₂ H (l)	CH ₃ CO ₂ CH ₃ (l)	H ₂ O (l)
Initial	3.0	3.0	0	0
Change	-x	-x	+x	+x
Equilibrium	3 – x	3 – x	x	x

Since concentration changes do not affect K_{c} ,

$$\mathcal{K}_{c} = \frac{[CH_{3}CO_{2}CH_{3}][H_{2}O]}{[CH_{3}OH][CH_{3}CO_{2}H]} = \frac{\left[\frac{x}{V}\right]\left[\frac{x}{V}\right]}{\left[\frac{3-x}{V}\right]\left[\frac{3-x}{V}\right]} = 0.0625$$

x = <u>0.6 mol</u>

The equilibrium mixture in a 3.0 dm³ flask at 250 °C was found to be 1.00 mol of PCl₅ (g); 2.00 mol of PCl₃ (g) and 0.3 mol of Cl₂ (g). Calculate the value of equilibrium constant, K_c , and state its units.

	Concentration of gases (mol dm ⁻³)	
PCl₅	$\frac{1.0}{3} = 0.33$	
PCl₃	$\frac{2.0}{3} = 0.67$	
Cl ₂	$\frac{0.3}{3} = 0.10$	

 $PCl_{5}(g) \rightleftharpoons PCl_{3}(g) + Cl_{2}(g)$

 $\mathcal{K}_{c} = \frac{[\text{PCl}_{5}][\text{Cl}_{2}]}{[\text{PCl}_{3}]} = \frac{[0.67][0.10]}{[0.33]} = \frac{\textbf{0.203 mol dm}^{-3}}{\textbf{0.203 mol dm}^{-3}}$

17.1.2 Gibbs Free Energy

- The thermodynamic state function ΔG is a measure of reaction spontaneity.
- Relationship between ΔG and reaction spontaneity:
 - \circ $\Delta G < 0$ (Reaction is spontaneous)
 - $\Delta G > 0$ (Reaction is not spontaneous)
 - $\Delta G = 0$ (Reaction mixture is at equilibrium)
- In reality, most reactions do not go to 100% completion; instead they reach a point of equilibrium, where there is minimum value of free energy and a maximum value of entropy.



(Figure-McMurray & Fay)

• The Gibbs free energy is related to the reaction quotient by the following equation:

where

 ΔG^{θ} is the free energy change under standard conditions R represents the gas constant T the absolute temperature in Kelvin.

• At equilibrium $\Delta G = 0$ and $Q = K_c$. Substituting into the equation given above,

 $0 = \Delta G^{\theta} + RT \ln K_c$

 $\Delta G^{\theta} = -RT \ln K_c$

• The relationship between K_c and ΔG obtained from this expression is summarised below.

ΔG ^θ	In <i>K</i> ₅	Kc
_	+	>1
+	-	<1
0	0	1

- If ΔG is negative, K_c is greater than 1 and the products will be at a higher concentration in the equilibrium mixture.
- Alternatively, if ΔG is positive, K_c will be less than 1 and the reactants will be at a higher concentration in the equilibrium mixture.

Example 16

Use $\Delta G^{\theta} = -32.96$ kJ mol⁻¹, calculate the equilibrium constant, K_c for the following reaction at 25 °C:

$$N_{2}(g) + 3H_{2}(g) \rightleftharpoons 2NH_{3}(g)$$

 $\Delta G^{\theta} = -RT \ln K_c$

 $\ln K_c = -\frac{\Delta G^{\theta}}{RT}$

Substituting the known value of ΔG^{θ} , R, and T into this equation gives the following result:

$$\ln \mathcal{K}_c = -\frac{(-32960)}{(8.31)(298)} = 13.3$$

 $K_{\rm c} = {\rm e}^{13.3} = 6.0 \ {\rm x} \ 10^5$

The equilibrium constant, K_c for this reaction at 25 °C is <u>6.0 x 10⁵</u>

Using the information given, calculate the standard Gibb's free energy formation of HI and the equilibrium constant K_c for the reaction.

$$\frac{1}{2}\,H_{2}\left(g\right)+\frac{1}{2}\,\,\mathrm{I}_{2}\left(g\right)\rightleftharpoons\mathrm{HI}\left(g\right),$$

 $\Delta H^{\theta}_{reaction}$ = 26.5 kJ mol⁻¹ and $\Delta S^{\theta}_{reaction}$ = 83.18 J mol⁻¹ K⁻¹

$$\begin{split} & \Delta G^{\theta} \\ &= \Delta H^{\theta} - T \Delta S^{\theta} \\ &= 26.5 - (298 \times 0.08318) \\ &= +1.71 \text{ kJ mol}^{-1} \end{split}$$

$$\ln K_c = -\frac{(+1710)}{(8.31)(298)} = -0.6905$$

 $K_c = e^{-0.6905} = 0.5$

(TOK – Role of intuition in problem solving refer to page 334 of Chemistry Course Companion)

<u>Summary</u>

- Dynamic equilibrium is a state in which the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products remain constant.
- The equilibrium constant, *K_c*, measures the extent of a reversible reaction. It is the ratio of the equilibrium concentrations of products over the equilibrium concentrations of reactants each raised to the power of their stoichiometric coefficients.
- Magnitude of K_c
 - If the K_c value is large ($K_c >> 1$), the equilibrium lies to the right and the reaction mixture contains mostly products.
 - If the K_c value is small ($K_c \ll 1$), the equilibrium lies to the left and the reaction mixture contains mostly reactants.
 - If the K_c value is close to 1 (0.10 < K_c < 10), the mixture contains appreciable amounts of both reactants and products.
- The value of K_c is only temperature dependent and is not affected by:
 - o changes in the concentrations of the reactants or products,
 - o changes in the pressure of the system for gaseous reactants and products,
 - the use of a catalyst.
- The reaction quotient (Q) measures the relative amount of products and reactants present during a reaction at a particular point in time.
 - If $Q > K_c$, the reaction will proceed to the left. The ratio of products over reactants is too large and the reaction will move toward equilibrium by forming more reactants.
 - If $Q < K_c$, the reaction will proceed to the right. The ratio of products over reactants is too small and the reaction will move toward equilibrium by forming more products.
 - o If $Q = K_c$, the reaction mixture is at equilibrium, so no shift occurs.
- Le Châtelier's principle states that if a change is made to the conditions of a system at dynamic equilibrium, then the position of equilibrium will shift to counteract the change and establish a new equilibrium.
- The relationship between K_c and ΔG is summarised below.

ΔG ^θ	In <i>K</i> c	Kc
-	+	>1
+	-	<1
0	0	1

Enrichment: Experimental Determination of Equilibrium Constants

To determine the K_c for the Esterification reaction.

The following procedure details how the equilibrium constant, K_c , for the esterification reaction can be determined:

$$C_2H_5OH(l) + CH_3CO_2H(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$$

- 1 Known quantities of pure or glacial ethanoic acid, CH_3CO_2H and absolute or pure ethanol, C_2H_5OH , are mixed together in a sealed flask of volume V dm³.
- 2 The flask is placed in a water bath for 20 hours to attain equilibrium. The temperature of the water is maintained at a fixed temperature; eg 70 °C, using a thermostat.
- 3 A fixed volume sample is run into a flask containing ice and water. This is to slow down the reaction before titration with aqueous NaOH. (The reaction between NaOH (aq) and CH₃CO₂H would disturb the equilibrium.)
- 4 A pipette is used to withdraw a known volume of the equilibrium mixture.
- 5 The amount of CH₃CO₂H left unreacted in the mixture is determined by titration using NaOH (aq) and phenolphthalein as an indicator.
- 6 The concentrations of the other substances in the equilibrium can be calculated.
- 7 These concentration values are substituted into the expression for K_c . A value for K_c can then be evaluated.





Mixtures allowed to equilibrate in a thermostatted water bath.



A 10 cm³ sample is run into a flask containing ice and water.



Ethanoic acid in the reaction mixture is titrated with alkali.