

Kirkcaldy High School



Chemistry

Advanced Higher

Unit 2 - Physical Chemistry

NOTES

Course Overview

Contents

The Advanced Higher Chemistry Course is split into four units. *Italic* shows the contents of this notes booklet.

Unit 1 - Inorganic Chemistry

- (a) Electromagnetic radiation and atomic spectra
- (b) Atomic orbitals, electronic configurations and the periodic table
- (c) Transition Metals

Unit 2 - Physical Chemistry

- (a) *Chemical Equilibrium* *page 5*
- (b) *Reaction Feasibility* *page 23*
- (c) *Kinetics* *page 33*

Unit 3 - Organic Chemistry and Chemical Analysis

- (a) Molecular Orbitals
- (b) Synthesis
- (c) Stereochemistry
- (d) Experimental Determination of structure
- (e) Pharmaceutical Chemistry

Unit 4 - Researching Chemistry

- (a) Weighing by difference and gravimetric analysis
- (b) Preparing a standard
- (c) Using a reference or control or blank determination
- (d) Carrying out a complexometric titration
- (e) Carrying out a back titration
- (f) Using a colorimeter or visible spectrophotometer and carrying out dilution to prepare a calibration graph
- (g) Distilling
- (h) Refluxing
- (i) Using vacuum filtration methods
- (j) Recrystallising
- (k) Determining % yield experimentally
- (l) Using thin-layer chromatography
- (m) Using melting point apparatus and mixed melting point determination
- (n) Using a separating funnel and solvent extraction
- (o) Carrying out stoichiometric calculations
- (p) Volumetric Analysis
- (q) Scientific Precision and Uncertainties

Assessment

- There is a final exam for Advanced Higher Chemistry. It lasts for 3 h and contains 110 marks scaled to a total of 120. There are.
 - 25 marks of multiple-choice questions
 - 85 marks of written answer questions
- There is a Project to write for Advanced Higher Chemistry.
 - The Assignment is externally marked by an SQA marker (NOT your teacher)
 - The Assignment contains 25 marks, but these are scaled to 40 marks such that the assignment is worth one quarter of the total marks.
 - You have unlimited time to research and gather data for your Assignment.
 - It must contain data and analysis from experiments you have carried out.

Success Criteria

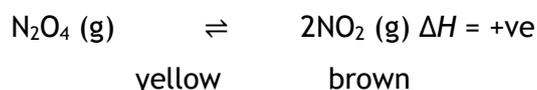
No.	Learning Outcome	Understanding?
1	What does it mean if a reaction is in dynamic equilibrium?	😊 😐 😞
2	How can the equilibrium constant, K , be used to predict the position of equilibrium and/or calculate the concentration of species at equilibrium?	😊 😐 😞
3	What is the mathematical relationship between pH and the concentration of H^+ ions in solution?	😊 😐 😞
4	How can the ionic product of water, $K_w=[OH^-][H^+]$, be used to calculate the concentrations of the two ions in aqueous solutions?	😊 😐 😞
5	How do Bronsted and Lowry define an acid and a base?	😊 😐 😞
6	What is a 'conjugate' acid or base?	😊 😐 😞
7	What is a 'strong' acid or base as opposed to a 'weak' acid or base?	😊 😐 😞
8	Are all salts neutral? How can the pH of a salt be predicted?	😊 😐 😞
9	How does the equilibrium constant for a weak acid or base relate to its strength?	😊 😐 😞
10	What is the pK_a value for an acid?	😊 😐 😞
11	How can the pH of a weak acid be calculated?	😊 😐 😞
12	How do buffer solutions work and how are they made?	😊 😐 😞
13	How can the pH of a buffer solution be calculated?	😊 😐 😞
14	What is equation for the equilibrium of a weak acid indicator?	😊 😐 😞
15	How do you predict the pH at which an indicator will change colour?	😊 😐 😞

16	What is the standard enthalpy of formation?	😊 😐 😞
17	What is the mathematical definition for enthalpy of formation for an element?	😊 😐 😞
18	What is entropy and how does it change with the physical state of substances?	😊 😐 😞
19	What is the Second Law of Thermodynamics?	😊 😐 😞
20	What is the Third Law of Thermodynamics?	😊 😐 😞
21	How can the change in entropy of a reaction system be calculated?	😊 😐 😞
22	What is the relationship between standard entropy, standard enthalpy and free energy (ΔG°)	😊 😐 😞
23	How can ΔG° be used to predict whether a reaction will occur or not?	😊 😐 😞
24	What does the term 'order of reaction' mean?	😊 😐 😞
25	How can a rate equation be derived from the experimental data for a reaction?	😊 😐 😞
26	How can the rate constant, k, be determined from initial rate data?	😊 😐 😞
27	What is the 'rate determining step' in a reaction?	😊 😐 😞
28	How can the rate equation be used to predict which reactants take part in the rate determining step?	😊 😐 😞

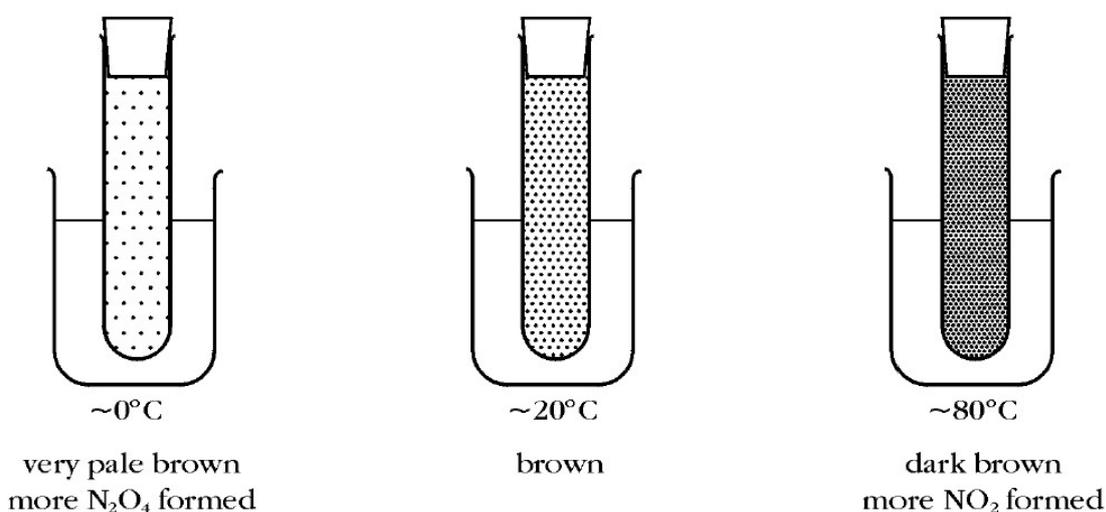
This fact is stated formally in Le Chatelier's principle, which states that 'when a reaction at equilibrium is subjected to change, the composition alters in such a way as to minimise the effects of the change'.

The effect of changing temperature

The effect of a temperature change on a reaction in equilibrium can be demonstrated in the laboratory using the following example:



Three boiling tubes filled to an equal colour intensity with this gas mixture are collected at room temperature. One is placed in ice water ($\sim 0^\circ\text{C}$) and one in hot water ($\sim 80^\circ\text{C}$) while the third is kept, as a control, at room temperature (Figure 3). The three tubes are left for about five minutes and the colour intensities are then compared.



From the colour changes that have taken place, it is evident that the relative concentrations of N_2O_4 and NO_2 have been changed by a change in temperature. This means that the actual value of K has changed. Equilibria are therefore temperature dependent. In fact most equilibrium constants are quoted at a specific temperature.

The equilibrium constant is:

$$K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

The reaction is endothermic for the forward reaction and exothermic for the reverse. The colour change from 20°C to 0°C shows that more N_2O_4 is formed at 0°C and therefore $[\text{N}_2\text{O}_4]$ increases and $[\text{NO}_2]$ decreases. This leads to a fall in the value of K .

Similarly, the colour change from 20°C to 80°C shows that more NO_2 is formed at 80°C and therefore $[\text{NO}_2]$ increases and $[\text{N}_2\text{O}_4]$ decreases. This leads to a rise in the value of K . These observations can be related to the ΔH value and are summarised in the following way.

For endothermic reactions a rise in temperature causes an increase in K while for exothermic reactions a rise in temperature causes a decrease in K .

K and Equilibrium Position

System	Value of K	Position of equilibrium
$\text{Ag}^+(\text{aq}) + 2\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+(\text{aq})$	1.7×10^7 at 25°C	Because $K \gg 1$ the equilibrium lies to the right
$\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$	1.8×10^{-5} at 25°C	Because $K \ll 1$ the equilibrium lies to the left
$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$	0.87 at 55°C	Because $K \approx 1$ the equilibrium lies to neither the left nor the right

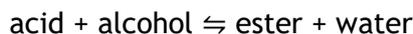
A high value of K means that the fraction used to calculate it is 'top heavy' so there is more product, i.e. equilibrium lies to the right. The table below summarises this for different reactions:

Effect of a Catalyst

Remember that all a catalyst does is lower activation energy. This will be true for forward and reverse reactions, so a catalyst speeds up the rate of establishment of equilibrium. It doesn't affect the position of equilibrium; therefore it must have no effect on K .

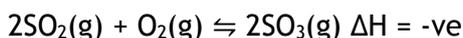
Questions:

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



- (a)
- (i) Predict the maximum yield of ester, given this value of K .
 - (ii) Give *one* reason why this yield might not be achieved in practice.
- (b)
- (i) A student suggested that a careful choice of catalyst could increase the yield of ester. Comment on this suggestion.
 - (ii) Another student 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.

■ The balanced equation for the principle reaction in the contact process is:



- (c) Write an expression for K , the equilibrium constant for this reaction, when the system has reached equilibrium.
- (d)
- (i) State Le Chatelier's Principle.
 - (ii) Use this generalisation to predict how an increase in temperature would affect the position of equilibrium.
 - (iii) Explain the effect this increase in temperature would have on the value of K .

Acid/Base Equilibria

From the National 5 course it will be remembered that the pH of an aqueous solution is a measure of the concentration of hydrogen ions in the solution. In fact the pH of any aqueous solution can be calculated using the expression:

$$\text{pH} = -\log[\text{H}^+] \quad \text{OR} \quad \text{pH} = -\log[\text{H}_3\text{O}^+]$$

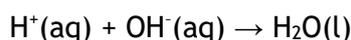
NB: You will sometimes see H^+ written as H_3O^+ and vice-versa. The standard at Advanced Higher is H_3O^+ .

The following examples illustrate its use:

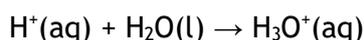
- pure water $[H^+] = 10^{-7}$ so $pH = 7$
- $mol\ l^{-1}\ HCl\ [H^+] = 1.0\ (10^0)$ so $pH = 0$
- $0.2\ mol\ l^{-1}\ HCl\ [H^+] = 0.2\ (2 \times 10^{-1})$
- So $pH = -\log 2 - \log (10^{-1})$
- $= -0.3 + 1.0 = 0.7$

For calculations involving strong acids and alkalis it can be assumed that they are 100% dissociated and that the small number of hydrogen ions supplied by the water can be ignored.

In S4, acids were defined as producing hydrogen ions in solution and bases as producing hydroxide ions in solution. These two ions combine in the neutralisation equation:



However, this definition is simplistic and can't explain all acids. For example, pure hydrogen chloride is a gas that contains no H^+ ions and ammonia has no OH^- ions but can neutralise an acid. It was also discovered that the H^+ ion could not exist in aqueous solution. The H^+ ion is so small that the electric field it creates is huge and in water it attracts a lone pair of electrons to form H_3O^+ , which is called the hydronium ion.



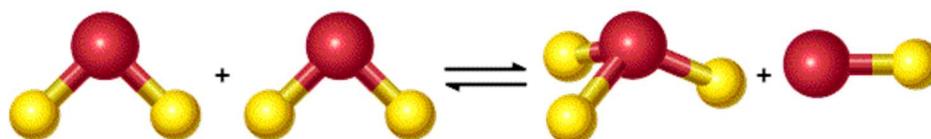
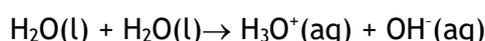
The shorthand $H^+(aq)$ is always used in stoichiometric and equilibrium equations, although this is not strictly accurate. In 1923 the new discoveries led two chemists, Brønsted and Lowry, to define acids and bases in a different way:

An acid is any substance capable of donating a proton.

A base is any substance capable of accepting a proton.

The dissociation of water

In Brønsted-Lowry terms the ionisation of water is represented by:



acid + base conjugate acid + conjugate base

The equilibrium constant is :

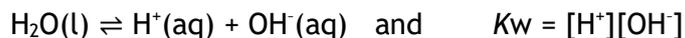
$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Since water is a liquid, $[H_2O] = 1$ (see page 37), giving:

$$K = [\text{H}_3\text{O}^+][\text{OH}^-]$$

This particular equilibrium constant is known as the **ionic product** (K_w) for water and has the value of 1.0×10^{-14} at 25°C .

The water equilibrium is more usually written as:



In **pure** water, for every molecule which ionises, one H^+ and one OH^- ion are produced, hence the $[\text{H}^+]$ in mol l^{-1} must equal the $[\text{OH}^-]$ in mol l^{-1} , i.e. the number of H^+ and OH^- ions in water are equal.

Substitution of $[\text{OH}^-]$ by $[\text{H}^+]$ in the above equilibrium expression gives:

$$[\text{H}^+]^2 = 10^{-14} \text{ mol}^2 \text{ l}^{-2}$$

taking square roots $[\text{H}^+] = 10^{-7} \text{ mol l}^{-1}$

so also $[\text{OH}^-] = 10^{-7} \text{ mol l}^{-1}$

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

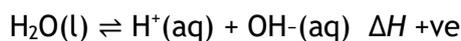
This relationship can be used to calculate the pH of an alkali as shown:

$0.01 \text{ mol l}^{-1} \text{ NaOH}$ $[\text{OH}^-] = 10^{-2}$, $[\text{H}^+] = 10^{-12}$, $\text{pH} = 12$

$0.5 \text{ mol l}^{-1} \text{ NaOH}$ $[\text{H}^+] = 2 \times 10^{-14}$ $\text{pH} = -\log 2 - \log(10^{-14})$

$= -0.3 + 14 = 13.7$

K_w is always quoted as 1.0×10^{-14} at 25°C since the value varies with temperature:



As the reaction is endothermic, an increase in temperature moves the equilibrium to the right and a decrease moves it to the left.

Questions

1. Calculate the pH of the following solutions:

(a) $0.35 \text{ mol l}^{-1} \text{ HNO}_3$

(b) $0.14 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ (assume fully ionised)

(c) $0.78 \text{ mol l}^{-1} \text{ NaOH}$

Conjugate Acids and Bases

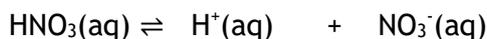
When an acid donates a proton the species left is called the conjugate base of that acid. When a base accepts a proton the species formed is called the conjugate acid of that base.

acid	+	base	\rightleftharpoons	conjugate base	+	conjugate acid
HCl	+	H ₂ O	\rightleftharpoons	Cl ⁻	+	H ₃ O ⁺
CH ₃ COOH	+	H ₂ O	\rightleftharpoons	CH ₃ COO ⁻	+	H ₃ O ⁺
H ₂ O	+	NH ₃	\rightleftharpoons	OH ⁻	+	NH ₄ ⁺
H ₂ O	+	CH ₃ COO ⁻	\rightleftharpoons	OH ⁻	+	CH ₃ COOH

This table also illustrates the **amphoteric** nature of water since it can act both as a proton acceptor and a proton donor.

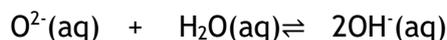
What is a 'Strong' Acid?

The strongest common acids are HCl, HBr, HI, HNO₃, HClO₃, HClO₄, and H₂SO₄. All strong acids dissociate completely in solution:

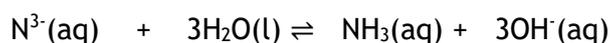
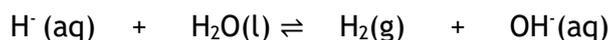


Therefore, the pH depends only on the initial molarity of the acid.

The strongest common bases are oxides and hydroxides of Group I metals. All strong bases dissociate completely in solution:



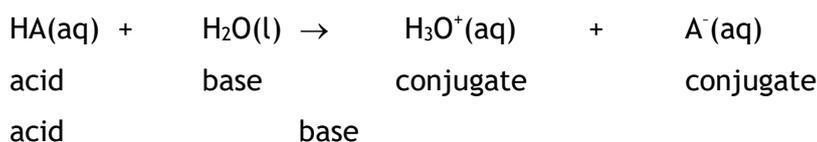
Bases do not need to include OH⁻ ions:



Therefore, the [OH⁻], and hence the [H⁺] and pH, depends only on the initial molarity of the base.

Dissociation and strength

The dissociation of any acid, HA, in aqueous solution can be represented by the equation:



The dissociation constant of acid HA is a measure of the strength of the acid. It is simply the equilibrium constant from the above equation and is:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

The [H₂O] has been omitted as it is the solvent and taken to be 1.

In **strong acids** the above equilibrium lies to the right with effectively complete dissociation so that *K_a* has no meaning. However, some acids do not dissociate well (less than 5%) in aqueous solution and these are called **weak acids**.

Conveniently, nearly all acids fall into one of these two categories. Within the weak acids, the value of *K_a* gives a measure of how weak (or how dissociated) the acid is: the smaller the value of *K_a*, the weaker the acid. A similar constant, *K_b* exists for the base equilibrium, but in general *K_a* is used to calculate pH for both acids and bases - we will see how this is done later.

pH of Salt Solutions

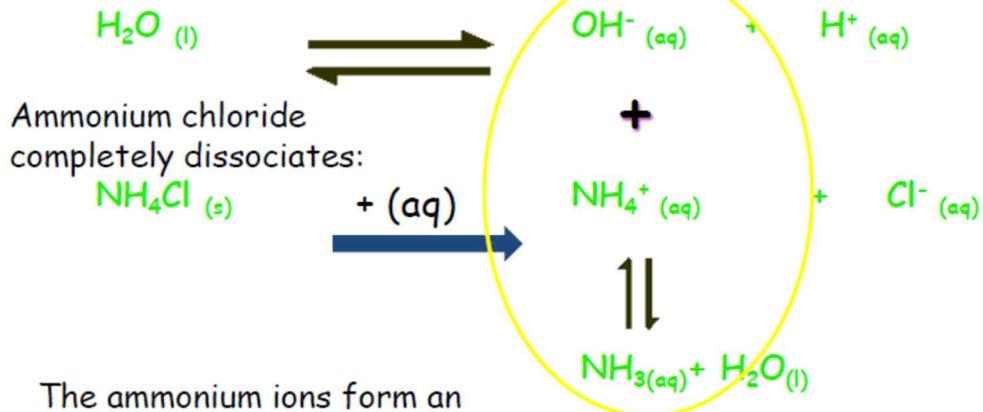
The **pH of a salt solution** depends on the **strength** of the **acid** and **base** from which it was formed.

Acid	Base	pH of salt
Strong	Weak	Acidic
Strong	Strong	Neutral
Weak	Strong	Alkaline

All salts are **strong electrolytes** and completely dissociate in solution. The ions of a **weak acid** or **base** when dissolved will set up an equilibrium with the ions in water.

Acidic Salt

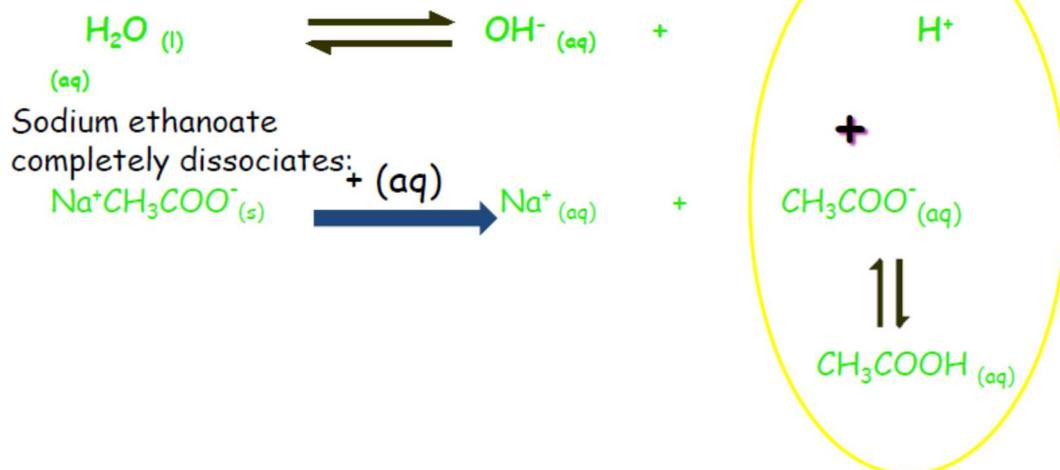
In water you have:



The ammonium ions form an equilibrium with the OH^- ions moving the water equilibrium to the right. Excess H^+ are formed so pH is less than 7.

Alkaline Salt

In water you have:



The ethanoate ions form an equilibrium with the H^+ ions moving the water equilibrium to the right. Excess OH^- ions are formed so the pH is greater than 7.

Calculating pH for a weak acid

Using the equilibrium constant (dissociation constant) from the reaction on page 47, the pH of a weak acid can be calculated:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$\text{Since } [\text{H}_3\text{O}^+] = [\text{A}^-]:$$

$$K_a = \frac{[\text{H}_3\text{O}^+]^2}{[\text{HA}]}$$

Taking logs of both sides:

$$\begin{aligned}\log K_a &= \log[\text{H}_3\text{O}^+]^2 - \log[\text{HA}] \\ &= 2\log[\text{H}_3\text{O}^+] - \log[\text{HA}]\end{aligned}$$

$$\begin{aligned}\text{but } -\log[\text{H}_3\text{O}^+] &= \text{pH, and assigning } -\log K_a \text{ as } \text{p}K_a \text{ we get:} \\ -\text{p}K_a &= -2\text{pH} - \log[\text{HA}] \\ \text{p}K_a &= 2\text{pH} + \log[\text{HA}]\end{aligned}$$

For a weak acid HA of concentration $c \text{ mol l}^{-1}$, $[\text{HA}]$ at equilibrium will be approximately equal to the original concentration $c \text{ mol l}^{-1}$, so:

$$\text{p}K_a = 2\text{pH} + \log c$$

Rearranging for pH:

$$\text{pH} = \frac{1}{2}\text{p}K_a - \frac{1}{2}\log c$$

Questions

1. Calculate the pH of a 0.2 mol l^{-1} solution of ethanoic acid if $K_a = 1.7 \times 10^{-5}$

0.02 mol l⁻¹ benzoic acid C₆H₅COOH, a monobasic acid, was found to have a pH of 2.94. Calculate the K_a of this weak acid.

Buffer solutions

A buffer solution is one in which the pH of the solution remains approximately constant when small amounts of acid or base are added or the solution is diluted with water.

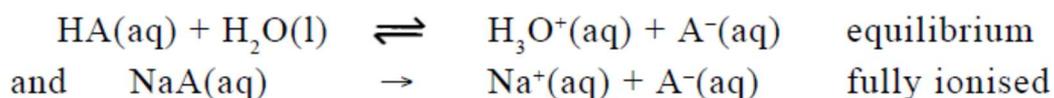
An **acidic buffer** consists of a solution of a weak acid and one of its salts with a strong alkali. A **basic buffer** consists of a solution of a weak base and one of its salts with a strong acid.

Both types of buffer solution work in the same way.

In an acid buffer solution, the weak acid supplies more hydrogen ions when the existing ones are removed by a base being added, while the salt of the weak acid provides the conjugate base to react with the hydrogen ions when small amounts of acid are added.

In a basic buffer solution, the weak base reacts with the hydrogen ions when acid is added and the salt provides the conjugate acid, which dissociates to replace the hydrogen ions when these are removed by addition of small amounts of base.

In consequence, the pH hardly changes in both cases. This principle is illustrated by an acid buffer of weak acid HA and the sodium salt of that acid NaA. In solution the following occurs:



Addition of small volumes of H^+ does not alter the pH greatly since an increase in $[\text{H}^+]$ favours the reverse reaction (HA formation) to maintain K_a . Since $[\text{A}^-]$ is high compared to $[\text{H}^+]$ in the original buffer solution, its ability to remove H^+ ions is substantial (but not infinite) and the pH of the solution is maintained.

In the same way, addition of OH^- does not alter the pH greatly since the OH^- ions combine with the H^+ of the weak acid until K_w is attained. Removal of H^+ means that more HA ionises, giving $\text{H}^+ + \text{A}^-$ until equilibrium is re-established, and the pH of the solution is maintained:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$
$$[\text{H}_3\text{O}^+] = \frac{[K_a][\text{HA}]}{[\text{A}^-]}$$

where $[\text{HA}]$ is the concentration of the acid as it is a weak acid and $[\text{A}^-]$ is the concentration of the salt as it is fully ionised and very little comes from the acid dissociating. Therefore:

$$[\text{H}_3\text{O}^+] = \frac{K_a[\text{acid}]}{[\text{salt}]}$$

If the buffer solution has water added to it, i.e. it is diluted, both $[\text{acid}]$ and $[\text{salt}]$ are equally affected and therefore $[\text{H}_3\text{O}^+]$ and the pH remain unaltered.

An efficient buffer must have a reasonable reserve of HA and A^- as the H^+ from HA removes added OH^- and the A^- removes added H^+ . If $[\text{acid}] = [\text{salt}]$ the buffer will have the same ability to resist addition of H^+ and OH^- .

Similar reasoning can be used to show how a basic buffer solution operates. The pH of an acid buffer solution can be calculated by conversion of the above equation,

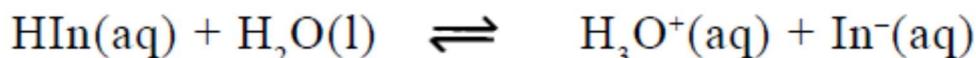
$$\text{pH} = \text{p}K_a - \log \frac{[\text{acid}]}{[\text{salt}]}$$

Questions

1. Calculate the pH of the buffer solution made from 1.0 mol l^{-1} methanoic acid and 1.78 mol l^{-1} sodium methanoate solution. The $\text{p}K_{\text{a}}$ of methanoic acid is 3.8.
2. Calculate the pH of the buffer solution made from 0.1 mol l^{-1} solution of ethanoic acid and potassium ethanoate. The $\text{p}K_{\text{a}}$ of ethanoic acid is 4.8.

Indicators

Indicators are used to determine the end-point in an acid-alkali titration. A suitable indicator must be chosen for any given reaction. Indicators are dyes whose colours are sensitive to pH. An indicator is usually a weak acid that dissociates as shown:



The unionised form of the indicator (HIn) has a different colour from its conjugate base (In⁻). The equilibrium constant (K_{In}) for the above equation is:

$$K_{\text{In}} = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]}$$

Rearranging this expression gives:

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_{\text{In}}}{[\text{H}_3\text{O}^+]}$$

This shows that the ratio of the two coloured forms is a function of the H_3O^+ concentration, i.e. the pH of the solution. It follows therefore that the colour of the indicator in any given solution depends on the relative concentrations (ratio) of the two coloured forms, which in turn is determined by the pH.

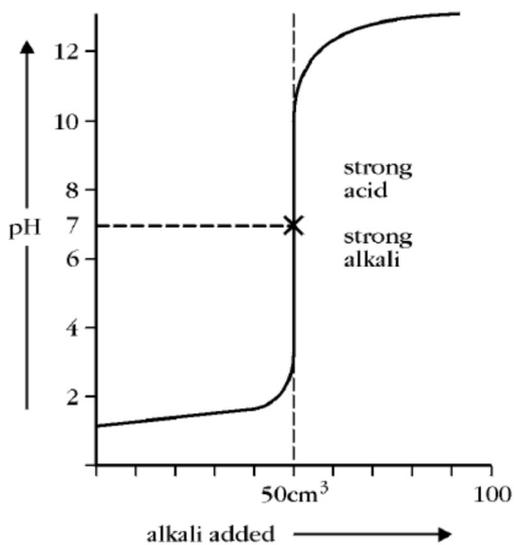
The theoretical point at which the colour change occurs is when $[\text{HIn}] = [\text{In}^-]$ and therefore $K_{\text{In}} = [\text{H}_3\text{O}^+]$. In other words, the colour change occurs when $\text{p}K_{\text{In}} = \text{pH}$. In practice the colour change cannot be seen when $[\text{HIn}] = [\text{In}^-]$ and it is only distinguishable when $[\text{HIn}]$ and $[\text{In}^-]$ differ by a factor of 10.

The pH range over which a colour change can be seen is therefore established using the expression:

$$\text{pH} = \text{p}K_{\text{In}} \pm 1 \quad (\log 10 = 1)$$

The appropriate indicator for any titration must be chosen such that the colour change occurs over the pH range when the pH is changing very rapidly. This means that the indicator must change colour during the addition of, say, half a drop of reagent. The indicator for a reaction can therefore be chosen by reference to titration curves, which are drawn from data obtained by measuring the pH of an acid continuously against the volume of alkali added during and after neutralisation.

Strong Acid + Strong Alkali

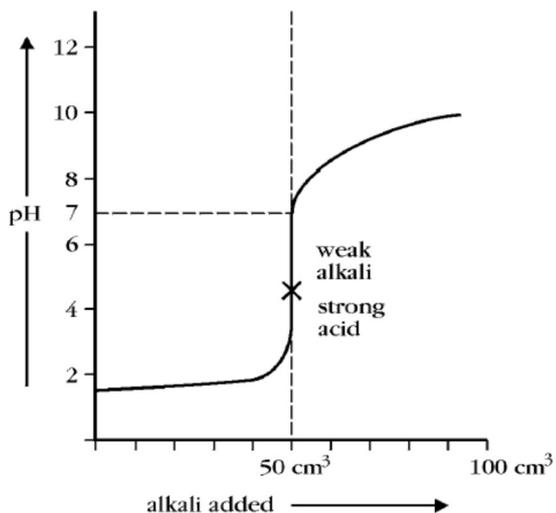


Note the rapid rise in pH as the end-point of the titration is approached.

Thereafter the alkali added has nothing to react with and the pH continues to rise to a final value of 12.

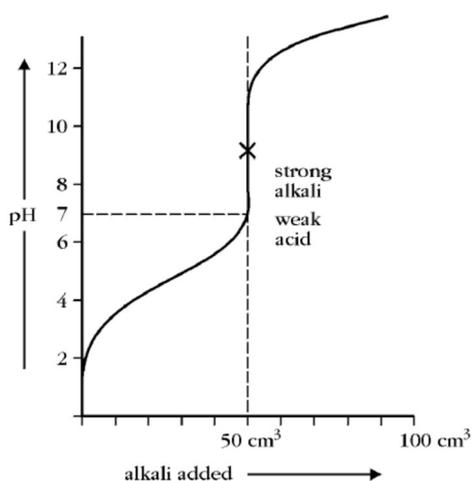
There is a region of rapid pH change around the end-point. For an indicator to be suitable, its pH range must fall within this region. It can be seen that for a strong acid and strong alkali a suitable indicator can have a colour change within the pH range 3-10.

Strong Acid + Weak Alkali



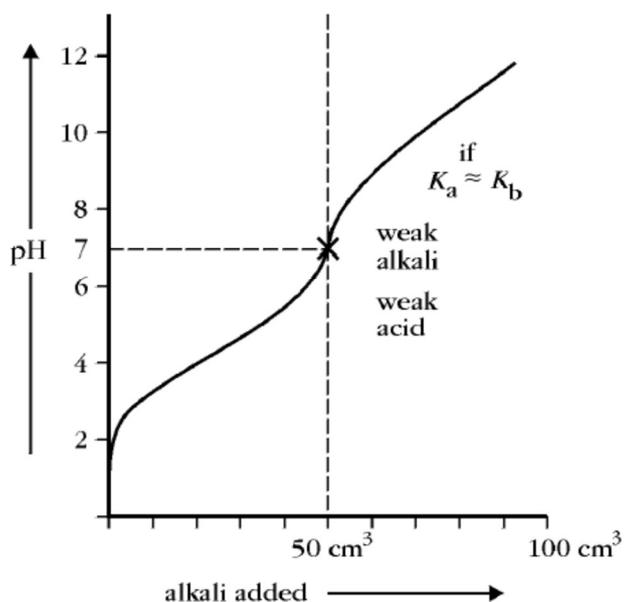
For a strong acid and weak alkali would change somewhere in the range 3-7.

Weak Acid + Strong Alkali



For a weak acid and strong alkali, a suitable indicator must change colour within the pH range 7-10.

Weak Acid + Weak Alkali



It is not possible to select any suitable indicator for a weak acid/weak alkali combination since the pH does not change rapidly enough at the end-point, i.e. the titration curve does not have an almost vertical section like the others.

The table below shows some common indicators, their pH range and colours.

Name of indicator	pH of colour change	Colour (HIn)	Colour (In)
Methyl orange	3.0–4.4	Orange	Yellow
Methyl red	4.2–6.3	Red	Yellow
Bromothymol blue	6.0–7.6	Yellow	Blue
Phenolphthalein	8.0–9.8	Colourless	Red

Question

From the table, calculate the pKa and Ka for the four indicators.

(b) Reaction Feasibility

Energy Changes

Thermochemistry is the study of energy changes in reactions. **The First Law of Thermodynamics states that the total energy of the universe is constant** - energy can neither be created nor destroyed.

Therefore, it only changes between different TYPES of energy.

Enthalpy changes are defined as the measured heat energy changes occurring during a reaction, usually per mole of product formed or reactant used up, depending on the particular enthalpy change being defined. The units are in

kilojoules per mole, kJ mol^{-1} . From Higher, you will already be aware of standard enthalpy of combustion and the use of standard reaction enthalpies and standard bond enthalpies in the context of Hess's Law.

The standard enthalpy change is defined as the enthalpy change measured under standard conditions.

Standard conditions are one mole of a substance at one atmosphere pressure and any specified temperature (in Kelvin). The

symbol used is ΔH° . The temperature specified is usually 298 K (25°C).

The standard state of a substance is the most stable state of that substance under standard conditions.

The standard enthalpy of formation (ΔH°_f) of a compound is the enthalpy change when one mole of a compound is formed from its elements in their standard states. The standard enthalpy of formation of elements is by definition zero, giving a base line from which enthalpy changes can be measured.

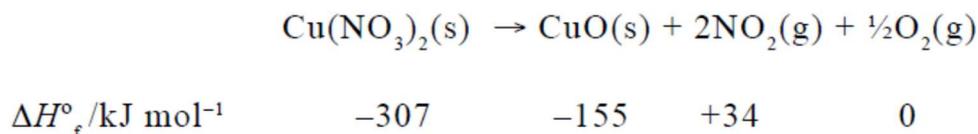
The standard enthalpy change for any reaction can be calculated from the standard enthalpies of formation of the substances in the equilibrium using the equation:

$$\Delta H^\circ = \sum \Delta H^\circ_f \text{ products} - \sum \Delta H^\circ_f \text{ reactants}$$

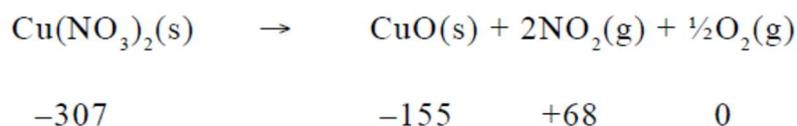
Example:

Calculate the standard enthalpy of reaction for the decomposition of copper(II) nitrate from the given standard enthalpies of formation.

Step 1: Write the equation with ΔH_f° values beneath each substance:



Step 2: Multiply each ΔH_f° value by its mole relationship:



Step 3: Use the equation $\Delta H^\circ = \Sigma\Delta H_f^\circ \text{ products} - \Sigma\Delta H_f^\circ \text{ reactants}$:

$$\begin{aligned} \Delta H^\circ &= \Sigma\Delta H_f^\circ \text{ prod} - \Sigma\Delta H_f^\circ \text{ reactants} \\ &= -155 + 68 - (-307) \\ &= -87 + 307 \\ &= + 220 \end{aligned}$$

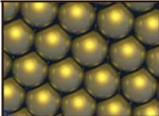
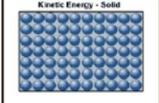
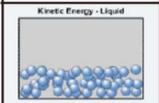
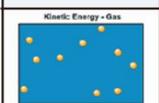
ΔH° for the reaction = +220 kJ mol⁻¹

Thermodynamics

Thermodynamics is concerned with the feasibility of a reaction i.e. whether a reaction will happen spontaneously or not. Increasingly we consider all reactions to be reversible, but, under certain conditions the reaction will be more likely to go in one direction than the other i.e. it will be spontaneous in one direction but not the other. Factors affecting feasibility are the enthalpy change, the temperature and the ENTROPY change involved in the reaction.

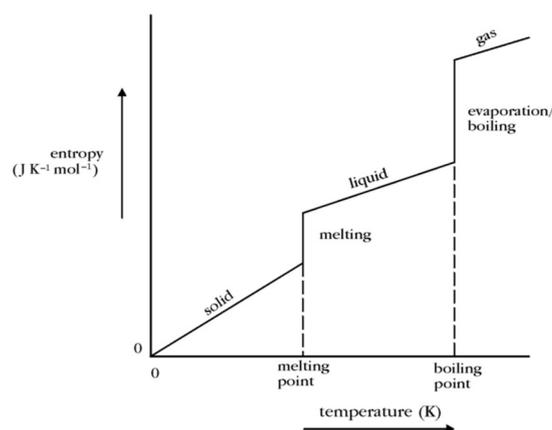
Entropy

In nature there is a tendency towards disorder. A brick wall changes into a disordered heap of bricks either with age or the demolition squad, but the reverse process does not take place spontaneously, i.e. without outside help. More widely, an untended garden, diffusion, corrosion and the dispersion of sewage into the sea are all examples of systems naturally tending towards disorder. In thermodynamic terms disorder is called entropy. The degree of disorder in a system is called the entropy of that system. The greater the disorder, the greater the entropy.

	Molecular Motion		
	Translation	Rotation	Vibration
Kinetic Energy - Solid 	no freedom to move	no freedom to rotate	free to vibrate
Kinetic Energy - Liquid 	restricted freedom to move	some freedom to rotate	free to vibrate
Kinetic Energy - Gas 	total freedom to move	total freedom to rotate	free to vibrate

The molecular motion of any substance depends on its state. Solids only have vibrational motion while gases have vibration, rotation and translational motion.

It therefore follows that entropy increases as temperature increases and that changes in state, such as melting and evaporation, involve large changes in entropy. When a state change occurs there is a change in entropy without a change in temperature and this is linked to the concept of latent heat (see diagram).



The Second Law of Thermodynamics states that the total entropy of a reaction system and its surroundings always increases for a spontaneous process. A spontaneous process is a process that is thermodynamically possible and this means that it can take place on its own irrespective of how long this requires. It should now become clearer why spontaneous endothermic processes take place. Consider the following endothermic reactions:

Free energy

We have now established that, in a thermodynamically feasible endothermic reaction, there is a favourable entropy change **inside** the reaction mixture. An endothermic reaction can only take place if its entropy change is sufficiently favourable to 'overcome' the unfavourable enthalpy change. The combination of enthalpy and entropy changes is known as the **free energy change** and is given the symbol ΔG :

$$\Delta G = \Delta H - T\Delta S$$

The sign of the free energy change obtained can be used to predict the possibility of the reaction proceeding. This can be summarised by saying that a **negative** value for the change in free energy shows that the reaction is likely to happen spontaneously. On the other hand, a positive value for ΔG shows that the reaction is unlikely to happen unless external energy is available to do work on the system (e.g. the reaction is heated).

If the values for the enthalpy and entropy changes are known for a reaction, it is possible to calculate the value of the free energy change at any temperature.

If the measurements are all made under standard conditions, then:

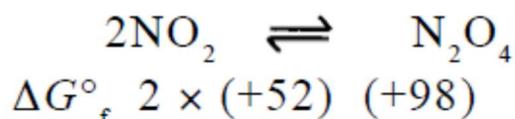
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Although a negative ΔG or ΔG° value allows one to predict that the reaction is feasible, i.e. the reaction will go in the direction of the products, it does not imply anything about the rate of the reaction. The activation energy for the reaction must be overcome for the reaction to occur and this could be very high and so the reaction could be very slow.

For example, if hydrogen and oxygen gases are mixed, the standard free energy change for the formation of 1 mole of water at 298 K is about -237 kJ mol^{-1} . However, virtually no reaction occurs until energy is supplied to overcome the activation energy or a suitable catalyst is added.

The standard free energy change for a reaction can be calculated from tabulated data of standard enthalpy and standard entropy changes for that reaction. In the same way as standard enthalpies of formation can be used to calculate the standard enthalpy change for a reaction, the standard free energy for a reaction can be calculated from the standard free energies of formation:

e.g.



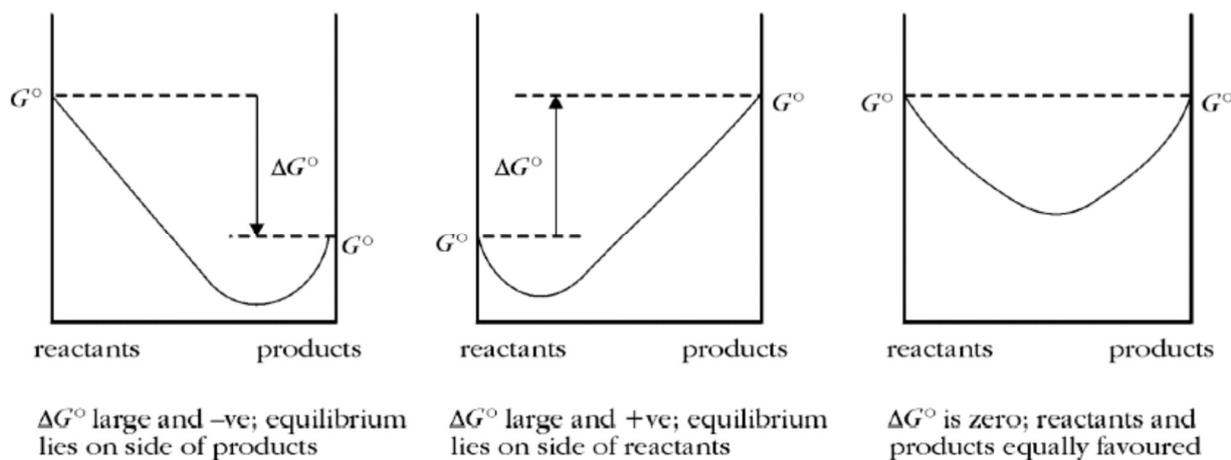
$$\begin{aligned} \text{At 298 K, } \Delta G^\circ &= +98 - (2 \times 52) \\ &= -6 \text{ kJ mol}^{-1} \end{aligned}$$

Free energy and equilibrium

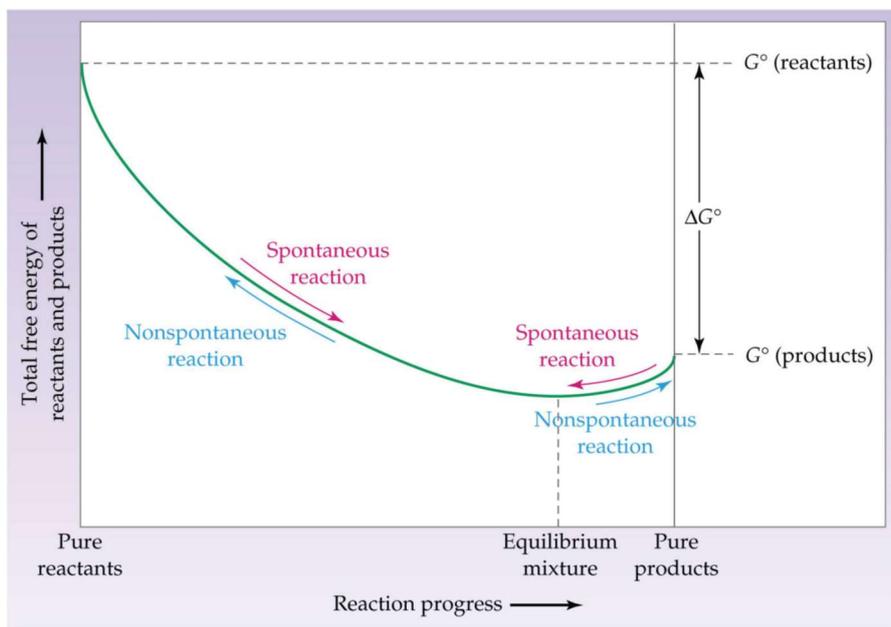
Only when the free energy of the reactants has fallen (by the reactants being used up) to the same value as the products (i.e. $\Delta G = 0$) do we reach equilibrium. At equilibrium, the free energy of the system has reached its minimum value under the given conditions.

In any chemical system once the reaction has started G will be lower than G° since:

- there is a change from standard conditions
- there is an increased entropy due to the mixing of reactant and product.



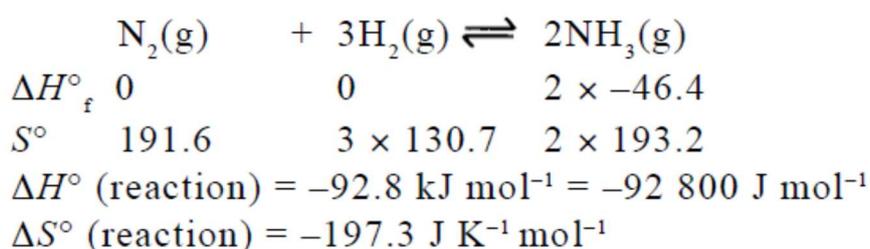
The minimum point of the free energy curve corresponds to the position of equilibrium and at this point $\Delta G = 0$.



We can now provide a picture of the difference between ΔG° (standard free energy change) and ΔG . The value of ΔG° tells the observer (outside the reaction) whether the equilibrium position will favour reactants or products. When equilibrium is established, the concentrations of the various species will not be of unit concentration and therefore standard conditions are not applicable. When equilibrium has been established, the ΔG value (inside the reaction) will be zero. Thus, at equilibrium, the free energy of reactants will be equal to the free energy of products and this is why there is no further change in the composition of the reaction with time.

When $\Delta G^\circ = 0$, neither products nor reactants are favoured. This is called the balance point, i.e. products and reactants are equally favoured. It is often possible to calculate the conditions at which the ΔG° value changes from being positive to being negative (which is when $\Delta G^\circ = 0$). This is done by considering only the standard free energies of the reactants and products. This can inform the observer about the conditions at which a reaction is just becoming feasible, i.e. when products are just slightly more favoured than reactants. *E.g.*

At what temperature does the Haber process become feasible?



When products are favoured as much as reactants, $\Delta G^\circ = 0$.

Thus from the equation:

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ T &= \Delta H^\circ / \Delta S^\circ = -92\,800 / -197.3 \\ &= 470 \text{ K} \\ &= 197^\circ\text{C} \end{aligned}$$

This result can be interpreted as meaning that at 470 K, the reactants and products are equally favoured. By considering the sign of ΔS° , we can work out whether the reaction is feasible at a temperature higher or lower than 470 K. Since ΔS° is negative, $-T\Delta S^\circ$ is positive. At low temperatures, ΔH° will dominate and ΔG° will be negative. Hence, the Haber process becomes feasible at temperatures below 470 K. By calculating ΔG° at temperatures slightly above and below 470 K, it is possible to see that ΔG° is positive at temperatures above 470 K and negative at temperatures below 470 K.

Therefore, ammonia production is feasible at temperatures below 470 K. Unfortunately, the industrial reaction cannot be carried out at such a low temperature as a suitable catalyst has not yet been found. It is interesting to note that leguminous plants can bring about this reaction. Current research is trying to identify the enzymes responsible to see if they could be used on an industrial scale.

The calculation does not say anything about either the reaction pathway or the reaction rate.

Thermodynamics tells us only how far a reaction will proceed (given enough time), it can never tell us how fast a reaction will take place or by which route. The fact that the standard free energy change is greater than zero does not mean that no reaction takes place. It means that the products are less favoured than the reactants. In industry, equilibrium is rarely allowed to occur.

Removal of a product can make a reaction with an unfavourable equilibrium position move in the desired direction.

Questions

1. Calculate the temperature at which the decomposition of barium carbonate becomes feasible.

$$\Delta H^\circ = 268 \text{ kJ mol}^{-1} \quad \Delta S^\circ = 168 \text{ J K}^{-1} \text{ mol}^{-1}$$

Is decomposition more favourable above or below this temperature?

2. The reaction of carbon with steam to produce carbon monoxide and hydrogen is endothermic ($\Delta H^\circ = 131 \text{ kJ mol}^{-1}$).

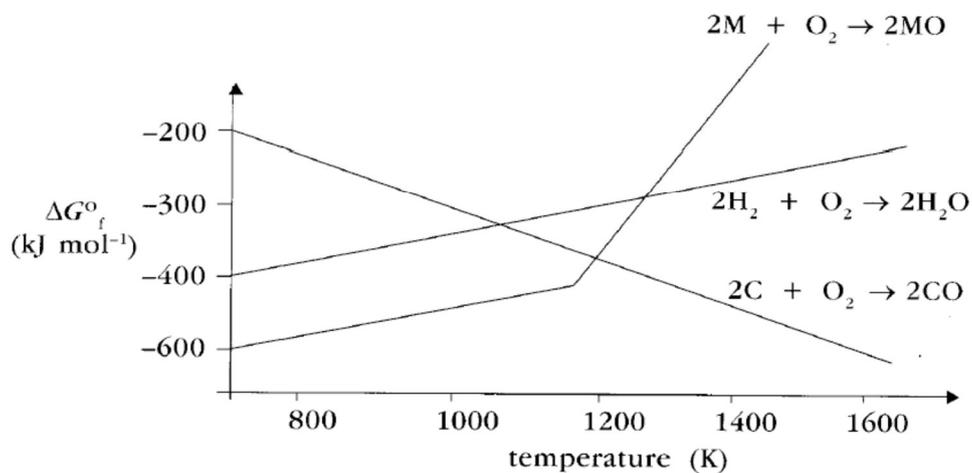
The reaction is successful at 1500 K when $\Delta G^\circ = -71.5 \text{ kJ mol}^{-1}$

- (a) Calculate the entropy change for the above reaction at 1500 K.
- (b) Is the reaction feasible at 25°C?
- (c) At which temperature does the reaction just become feasible?

Problem Solving

Ellingham Diagrams are used to predict whether it is feasible to extract metals from their ores and which reducing agents may be suitable. The following Ellingham diagram shows the dependence of ΔG° on temperature for a range of oxidation reactions:

3.



What is the minimum temperature at which the metal oxide, MO, can be reduced by:

- (d) hydrogen
- (e) carbon?

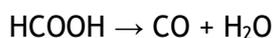
(c) Kinetics

Chemical kinetics is the study of the speed of chemical reactions. From Higher Chemistry it is already known that the speed or rate of a chemical reaction depends on factors such as temperature, concentration of the reactants, particle size and whether a catalyst is present or not. It is also known that all reactions have an activation energy and that an activated complex is formed.

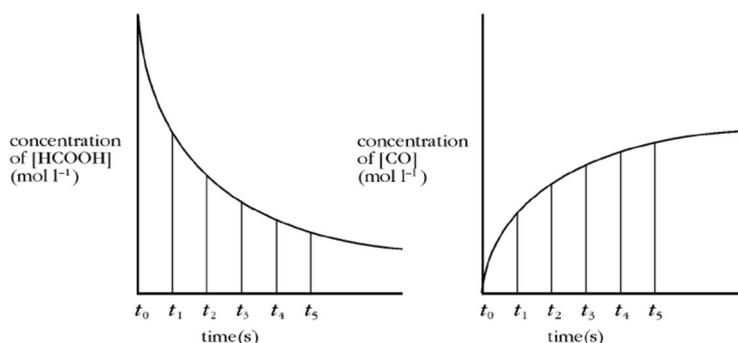
In this section, we are now concerned with the development of these ideas on a more quantitative basis, in which mathematical models are used to state precisely how the concentration of reactants influences the speed of a chemical reaction. We are also interested in how such information can be used to gain an insight into the pathway by which the reaction takes place.

It is customary when dealing with reaction rates to express the rate as a change in concentration of reactant or product in unit time. Expressed in this way, the rate is independent of the size of the sample under consideration.

For example, in the decomposition of methanoic acid:



We can determine the reaction rate by following either the decrease in concentration of the acid or the increase in carbon monoxide concentration with time:



The average reaction rate is the change in concentration of either reactants or products divided by the elapsed time. For example, over the time interval t_1 to t_2 :

$$\text{average reaction rate} = \frac{([\text{HCOOH}]_2 - [\text{HCOOH}]_1)}{(t_2 - t_1)}$$

or

$$\text{average reaction rate} = \frac{+([\text{CO}]_2 - [\text{CO}]_1)}{(t_2 - t_1)}$$

(Note that the negative sign is used if we are dealing with reactant concentrations since their concentrations decrease with time.)

It should be clear from the graphs above that, as is the case with most reactions, the rate decreases as the reaction proceeds.

We need to make the elapsed time interval as short as possible, and in effect measure the instantaneous rate, i.e. as Δt approaches zero. We can write, for a very small time interval, dt , that the instantaneous rate is:

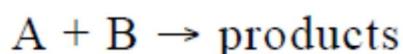
$$\frac{-d[\text{HCOOH}]}{dt} \quad \text{or} \quad \frac{+d[\text{CO}]}{dt}$$

Thus, the rate, at any time t , is given by the gradient of the tangent to the curve at time t . This will have a maximum value at time $t = 0$ and it is therefore usual to determine initial rates of reaction and to use these values in the determination of other kinetic parameters.

Reaction rates and concentration

The qualitative dependence of reaction rate on concentration can be readily demonstrated using many reactions, e.g. the iodine clock reaction, or by measuring the volume of hydrogen produced when magnesium reacts with different concentrations of dilute hydrochloric acid.

If we consider a very simple reaction:



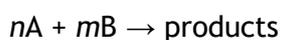
the rate of the forward reaction at any time depends on the concentration of A and B at that time and can be expressed as follows:

$$\text{rate} \propto [A][B]$$

$$\text{rate} = k[A][B]$$

where k is the rate constant.

In more general terms, for a simple reaction:



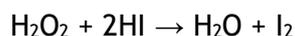
$$\text{rate} = k[A]^n[B]^m$$

This equation is the **rate law**.

The quantities n and m are termed the orders with respect to the reactants A and B respectively. The overall order of reaction is given as the sum of the powers of the concentration terms that occur in the rate equation, i.e. in the above example the overall order is $n + m$. In simple reactions, the rate law, sometimes called the rate equation, can take one of the forms shown in the table:

Rate law	Order of reaction
rate $\propto [A]^0$	0
rate $\propto [A]^1$	1
rate $\propto [A]^2$	2
rate $\propto [A]^1[B]^1$	2
rate $\propto [A]^1[B]^2$	3

These small integral values for the order of reaction are readily understandable if we realise that they refer to the actual number of particles involved in the single step of the reaction that controls the overall reaction rate, i.e. the rate-determining step. This is not necessarily the number of particles involved in the stoichiometric equation. For example, consider the reaction of hydrogen peroxide with hydrogen iodide:



The experimentally observed rate law is:

$$\text{rate} \propto [\text{H}_2\text{O}_2][\text{HI}]$$

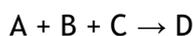
and consequently the order of reaction is two, whereas the balanced equation has three reactant molecules. The order of reaction is entirely an experimental quantity that is determined solely by finding the rate equation that best fits

the experimental data. It cannot be deduced from an examination of the chemical equation for the reaction.

Determining rate constants and orders of reaction

The rate constant of a reaction can be determined from a series of experiments in which the initial concentrations of the reactants are changed. The initial rate of each reaction is calculated and comparisons made:

e.g Consider the following data for an imaginary reaction:



and calculate the rate constant for this reaction.

Experiment	[A] (mol l^{-1})	[B] (mol l^{-1})	[C] (mol l^{-1})	Initial rate of D formed ($\text{mol l}^{-1} \text{ s}^{-1}$)
1	1.0	1.0	1.0	20
2	2.0	1.0	1.0	40
3	1.0	2.0	1.0	20
4	1.0	1.0	2.0	80

From these results we can see that:

- (a) doubling [A] doubles the rate (compare 1 and 2)
- (b) doubling [B] has no effect on rate (compare 1 and 3)
- (c) doubling [C] increases the rate fourfold (compare 1 and 4).

Relating the effect of change in concentration of reactants to the rate of reaction, the experimental rate law becomes:

$$\text{rate} \propto [\text{A}][\text{B}]^0[\text{C}]^2$$

or, more simply:

$$\text{rate} \propto [\text{A}][\text{C}]^2$$

The reaction is first order with respect to A, second order with respect to C and zero order with respect to B. The overall order is $(1 + 2 + 0) = 3$.

The rate constant, k , for this reaction is obtained by substituting values from experiment 1 in the rate equation:

$$\text{rate} = k[\text{A}][\text{C}]^2$$

$$20 = k[1.0][1.0]$$

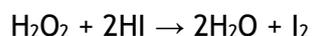
$$k = 20 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-2}$$

Identical values are obtained using any of the other three sets of results.

Kinetics and reaction mechanism

Chemical kinetics may be thought of as an example of the 'bottle-neck principle', which is frequently observed in everyday life. For instance, a large crowd of people leaving a football ground can only do so at a rate equal to the number who can squeeze through the exit in unit time. It makes no difference whether they run or walk to or from the exit.

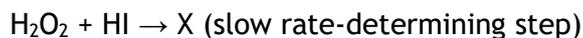
Similarly, if a chemical reaction proceeds in a series of sequential stages, the overall rate of reaction will be determined by the slowest step, which we call the rate-determining step. The kinetic parameters, which are determined experimentally, refer to this rate-determining step. By reversing the argument, experimentally determined rate equations and orders of reaction can give information about the way in which the reaction occurs. The following three reactions illustrate this.



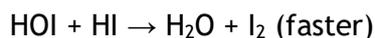
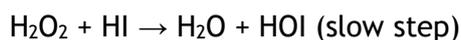
Experimentally the rate equation is of the form:



This tells us that the rate must be controlled by a step in which one molecule of hydrogen peroxide reacts with one molecule of hydrogen iodide. We can suggest that:



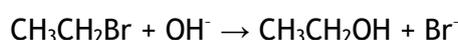
where X is an intermediate formed in the reaction. However, the kinetics themselves give us no direct information about either nature of X or about the total number of steps involved. These must be deduced by other means, such as spectroscopy. The generally accepted mechanism for this reaction is:



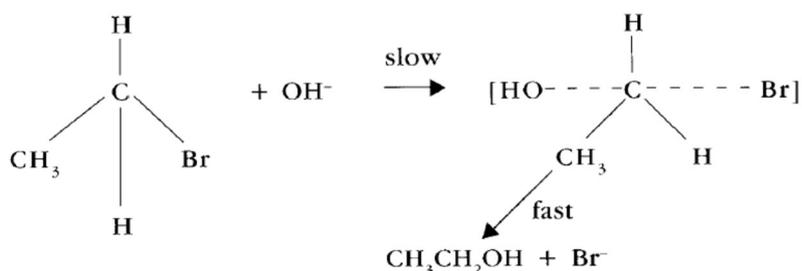
where HOI is an intermediate formed with a transient lifetime.

Hydrolysis of halogenoalkanes (see Unit 2)

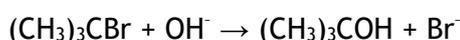
(a) A primary halogenoalkane



From the rate equation we can deduce that both of the reactants are involved in the rate-determining step. How this takes place is shown below. It can be seen that in the slow rate-determining step (in fact the only step in the reaction) the hydroxide ion displaces the bromide ion by attack at the 'back' of the molecule in an $\text{S}_{\text{N}}2$ process (see Unit 2).



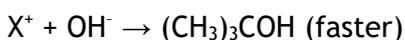
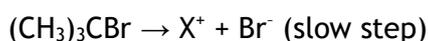
(b) A tertiary halogenoalkane



The observed rate law depends only on the concentration of the halogenoalkane:



The rate-determining step does not, in this case, involve the hydroxide ion. The mechanism can be written as follows:

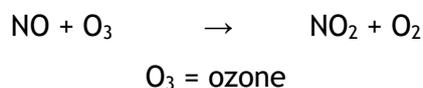


The reaction is a two-step (or, more accurately, more than one-step) process, involving some intermediate (X^+), which by other means we can determine to be the carbocation $(\text{CH}_3)_3\text{C}^+$.

It has to be emphasised that, on the basis of kinetics alone, we cannot establish the exact mechanism of a reaction. We can only propose a possible mechanism that is consistent with the kinetics.

Questions

1. The following exothermic reaction takes place in the upper atmosphere where the temperature is much lower than on the Earth's surface.



In a laboratory- simulated study carried out at room temperature, the following results were recorded.

<i>Relative concentration</i> NO	<i>Relative concentration</i> O ₃	<i>Reaction Rate</i>
1	1	1
2	1	2
1	2	2

- (a) Write out the rate expression for the reaction.
- (b) What is the overall order of the reaction ?
- (c) The reaction in the upper atmosphere is slower than the laboratory reaction for the same relative concentrations of NO and O₃. Account for this observation.
- (d) From the above equation, comment on the statement "NO catalyses the decomposition of ozone".
- (e) In the above reaction, NO removes ozone from the upper atmosphere. Suggest one possible man-made source of oxides of nitrogen which could contribute to this effect.

Glossary

Word	Meaning
bond enthalpy	For a diatomic molecule XY the molar bond enthalpy is the energy required to break one mole of XY bonds, the products being X and Y. All reactants and products must be in the gas state.
buffer solution	A solution in which the pH remains approximately constant when small amounts of acid or base are added
closed	A closed system has no exchange of matter or energy with its surroundings
conjugate acid	For every base, there will a conjugate acid formed by gain of a proton (H +)
conjugate base	for every acid, there is a conjugate base formed by loss of a proton (H + ion)
dynamic equilibrium	A dynamic equilibrium is achieved when the rates of two opposing processes become equal, so that no net change results
end point.	The end point of a titration is the point when the reaction is shown to be complete. This is frequently signalled by the change in colour of an indicator.
enthalpy of neutralisation	The enthalpy change when the acid is neutralised to form one mole of water
enthalpy of solution	The enthalpy change when one mole of a substance is dissolved completely in water
entropy	The entropy of a system is the degree of disorder of the system. The greater the disorder, the greater the entropy. Low entropy is associated with strongly ordered substances

Word	Meaning
equivalence point	the equivalence point in a titration experiment is reached when the reaction between the titrant (added from the burette) and the titrate (in the flask) is just complete.
First Law of Thermodynamics	states that the total energy of the universe is constant - energy can neither be created nor destroyed
ground state	This is the lowest possible electronic configuration the electrons in an atom can adopt.
Hess's Law	Hess's Law states that the overall reaction enthalpy is the sum of the reaction enthalpies of each step of the reaction.
intermediate	A species that is formed in one step of a reaction mechanism and then used up in a subsequent step
mean molar bond enthalpy	An average value that is quoted for a bond that can occur in different molecular environments
molar bond enthalpy	The molar bond enthalpy for a diatomic molecule X-Y is the energy required to break one mole of X-Y bonds, that is for the process: X - Y(g) X(g) + Y(g)
molar solution	A molar solution contains 1 mole of solute in 1 litre of solution.
monoprotic	an acid which is able to produce one H ⁺ ion from each molecule
order of a reaction	The power to which the concentration of a particular reactant is raised in the rate equation
overall order of a reaction	The sum of the powers to which the concentrations of all reactants in the rate equation are raised in the rate equation

Word	Meaning
quantitative reaction	A quantitative reaction is one in which the reactants react completely according to ratios in the balanced stoichiometric equation.
rate constant	In a rate equation, k is the rate constant and has a constant value for a given reaction at a particular temperature
rate determining step	The slowest step in a reaction mechanism that governs the overall rate
rate equation	An equation that tells how the reaction rate depends on the concentration of each reactant
reaction mechanism	The series of simple steps by which a chemical reaction occurs
Second Law of Thermodynamics	The total entropy of a reaction system and its surroundings always increases for a spontaneous change
stable equilibrium	A stable equilibrium state is one which is regained after a small disturbance from this state occurs.
standard conditions	Conditions at a pressure of one atmosphere and a specific temperature (298 K)(25 °C).
standard enthalpy change	The enthalpy change for a reaction in which reactants and products are considered to be in their standard states at a specified temperature
standard Gibbs free energy	The standard Gibbs free energy change for a reaction is related to the standard enthalpy and entropy changes by $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ The direction of spontaneous change is in the direction of decreasing free energy.

Word	Meaning
standard molar enthalpy of combustion	The enthalpy change when one mole of a substance is completely burned in oxygen under standard conditions.
standard molar enthalpy of formation	The enthalpy change that occurs when one mole of a substance is produced from its elements in their standard states
standard solution	A standard solution is one with an accurately known concentration. It can be prepared by weighing a primary standard and dissolving it in a known volume of solution, or by titrating against another standard solution.
standard state	The most stable state of a substance or element under standard conditions
Third Law of Thermodynamics	The Third Law of Thermodynamics states that the entropy of a perfect crystal at 0 K is zero