

A microscopic view of a mineral specimen showing a central cluster of green, translucent crystals with a radial, fibrous structure. The crystals are surrounded by a dense field of smaller, clear, needle-like crystals that radiate outwards from the center. The overall appearance is that of a complex crystalline growth.

# **IB Chemistry Investigations**

**Volume 1 (Standard Level)**

## **TEACHING NOTES**

*(For use with the IB Diploma programme)*

**(Fourth edition)**

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## Foreword to the Fourth Edition

This is not a practical course to be followed from cover to cover, more an à la carte menu for teachers to select from. There are far too many Investigations for the full 40/60 hours of mandatory practical work, let alone what remains when time for the Group 4 Investigation and the Internal Assessment project have been subtracted. It is hoped that teachers will be able to choose a variety of different practical exercises that fit in with the course they have planned and the ability of their students. There are now certain areas where practical work is prescribed and these are coloured in the Syllabus Correlation Table in the Teaching Notes – your programme should include at least one Investigation of each colour.

Whilst many of the Investigations in this book are quite similar to those in previous editions there are a number of new additions. There are also some significant changes to the way that a number of the Investigations have been presented. This is in response to the changes that have been made to the Internal Assessment in IB Chemistry. The focus of most Investigations under the previous system was to provide assessment opportunities for one of the IA criteria, hence they were often presented in a very open ended manner so as to conform to the assessment requirements. Now that the IA is just a single extended investigation, it frees up the regular routine laboratory work to provide practical reinforcement for the theory content and to prepare students for the IA assignment. As a result many of the Investigations are more directed, with results tables and specific questions that will hopefully direct the attention of the students to the important concepts that the Investigation deals with. There are also some more open-ended tasks and still a few Investigations where students come up with their own specific research ideas. It is hoped that exercises of this sort will help prepare students for their IA assignment. I must admit I have some reservations about the new IA system. Whilst it is good to free laboratory time from the constraints of assessment, it might have the effect of devaluing the practical component of the programme and, even though the requirement remains 25% of the teaching time, I fear that some schools may erode this time now it is less directly linked to the IA. Hopefully the fact that you have purchased this book indicates that you are not such a teacher!

I hope that you find this new edition useful in your teaching and I would be delighted to hear from any of you, who have ideas or suggestions as to how this work can be improved further for future editions. This is probably simplest through the publisher's <website; [www.ibid.com.au](http://www.ibid.com.au)>

*John Green (author)*

New Zealand 2014

## Author Profile

After extensive teaching experience in the UK at Repton and Manchester Grammar School, Dr John Green began his involvement with the IB when he joined the staff at Kristin School, in 1987. There, as IB coordinator, he was responsible for the introduction of the IB into the school, the first in New Zealand to offer the programme. Then followed a twelve year period when he was Director of Studies at the Li Po Chun United World College in Hong Kong. Now, as an independent educational consultant, John is an IB Deputy Chief Examiner for Chemistry, a moderator for the Chemistry Internal Assessment, a marker of the Chemistry Extended Essays and an assessor for Theory of Knowledge. He was extensively involved in the current syllabus revision and the setting of examination papers. He has run many IB workshops in both Chemistry and Theory of Knowledge.

## Acknowledgements

Whilst one or two of these practicals have been specially developed for this publication, the vast majority have been refined during my years of teaching at Repton, Manchester Grammar, Kristin and Li Po Chun. I would therefore like to thank my colleagues at these institutions and the students I taught for their many invaluable observations. In all of these schools I was blessed by the support of superb laboratory technicians, the unsung heroes of science teaching. I would therefore like to particularly thank them for the innumerable ways in which they have helped to refine and improve these Investigations. I would also like to thank my friends and former colleagues at ACG Senior College in Auckland for allowing me access to their science laboratories to try out some of my ideas. Our thanks also to Nicole Lukins for her expert checking and helpful suggestions with the sample data and the Teaching Notes

## Contents with Syllabus references

No.	Title	Topic	Syllabus reference
1A	Determining the Water of Crystallisation	1.2	Obtaining and using experimental data for deriving empirical formulas from reactions involving mass changes.
1B	Determining the Composition of "Copper Carbonate"	1.2	
1C	How Concentrated is "Concentrated" Nitric Acid?	1.3	Use of the experimental method of titration to calculate the concentration of a solution by reference to a standard solution
1D	Determining the Molar Mass of a Soluble Acid	1.3	
1E	Identifying fuels from their molar masses	1.3	Obtaining and using experimental values to calculate the molar mass of a gas from the ideal gas equation.
2A	Observing Emission Spectra	2.2	Emission spectra could be observed using discharge tubes of different gases and a spectroscope. Flame tests could be used to study spectra.
3A	Some Reactions of the Halogens	3.2	Experiment with chemical trends directly in the laboratory or through the use of teacher demonstrations.
4A	Forces Between Particles and Physical Properties	4.1	Students could investigate compounds based on their bond type and properties.
5A	Measuring Enthalpy Changes	5.1	A calorimetry experiment for an enthalpy of reaction should be covered and the results evaluated. Experiments could include calculating enthalpy changes from given experimental data (energy content of food, enthalpy of melting of ice or the enthalpy change of simple reactions in aqueous solution).
5B	Using Hess' Law to Determine Enthalpy Changes	5.2	A calorimetry experiment for an enthalpy of reaction should be covered and the results evaluated. Experiments could include Hess's Law labs.
6A	Techniques for Measuring Reaction Rates	6.1	Investigation of rates of reaction experimentally and evaluation of the results. Experiments could include investigating rates by changing concentration of a reactant or temperature.
6B	Factors Affecting Rates of Chemical Reactions	6.1	Investigation of rates of reaction experimentally and evaluation of the results. Experiments could include investigating rates by changing concentration of a reactant or temperature.
6C	A Quantitative Investigation of Reaction Rates	6.1	Investigation of rates of reaction experimentally and evaluation of the results. Experiments could include investigating rates by changing concentration of a reactant or temperature.
7A	An Introduction to Equilibrium	7.1	The characteristics of chemical and physical systems in a state of equilibrium. Physical and chemical systems should be covered.
7B	An Introduction to Vapour Pressure	7.1	The characteristics of chemical and physical systems in a state of equilibrium. Physical and chemical systems should be covered.
7C	Predicting the Effect of Changes on an Equilibrium	7.1	Le Châtelier's principle can be investigated qualitatively by looking at pressure, concentration and temperature changes on different equilibrium systems.
8A	The Solubility of Ethanedioic (Oxalic) Acid	8.2	Candidates should have experience of acid-base titrations with different Indicators. The evidence for these properties could be based on a student's experimental experiences.
8B	Percentage of Nitrogen Content in a Fertilizer	8.2	Candidates should have experience of acid-base titrations with different Indicators. The evidence for these properties could be based on a student's experimental experiences.

No.	Title	Topic	Syllabus reference
8C	A Comparison of Strong and Weak Acids and Bases	8.4	Students should be familiar with the use of a pH meter and universal indicator. Students should have experimental experience of working qualitatively with both strong and weak acids and bases. Examples to include: $\text{H}_2\text{SO}_4$ (aq), $\text{HCl}$ (aq), $\text{HNO}_3$ (aq), $\text{NaOH}$ (aq), $\text{NH}_3$ (aq).
9A	Common Oxidizing and Reducing Agents	9.1	Experiments could include demonstrating the activity series, redox titrations and using the Winkler Method to measure BOD.
9B	Redox Titrations	9.1	Experiments could include demonstrating the activity series, redox titrations and using the Winkler Method to measure BOD.
9C	Investigating some Electrochemical Cells	9.2	Performance of laboratory experiments involving a typical voltaic cell using two metal/metal-ion half-cells.
10A	Investigating Organic Structures using Models	10.1	Construction of 3-D models (real or virtual) of organic molecules.
10B	Reactions of Hydrocarbons	10.2	Experiments could include distinguishing between alkanes and alkenes.
10C	Reactions of Organic Compounds containing Oxygen	10.2	Experiments could include reflux and distillation.
11A	Analysis of Organic Spectra	11.3	Deduction of information about the structural features of a compound from percentage composition data, MS, $^1\text{H}$ NMR or IR.
<b>OPTION TOPICS</b>			
22A	Investigating the Behaviour of Catalysts	A.3	Experiments could include investigating the decomposition of potassium sodium tartrate with cobalt chloride and the decomposition of hydrogen peroxide with manganese (IV) oxide.
23A	The Chromatographic Separation of Amino acids	B.2	Experiments could involve identification of amino acid mixtures by paper chromatography.
24A	The Enthalpy of Combustion of fuels	C.1	The energy density of different fuels could be investigated experimentally.
25A	The Synthesis of Aspirin	D.2	Experiments could include the synthesis of aspirin.

### Key to Required Practicals

No.	Topic	Requirement
1	Topic 1.2	Determination of the molecular formula of a compound from its empirical formula and molar mass.
2	Topic 1.3	Obtaining and using experimental values to calculate the molar mass of a gas from the ideal gas equation.
3	Topic 1.3	Use of the experimental method of titration to calculate the concentration of a solution by reference to a standard solution
4	Topic 5.1	A calorimetry experiment for an enthalpy of reaction should be covered and the results evaluated.
5	Topic 6.1	Investigation of rates of reaction experimentally and evaluation of the results.
6	Topic 9.2	Performance of laboratory experiments involving a typical voltaic cell using two metal/metal-ion half-cells.
7	Topic 10.1	Construction of 3-D models (real or virtual) of organic molecules.
8	Topic 15.1 / Topic 19.1	Perform lab experiments which could include single replacement reactions in aqueous solutions.

## Health and Safety Warnings and Symbols

Laboratories can be hazardous places. Often scientists, Science teachers and students handle equipment and materials which can be dangerous to their health and safety. Throughout these Volumes of Investigations you will see a number of symbols and warnings which will represent particular hazards. For each of these we will briefly describe the hazard and indicate what precautions you should take to avoid damage and/or what responses are appropriate. In all cases, of course, you should seek advice and assistance from the teacher or laboratory technician.

A biohazard is any organism or body fluid which could possibly cause illness or disease in your body. This particularly includes micro-organisms.



A flammable substance is one which will readily burn in air. It may be a solid, liquid or gas. If you are using such a substance it is vital that there are no sparks or naked flames which could ignite it. It is vital that you know what to do in the event of fire. This may include the use of fire extinguishers and evacuation procedures.



A radioactive substance is one which emits particles or 'radiation'. This radiation is known to cause damage to cells and may also be cancer causing. If you are using radioactive substances it is vital that you wear protective clothing, use metal tongs and listen carefully to instructions given by your teacher or laboratory technician.



Sharp instruments are often used in Science and particularly in Biology, to cut sections through plant or animal tissue. These instruments, which include scalpels and razor blades are very sharp and obviously will also cut through your tissues. When using these instruments it is essential that you always cut away from your body and preferably onto a cutting board. It is also important to be very careful when carrying these instruments and also ensure they are placed on the workbench in a safe place.



When certain chemicals are mixed together they can become explosive. An explosion is caused by rapid expansion of gas in a confined space and can be very dangerous. Sometimes it is important to ensure that the space is not confined and sometimes it is important to conduct these reactions behind a protective screen.



It is often necessary to protect your hands from heat, chemicals or other hazards and gloves will be made available for these situations. The type of glove needed will depend on the particular hazard and your teacher will provide further advice. In some cases you will be advised to dispose of the gloves after use and in other cases to wash and dry them carefully.



Your eyes are the most vulnerable and easily damaged external part of your body. This is why they must be protected if you are using solids and liquids which could get into them. Whenever you are heating things or using corrosive liquids, and in other cases as instructed by a teacher, you should wear safety goggles. You should also do this if possible even if you wear spectacles to correct your vision. In the event that something gets in your eye you should immediately make use of the eyewash facility in the laboratory as instructed and then notify your teacher.



Some chemicals, which are used in a laboratory, are *corrosive*. This means that they can react with and 'eat away' materials like the bench, your books, clothing and skin. It is essential that you handle these materials, which are usually liquids, with care. Always tip from the container with the label uppermost, never add water to concentrated acid and never have your face anywhere near the container. It is usually advisable to wear both safety goggles and gloves. If protective aprons are available you should also wear one.



As a general rule, 12 or 24 volt *electrical* appliances are unlikely to cause serious injury. However, 'mains' voltage (110V or 240V or higher) can cause serious injury or death. The appliances you use should be regularly tested and certified safe. If you notice sparks or smell insulation burning, turn the power off immediately and notify staff. Be particularly careful not to allow water to get into any appliance as it may cause a short circuit.



Some chemicals are *poisonous* and should not be inhaled or ingested. It will be necessary to use a fume cupboard when using poisonous gases or volatile liquids. They could make you very ill and you may require medical assistance. It is vital that you listen to instructions, follow them carefully and notify your teacher immediately if there is accidental exposure to poisonous or toxic substances.



Lasers are very intense beams of light. They are capable of causing burns to the skin and permanent damage to the eyes. It is essential that these are only ever used under the supervision of a teacher and in a situation where people can not see the beam directly or when it is reflected from a shiny surface. Sunglasses or welding masks do not provide sufficient protection and special 'laser glasses' must be used where there is a risk.



UV light is harmful to skin and especially eyes. Do not expose these areas directly to a UV light source. If it is not avoidable, sunscreen can be applied to the skin and special goggles should be worn.



There are other *dangers* or hazards as well, for example carrying heavy or hot objects. This may also include chemicals which are not poisonous but which may smell unpleasant or irritate the skin. Whenever you see this icon more information will be provided in the adjacent text about the specific danger.



In Science and particularly in Biology, there are situations when ethics and ethical issues need to be considered in experimental work. This is particularly the case when human volunteers are being used, not just for experimental work but also when they are being surveyed to collect personal information. In these cases a consent form should be used to explain the nature of their involvement and to get their approval. Ethics will also be an issue whenever animals are used in experimentation or when they are collected in the field. They should not be exposed to conditions that are outside their natural range of tolerance and wild animals must be released back where they were sampled with the minimum of disturbance.



The environment and environmental issues become important when hazardous substances are used or produced during an experiment. Their disposal must result in minimal impact on the environment. In field work the protocol that is used must reflect practices that minimise the impact of the investigation on the site.



## IMPORTANT NOTICE

Although every care has been taken in preparing and trialling these investigations, **absolutely no responsibility or liability whatsoever can be accepted for any damage or accident which may occur for whatever reason during the conduct of any of these activities.** The Safety Warnings and Icons are advisory only and are not intended to be exhaustive or exclusive. It is a strict condition of sale that safety in the laboratory is the responsibility of the staff and students doing the laboratory work and not the author, editor or publisher of this work.



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## SYLLABUS REFERENCE: TOPIC 1.2

Obtaining and using experimental data for deriving empirical formulas from reactions involving mass changes.

## Apparatus required

### Per group

- Bunsen burner
- Tripod
- Pipeclay triangle
- Crucible with lid

### General

- Balance capable of weighing to at least 0.01 g

## Chemicals required

- Hydrated copper(II) sulfate crystals (~10 g per student)

## Notes

*Probable timing - 60 minutes laboratory time*

This quantitative gravimetric exercise is included to get students to question assumptions and also to look at ways to improve the method they are given. Unless they are very careful with the heating then the anhydrous copper(II) sulfate will decompose further giving a product with a non-uniform colour - white in some places and changing from green to yellow to brown at the edges, where the temperature is highest. This should tell them that the product is not a single substance. As a result of this the value calculated for the number of moles of water of crystallization is usually around 5.5, depending on the temperature of the Bunsen flame and how long the solid is heated.

The practical is also useful to introduce students to the idea that there is a finite precision to quantitative work, as a result of random and systematic errors. It is sometimes useful to have students put their results on a spreadsheet so they can compare the values they obtain (it also helps in fulfilling Aim 7 of the syllabus). I have given an exemplar set of such data on the following page. This usually shows that the variation in the results is far greater than the precision uncertainty, hence the method has some major, variable, systematic error. It is also important to get students to work through whether a particular possible error, such as spilling a little of the solid, would lead to a higher or lower value for the final result. Hopefully some students will come up with the need for more careful, even heating and/or heating to constant mass.

It is also possible to use other salts, or even a variety of salts labelled A, B, C etc., though the extent to which further decomposition occurs will vary and some will not have any colour change involved. Suitable salts are:

- Hydrated magnesium sulfate crystals
- Hydrated barium chloride crystals
- Hydrated nickel sulfate crystals

**Warning: If you use hydrated barium chloride, do not forget to warn the students that it is toxic!**



# TEACHING NOTES for Investigation 1A

## DETERMINING THE AMOUNT OF WATER OF CRYSTALLIZATION

SL

### Class data

The data produced by a year group of students is given below:

$m_1$ /g	$m_2$ /g	$m_3$ /g	$\text{CuSO}_4$ /g	$\text{H}_2\text{O}$ /g	$\text{CuSO}_4$ /mol	$\text{H}_2\text{O}$ /mol	ratio	Appearance of residue
36.971	37.952	37.491	0.52	0.461	0.003270	0.025611	7.83	white powder, burnt on edges
36.134	37.441	36.968	0.834	0.473	0.005245	0.026278	5.01	white/grey powder
35.422	36.257	35.984	0.562	0.273	0.003535	0.015167	4.29	parts grey, white and black (on the side)
36.737	37.331	37.102	0.365	0.229	0.002296	0.012722	5.54	white, burnt brown around the edges
35.176	36.207	35.831	0.655	0.376	0.004119	0.020889	5.07	grey, green on the edges
35.796	36.84	36.345	0.549	0.495	0.003453	0.027500	7.96	grey, some parts brown and burnt
37.409	38.425	38.03	0.621	0.395	0.003906	0.021944	5.62	greyish-light green, brown on the side
35.62	36.848	36.398	0.778	0.45	0.004893	0.025000	5.11	greyish, burnt -black on the edges
35.977	37.018	36.634	0.657	0.384	0.004132	0.021333	5.16	white with greenish-black edges
35.727	36.647	36.316	0.589	0.331	0.003704	0.018389	4.96	white/grey powder
37.489	38.488	38.111	0.622	0.377	0.003912	0.020944	5.35	greenish white powder with grey/brown edges
36.344	37.335	36.958	0.614	0.377	0.003862	0.020944	5.42	white powder, burnt edges and top
34.445	35.44	35.04	0.595	0.4	0.003742	0.022222	5.94	white powder with grey edges, and an outer rim of orange
34.97	35.913	35.553	0.583	0.36	0.003667	0.020000	5.45	white powder, grey/brown edges
35.448	36.489	36.115	0.667	0.374	0.004195	0.020778	4.95	greyish white powder with a bit of black and yellowish-green powder
35.796	36.841	36.456	0.66	0.385	0.004151	0.021389	5.15	white powder with black solids
36.41	37.439	37.117	0.707	0.322	0.004447	0.017889	4.02	bluish grey powder with a bit brown powder
34.433	35.323	34.998	0.565	0.325	0.003553	0.018056	5.08	white powder, some parts brown/green
35.098	37.984	36.863	1.765	1.121	0.011101	0.062278	5.61	black powder with traces of white and blue powder.
34.972	35.972	35.602	0.63	0.37	0.003962	0.020556	5.19	white powder, some parts grey
36.02	37.04	36.638	0.618	0.402	0.003887	0.022333	5.75	very pale green with brown powder
35.135	36.25	35.846	0.711	0.404	0.004472	0.022444	5.02	greyish white, charred to greenish white on the edges
34.976	35.977	35.582	0.606	0.395	0.003811	0.021944	5.76	white product was a lump, which was both yellow and black underneath
37.3	38.4	37.9	0.6	0.5	0.003774	0.027778	7.36	greyish powder, slightly clumped
36.107	37.231	36.804	0.697	0.427	0.004384	0.023722	5.41	powder changed in color to white/gray/yellow
					<b>Mean</b>		<b>5.52</b>	

## Sample results

$$\text{Mass of empty crucible and lid} = 35.096 \pm 0.005 \text{ g}$$

$$\text{Mass of crucible, lid and hydrated salt} = 37.986 \pm 0.005 \text{ g}$$

$$\text{Mass of crucible and salt after heating} = 36.866 \pm 0.005 \text{ g}$$

## Data Analysis

$$\begin{aligned} \text{a) Mass of salt remaining} &= (36.866 \pm 0.0005) - (35.096 \pm 0.0005) \\ &= 1.790 \pm 0.001 \text{ g} (= \pm 0.0559\%) \end{aligned}$$

$$\begin{aligned} \text{Molar mass CuSO}_4 &= 63.55 + 32.07 + (4 \times 16.00) \text{ [each } \pm 0.005] \\ &= 159.62 \pm 0.03 \text{ g mol}^{-1} (= \pm 0.0188\%) \end{aligned}$$

$$\text{Amount of salt remaining} = 1.790/159.62 (= \pm 0.0747\%) = 0.011214 \pm 0.000008 \text{ mol}$$

$$\begin{aligned} \text{b) Mass of water lost} &= (37.986 \pm 0.005) - (36.866 \pm 0.0005) \\ &= 1.120 \pm 0.001 \text{ g} (= \pm 0.0893\%) \end{aligned}$$

$$\begin{aligned} \text{Molar mass water} &= 16.00 + (2 \times 1.01) \text{ [each } \pm 0.005] \\ &= 18.02 \pm 0.015 \text{ g mol}^{-1} (= \pm 0.0849\%) \end{aligned}$$

$$\begin{aligned} \text{Amount of water lost} &= 1.120/18.02 (= \pm 0.174\%) \\ &= 0.06215 \pm 0.00011 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{c) Ratio of mol(H}_2\text{O) : mol(CuSO}_4\text{)} &= 0.06215/0.011214 (\pm 0.249\%) : 1 \\ &= 5.5421 \pm 0.00138 : 1, \text{ or } 5.542 \pm 0.001 : 1 \end{aligned}$$

d) If the number is an integer it would be  $\text{CuSO}_4 \cdot 6 \text{ H}_2\text{O}$

e) The precision of the weighings was  $\pm 0.0005 \text{ g}$ . When propagated (see calculations above), this results in an uncertainty in the final value of  $\pm 0.001$  or about  $\pm 0.25\%$ .



## Evaluation

- a) Rising air currents lead to unstable readings on balances as sensitive as those used in chemistry investigations
- b) Many hydrated salts, in their anhydrous form, will absorb water vapour from the atmosphere, rehydrating them and resulting in an increase in their mass.
- c) At the start of heating the rate of evolution of water vapour is quite high and this can result in “spitting” of the solid. Having the lid partially on at this time minimises this loss of solid.
- d) The “text book” colour change is from blue to white. In practice a wide range of colours from yellowish-green through to browns and blacks are observed. These colours seem to arise from further decomposition of the anhydrous sulfate, with the former colours probably arising from sulfites, with the darker colours indicating the presence of copper(II) oxide.
- e) A small value would indicate that the decrease in mass on heating was less than expected. This could result from the solid not being heated for long enough, or to a high enough temperature, so that some of the water of crystallization remains. Another possible source of such an error would be from the anhydrous salt re-absorbing water vapour from the atmosphere.
- f) A large value would indicate that the decrease in mass on heating was greater than expected. This could result from further decomposition of the anhydrous sulfate if the heating was too strong. Loss of solid from the crucible, either through spitting during the heating, or from accidental spillage, would also give a ratio that was too high.
- g) The deviation from the accepted value of 5, of both the individual value obtained (5.542 or 11% deviation) and the mean of the group determination (5.52), is much greater than can be accounted for by the experimental uncertainty ( $\pm 0.001$  or  $\pm 0.02\%$ ), hence it would appear that systematic errors are the major factor and this would again fit with the observation that 21 of the 25 collected results are greater than 5. The variation of the values obtained by different groups, is also much larger than the uncertainty probably indicating that the systematic error can vary quite significantly in its magnitude.
- h) In e) and f) four possible sources of significant error were identified, so the techniques could be improved by altering it to minimise these. In order of decreasing probable importance:  
The temperature of the heating may be too high leading to further decomposition. A heating technique that involves better temperature control, such as a thermostatically controlled oven, would give better temperature control. The temperature would be best optimised by trial and error, but an initial value of about  $150^{\circ}\text{C}$  might be a good starting point.  
Some solid may be lost from the crucible. A way to minimise this is to heat the solid very slowly at the start with the lid fully on, perhaps by having the crucible containing the salt in the oven when it is first turned on. After the first weighing, when most of the water vapour will have been lost, the lid can be removed.  
The hydrated salt may not be heated for long enough. A way to combat this would be to heat to “constant mass”; the solid is heated, allowed to cool, reweighed and then heated again. This is continued until there is no further loss in mass.  
When cooling the crucible could be placed in a desiccator – a closed vessel containing a substance that absorbs water vapour.
- i) Quite a number of hydrated salts undergo further decomposition when heated. Hydrated iron(II) sulfate for example decomposes to iron(III) oxide, sulfur dioxide, sulfur trioxide and water vapour on heating. Many hydrated transition metal chlorides decompose to hydrogen chloride and the transition metal oxide on heating. In these cases the composition of the hydrated salt is best found by determining its molar mass, often by finding the amount of the metal present in a given mass of the solid using titration techniques.

## SYLLABUS RELEVANCE: TOPIC 1.2

Obtaining and using experimental data for deriving empirical formulas from reactions involving mass changes.

## Apparatus required

## Per group

- Bunsen burner
- Tripod
- Pipeclay triangle
- Crucible with lid

## General

- Balance capable of weighing to at least 0.01 g

## Chemicals required

- Copper carbonate (~10 g per student)

## Notes

*Probable timing—60 minutes laboratory time*

This is very closely related to the previous practical. Because of the greater complexity in working out the required results this is more suitable for a more able group of students—with very good students even the guidelines as to how to calculate the result could be omitted. If both practicals are to be done, then this one could perhaps be adapted as a planning exercise. “Copper carbonate” varies quite a lot between suppliers, so you really need to do your own determination to find out the “right” answer (or average out the results of your 2 or 3 most reliable students!).

## Sample results

Mass of empty crucible	= 28.993 ± 0.0005 g
Mass of crucible and carbonate	= 32.404 ± 0.0005 g
Mass of after initial heating	= 31.461 ± 0.0005 g
Mass of after final heating	= 31.442 ± 0.0005 g

## Data Analysis

$$\begin{aligned} \text{a) } M_r \text{ CuCO}_3 &= 63.55 + 12.01 + (3 \times 16.00) = 123.56 \\ M_r \text{ CuO} &= 63.55 + 16.00 = 79.55 \end{aligned}$$

$$\text{Mass of CuCO}_3 = 32.404 - 28.993 = 3.411 \text{ g}$$

$$\text{Mass of CuO} = 3.411 \times \frac{79.55}{123.56} = 2.196 \text{ g}$$

$$\text{b) } M_r \text{ Cu(OH)}_2 = 63.55 + (2 \times 16.00) + (2 \times 1.01) = 97.57$$

$$\text{Mass of CuO} = 3.411 \times \frac{79.55}{97.57} = 2.781 \text{ g}$$

$$\text{c) } 31.442 - 28.993 = 2.449 \text{ g}$$

- d)  $2.196y + 2.781(100 - y) = 2.449 \times 100$   
 $2.781y - 2.196y = 0.585y = 278.1 - 244.9 = 33.2$   
 $y = \frac{33.2}{0.585} = 56.75\%$
- e) Deduce the uncertainty of the value you have obtained by propagating the uncertainties in the weighings.

$$\text{Uncertainty in mass of substances} = 0.0005 + 0.0005 = \pm 0.001 \text{ g}$$

$$\text{Percent uncertainty in original mass of solid} = \frac{0.001}{3.411} \times 100 = 0.029\%$$

$$\text{Percent uncertainty in final mass of product} = \frac{0.001}{2.449} \times 100 = 0.041\%$$

$$\text{Uncertainty in molar masses} = \pm 0.005$$

$$\text{Percent uncertainty in molar mass of CuCO}_3 = \frac{5 \times 0.005}{123.56} \times 100 = 0.020\%$$

$$\text{Percent uncertainty in molar mass of Cu(OH)}_2 = \frac{5 \times 0.005}{97.57} \times 100 = 0.0256\%$$

$$\text{Percent uncertainty in molar mass of CuO} = \frac{2 \times 0.005}{79.55} \times 100 = 0.013\%$$

$$\text{Percent uncertainty in 2.196} = 0.029 + 0.020 + 0.013 = 0.062\%$$

$$\text{Absolute uncertainty in 2.196} = 2.196 \times \frac{0.062}{100} = 0.0014$$

$$\text{Percent uncertainty in 2.781} = 0.029 + 0.026 + 0.013 = 0.068\%$$

$$\text{Absolute uncertainty in 2.781} = 2.781 \times \frac{0.0678}{100} = 0.0019$$

$$\text{Absolute uncertainty in 0.585} = 0.0014 + 0.0019 = 0.0033$$

$$\text{Percent uncertainty in 0.585} = \frac{0.0033}{0.585} \times 100 = 0.56\%$$

$$\text{Absolute uncertainty in 33.2} = 100 \times (0.0019 + 0.001) = 0.29$$

$$\text{Percent uncertainty in 33.2} = \frac{0.29}{33.2} \times 100 = 0.87\%$$

$$\text{Percent uncertainty in } y = 0.56 + 0.87 = 1.43\%$$

$$\text{Absolute uncertainty in } y = 56.8 \times \frac{1.43}{100} = 0.805$$

$$\text{Final percentage of CuCO}_3 = 56.8 \pm 0.8\%$$



## Evaluation

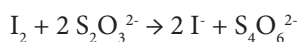
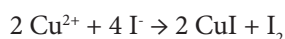
- (a) Because there is no “right answer” (the exact composition will vary slightly from supplier to supplier as it depends on the exact conditions of preparation) it is not possible to be sure how accurate the result is. Some indication might come from carrying out the same determination by using a different method, which would probably have different systematic errors, and seeing whether the values are in agreement.

One indication of uncertainty that has not been investigated is the consistency of the values obtained by the same group of experimenters, or by different groups of experimenters, who might employ slightly different techniques. Theoretically the values they obtain should be within the uncertainty calculated from the precision of the values used. If it is greater than this it probably indicated some systematic/random error that has not been taken into account, but which can vary in magnitude.

- b) The uncertainties arising from the weighings and the molar mass values are of a similar order of magnitude (~0.04%) and so improvements in either would be beneficial. Relative atomic mass data to greater precision than that given in the IB data booklet is readily available (e.g. H = 1.0079, C = 12.011, O = 15.999, Cu = 63.546) so reducing that source of uncertainty by an order of magnitude can be dealt with easily. Similarly balances that read to 4 dp can be purchased.

There are also a number of other sources of potential systematic error. Often students will observe black dust on the bench around the Bunsen indicating that solid is being lost. This would lead to an unexpectedly high mass loss, resulting in a greater percentage of copper(II) carbonate than the true value. One way to reduce this would be to carry out the reaction in a boiling tube rather than a crucible. More careful initial heating would also help. One other possible source of error might be that the initial “copper carbonate” was damp (it often gives that appearance from its physical behaviour). Again the mass loss would be greater than expected, increasing the apparent percentage of copper(II) carbonate. Heating to dry it probably wouldn't be advisable; maybe storing it in a sealed container alongside a suitable drying agent (anhydrous  $\text{CaCl}_2$ ?) would help.

- (c) The best way to do this would be to find the percentage of  $\text{CuCO}_3$  present using other methods and to see if these agree. Any method that gives the apparent molar mass of the compound could be used. Techniques could include titrating a solution, accurately made up in excess sulfuric acid, to find the  $[\text{Cu}^{2+}]$  by adding excess potassium iodide and titrating the liberated iodine with aqueous sodium thiosulfate:



Alternatively the  $[\text{Cu}^{2+}]$  in the solution could be found spectrophotometrically by comparing the absorption with standard solutions of copper(II) sulfate.

One other contrasting method would be to heat the “copper carbonate” and find the amount of carbon dioxide evolved for example from its volume (at known T & P) or by absorbing it into aqueous alkali and back titrating.

## SYLLABUS RELEVANCE: TOPIC 1.3

Use of the experimental method of titration to calculate the concentration of a solution

by reference to a standard solution

## Apparatus required

## Per group

- Burette
- Burette funnel
- 25 cm<sup>3</sup> pipette
- 10 cm<sup>3</sup> pipette
- Pipette filler
- 100 cm<sup>3</sup> volumetric flask
- 250 cm<sup>3</sup> volumetric flask
- Weighing bottle
- 2 × 100/150 cm<sup>3</sup> conical flask

## General

- Balance capable of weighing to at least 0.01 g

## Chemicals required

Concentrated nitric acid (~10 cm<sup>3</sup> per group)

Solid anhydrous sodium carbonate (~10 g per group) [should be dried in an oven at ~110°C for 24 hours]



## Notes

*Probable timing—90 minutes laboratory time*

This is a useful introduction to volumetric analysis. I have not specified a particular method as I find that many teachers have their own particular preferences when it comes to making up standard solutions etc. Besides which I prefer to demonstrate the 'correct' use of the apparatus and explain the reasons why I like things done in a certain way. Having the students write up the Method, should reinforce this information. As it is an initial exercise, I have led the students very much step by step through the Data Processing.

## Sample results

Mass of weighing bottle & sodium carbonate = 2.269 ± 0.0005 g

Mass of weighing bottle after emptying = 1.178 ± 0.0005 g

Volume of sodium carbonate solution prepared = 100.00 ± 0.16 cm<sup>3</sup>

Volume of concentrated nitric acid used = 1.000 ± 0.012 cm<sup>3</sup>

which was diluted to 100.00 ± 0.16 cm<sup>3</sup>

Titration No.	1	2	3	4
Final reading (cm <sup>3</sup> )	41.2	18.1	35.6	39.5
Initial reading (cm <sup>3</sup> )	23.4	0.7	18.1	22.1
Titre of Na <sub>2</sub> CO <sub>3</sub> (cm <sup>3</sup> )	17.8	17.4	17.5	17.4

Precision of burette readings =  $\pm 0.05 \text{ cm}^3$   
 Volume of pipette =  $20.00 \pm 0.06 \text{ cm}^3$   
 Indicator used – methyl orange

### Relevant Qualitative Observations

The sodium carbonate is a free moving white powder and all the solutions, apart from the methyl orange, are clear and colourless. When the water is added to the sodium carbonate in the volumetric flask it dissolves readily to give a clear and colourless solution. When methyl orange is added to the aqueous sodium carbonate it makes the solution a yellow colour. As the acid is added to this there are pink-red “flashes” near where the acid is dripping, but these quickly disperse. As more acid is added the colour persists longer and eventually, for the accurate titrations, the addition of a single drop leaves the solution permanently red.

### Data Analysis

- a) Mass of sodium carbonate used =  $1.091 \pm 0.001 \text{ g}$   
 Amount of sodium carbonate used =  $\frac{1.091}{105.99} = 0.01029 \text{ mol}$   
 Concentration of solution =  $\frac{0.01029}{0.100} = 0.1029 \text{ mol dm}^{-3}$
- b) Equation for the reaction  $\text{Na}_2\text{CO}_3 + 2 \text{HNO}_3 \rightarrow 2 \text{NaNO}_3 + \text{CO}_2 + \text{H}_2\text{O}$   
 Mean titre of aqueous sodium carbonate =  $\frac{1}{3} (17.4 + 17.5 + 17.4) = 17.43 \text{ cm}^3$   
 Amount of sodium carbonate from burette =  $0.01743 \times 0.1029 = 0.001790 \text{ mol}$   
 Amount of nitric acid this reacted with =  $2 \times 0.001790 \text{ mol} = 0.003580 \text{ mol}$   
 Concentration of diluted nitric acid =  $\frac{0.003580}{0.02000} = 0.1790 \text{ mol dm}^{-3}$   
 Concentration of original nitric acid =  $100 \times 0.1790 = 17.90 \text{ mol dm}^{-3}$

**Uncertainties** – neglecting uncertainty in molar mass, as an order of magnitude less than volumetric method uncertainties, and taking the uncertainty of repeated values as being  $\pm \text{Range}/2\sqrt{n}$ :

Quantity	Value	Absolute uncertainty	Percentage uncertainty
Mass of $\text{Na}_2\text{CO}_3$	1.091	0.001	0.0917
Volume of volumetric flask	100.00	0.16	0.160
Concentration of $\text{Na}_2\text{CO}_3$			0.252
Mean titre	17.43	0.029	0.166
Amount of $\text{Na}_2\text{CO}_3$			0.417
Amount of $\text{HNO}_3$			0.417
Volume of titration pipette	20.00	0.06	0.300
Concentration of dil $\text{HNO}_3$			0.717
Volume of dilution pipette	1.000	0.012	1.20
Volume of volumetric flask	100.00	0.16	0.160
Concentration of conc $\text{HNO}_3$	17.90	0.25	2.08

Concentration of concentrated nitric acid =  $17.9 \pm 0.3 \text{ mol dm}^{-3}$



## Evaluation

- a) Nitric acid is usually sold as a 70% solution, with a nominal concentration of  $15.8 \text{ mol dm}^{-3}$ . The solutions are "commercial" solutions and not necessarily prepared to a high degree of precision, so the value obtained, whilst slightly higher than the 70% value (13%) is not necessarily inaccurate, even though the literature value is outside of the uncertainty range.
- b) Precision uncertainties associated with the weighing of the solid and the volume of the flask are one source of error. Another potential source of uncertainty is the sodium carbonate being damp (it should really be dried before use, or at least kept in a "dry-box"). Others depend a little on the technique used in making the solution. Failure to rinse funnels used to transfer the solid/solution into the volumetric flask can be a problem, as can failure to rinse out any glassware used to dissolve the solid, if this is done outside of the volumetric flask. Another possibility is a failure to shake the solution after topping up the volumetric flask with water. (Note that spilling solid, overfilling the volumetric flask etc. are mistakes rather than errors.)
- c) The precision uncertainties are random errors. The damp solid and rinsing errors are systematic and would both result in the concentration being lower than the expected value. The failure to mix is an unusual error, random in the sense it would depend on where in the flask the tip of the pipette was, but systematic in the fact that it would affect it in the same direction. If the solution was pipetted from the bottom the concentration would always be too high. This is one reason why it is advisable to transfer solutions into a beaker before pipetting.
- d) It would be surprising if novice students managed to get them the same! There are however few good excuses, other than mistakes, for them not being identical. Even with B-grade pipette and burette, the uncertainty is below the precision with which most students can read a burette, not to mention the fact that presumably the same pipette is used each time (and hence the same uncertainty). Random fluctuation in the bore of the burette would explain variations in values using different sections of the burette (an advisable technique in order to randomise such effects), but it would be a poor burette if these were significant! A common source of small fluctuations is that drops splash on to the inside wall of the titration flask and hence are not neutralised at the end-point. This may be overcome by using a wash bottle to rinse down the walls just before the end-point (students often need coaxing into realising that this does not affect the titration result). Another possibility is the uncertainty at which point the indicator has just changed colour. This can be overcome by keeping the flask with the first accurate titration to act as a colour standard for later titrations. Whilst this helps to obtain more consistent results, if it is poorly chosen it can introduce a systematic error, which might be worse. One common excuse is that an extra drop was added to check the indicator really had changed colour. It is advisable to take a reading before this extra drop, so that this value can be recorded if the extra drop does confirm the change.
- e) The variation in the bore of the burette and the precise point that the indicator changes are both random errors. Drops on the flask wall lead to a systematic error causing the titre to be too small and the concentration of the acid higher than the true value. The "extra drop" will be a systematic error making the titre too high and hence the concentration of the acid lower than the true value.
- f) Probably having experienced people carrying out the titration! Cynicism aside practice does make perfect. The main reason for this is learning to take care when adding liquid from the burette near to the end point. Some people even rinse "half-drops" off the burette at this stage! If the precision was thought to be a limiting factor (many people obtain consistent results) then the uncertainty of the  $1 \text{ cm}^3$  pipette is by far the major source of precision uncertainty. Using a larger pipette and a larger flask to dilute the acid in would reduce this source of error.
- g) This has no effect on the result. The volume of alkali is dictated by the pipette and this is what governs the amount of acid added from the burette. Obviously the pipette and burette being wet with water would affect things by diluting the solution, which is why it is advisable to rinse them with the solution to be used before starting.

### SYLLABUS RELEVANCE: TOPIC 1.3 SKILL

Use of the experimental method of titration to calculate the concentration of a solution by reference to a standard solution.

## Apparatus required

### General

- Burette
- Burette funnel
- Various pipettes
- Pipette filler
- Various volumetric flasks
- Weighing bottles
- Various beakers
- Various conical flasks
- Top pan balance reading to at least 0.01 g

### Chemicals required

- Aqueous sodium hydroxide, approximately 0.1 mol dm<sup>-3</sup> (~300 cm<sup>3</sup> each)
- Solid potassium hydrogenphthalate (~2 g per student)
- Solid citric acid (~2 g per student) labelled as "Acid HX"  
(or any solid water soluble acid of your choice)
- Phenolphthalein indicator

## Notes

*Probable timing—90 minutes laboratory time*

This is a useful introduction to volumetric analysis. I have not specified a particular method as I find that many teachers have their own particular preferences when it comes to making up standard solutions etc. Besides which I prefer to demonstrate the 'correct' use of the apparatus and explain the reasons why I like things done in a certain way. Having the students write up the Method, should reinforce this information. As it is an initial exercise, I have led the students very much step by step through the Data Processing.

## Sample results

### Standardisation

Mass of weighing bottle & potassium hydrogenphthalate = 3.168 ±0.0005 g

Mass of weighing bottle after emptying = 1.181 ±0.0005 g

Volume of potassium hydrogenphthalate solution prepared = 100.00 ±0.016 cm<sup>3</sup>

Titration No.	1	2	3	4
Final reading (cm <sup>3</sup> )	43.6	29.5	49.6	22.3
Initial reading (cm <sup>3</sup> )	21.7	9.4	29.5	2.2
Titre of NaOH (cm <sup>3</sup> )	21.9	20.1	20.1	20.1

Precision of burette readings =  $\pm 0.05 \text{ cm}^3$

Volume of potassium hydrogenphthalate solution taken =  $20.00 \pm 0.06 \text{ cm}^3$

Indicator used – Phenolphthalein

### Relevant qualitative observations

The potassium hydrogen phthalate is a free moving white powder and when the water is added it dissolves readily to give a clear and colourless solution in the volumetric flask. When phenolphthalein is added the solution remains colourless, but as the alkali is added to this there are pink-purple “flashes” near where the alkali is dripping, but these quickly disperse. As more alkali is added the colour persists longer and eventually, for the accurate titrations, the addition of a single drop leaves the solution permanently pink.

### Molar mass determination

Mass of weighing bottle & Acid X =  $2.203 \pm 0.0005 \text{ g}$

Mass of weighing bottle after emptying =  $1.188 \pm 0.0005 \text{ g}$

Volume of solution prepared =  $100.00 \pm 0.16 \text{ cm}^3$

Titration No.	1	2	3	4
Final reading ( $\text{cm}^3$ )	32.6	47.3	31.0	38.4
Initial reading ( $\text{cm}^3$ )	1.5	17.0	0.7	9.1
Titre of NaOH ( $\text{cm}^3$ )	31.1	30.3	30.3	30.3

Precision of burette readings =  $\pm 0.05 \text{ cm}^3$

Volume of Acid X solution taken =  $20.00 \pm 0.06 \text{ cm}^3$

Indicator used – phenolphthalein

### Relevant Qualitative Observations

Acid X is a free moving white powder. When water is added to the volumetric flask it dissolves readily to give a clear and colourless solution. When phenolphthalein is added the solution remains colourless, but as the acid is added to this there are pink-purple “flashes” near where the alkali is dripping, but these quickly disperse. As more alkali is added the colour persists longer and eventually, for the accurate titrations, the addition of a single drop leaves the solution permanently pink.

## Data Analysis

### Standardisation

Mass of potassium hydrogenphthalate used =  $1.987 \pm 0.001 \text{ g}$

Amount of potassium hydrogenphthalate used =  $\frac{1.987}{204.23} = 0.00973 \text{ mol}$  (Neglect  $M_r$  uncertainty)

Concentration of solution =  $\frac{0.00973}{0.100} = 0.0973 \text{ mol dm}^{-3}$

Equation for the reaction  $\text{KHC}_8\text{H}_4\text{O}_4 + \text{NaOH} \rightarrow \text{NaKC}_8\text{H}_4\text{O}_4 + \text{H}_2\text{O}$

Amount of potassium hydrogenphthalate from pipette =  $0.0200 \times 0.0973 = 0.00195 \text{ mol}$

Which reacts with  $0.00195 \text{ mol}$  of sodium hydroxide.

Mean titre of aqueous sodium hydroxide =  $20.1 \pm 0.1 \text{ cm}^3$

Concentration of aqueous sodium hydroxide =  $\frac{0.00195}{0.0201} = 0.0968 \text{ mol dm}^{-3}$



Quantity	Value	Absolute uncertainty	Percentage uncertainty
Mass of $\text{KHC}_8\text{H}_4\text{O}_4$	1.987	0.001	0.0503
Volume of volumetric flask	100.00	0.16	0.160
Concentration of $\text{KHC}_8\text{H}_4\text{O}_4$		0.0002	0.210
Volume of titration pipette	20.00	0.06	0.300
Amount of $\text{KHC}_8\text{H}_4\text{O}_4/\text{NaOH}$			0.510
Mean titre	20.1	0.1	0.498
Concentration of NaOH	0.0968	0.000975	1.008

Concentration of aqueous sodium hydroxide =  $0.097 \pm 0.001 \text{ mol dm}^{-3}$

### Molar mass determination

Mean titre of aqueous sodium hydroxide =  $30.3 \pm 0.1 \text{ cm}^3$

Equation for the reaction  $\text{HX} + \text{NaOH} \rightarrow \text{NaX} + \text{H}_2\text{O}$

Amount of sodium hydroxide used =  $0.0968 \times 0.0303 = 0.00293 \text{ mol}$

Which reacts with 0.00293 mol of HX in the 20  $\text{cm}^3$  titre.

Concentration of HX =  $\frac{0.00293}{0.020} = 0.147 \text{ mol dm}^{-3}$

Amount of HX in 100  $\text{cm}^3 = 0.147 \times \frac{100}{1000} = 0.0147 \text{ mol}$

Mass of HX used =  $1.015 \pm 0.001 \text{ g}$

Molar mass of X =  $\frac{1.015}{0.0147} = 69.2 \text{ mol dm}^{-3}$

Quantity	Value	Absolute uncertainty	Percentage uncertainty
Mean titre	30.3	0.1	0.330
Concentration of NaOH	0.0968		1.008
Amount of NaOH/HX			1.338
Volume of titration pipette	20.00	0.06	0.300
Concentration of HX			1.638
Volume of volumetric flask	100.00	0.16	0.160
Amount of HX			1.798
Mass of HX	1.015	0.001	0.0985
Molar mass of HX	69.2	1.312	1.897

Molar mass of Acid HX =  $69 \pm 1 \text{ mol dm}^{-3}$

Actual molar mass of citric acid is  $192.1 \text{ mol dm}^{-3}$ , so considering it monobasic should give an answer of  $64.0 \text{ mol dm}^{-3}$ .

## Evaluation

- a) The value of  $0.097 \pm 0.001 \text{ mol dm}^{-3}$  is very credible for a solution that is nominally  $0.1 \text{ mol dm}^{-3}$ . The uncertainty in the value, of about 1% is a little high for a standardisation.
- b) The major source of uncertainty is associated with the volumetric apparatus, especially the burette (~0.5%) and the pipette (~0.3%). Using Class A rather than Class B glassware would halve these. Doubling the mass of potassium hydrogenphthalate used would double the titre and would also halve the uncertainty. Other potential sources of error, depending on the exact technique used, might be a failure to rinse glassware used to dissolve the solid or to transfer the solid/solution to the volumetric flask. Another possibility is a failure to shake the solution after topping up the volumetric flask with water, though this, like spilling solid, overfilling the volumetric flask etc., could be considered a mistake rather than an error.
- c) The value of the molar mass obtained ( $69 \pm 1 \text{ mol dm}^{-3}$ ) is significantly different to the literature value of  $64.0 \text{ mol dm}^{-3}$ . The percentage error (7.8%) is significantly greater than the uncertainty (1.3%). This would imply the presence of significant systematic or random errors other than those resulting from instrumental uncertainties. Differentiating between these possibilities would probably involve repeating the procedure a number of times to establish whether it consistently gave results in excess of the literature value.
- d) The variation in the bore of the burette and the precise point that the indicator changes are both random errors, but are unlikely to result in significant error. Small deviations can be also be caused by drops of the liquid in the flask splashing on the flask wall. This systematic error would result in the titre to be too small and in the standardisation the concentration of the alkali would be higher than the true value. In the molar mass determination the molar mass would come out as larger than the true value. An extra drop added to check the colour change was complete, will be a small systematic error making the titre too high and hence the concentration of the alkali lower than the true value, or the molar mass smaller than the true value. For either of these, if the error occurred in both titrations it would to some extent be self-cancelling. None of these would really provide an adequate explanation of a result that is as far from the literature value as this is.
- e) Some minor improvements such as reducing uncertainties by using Class A rather than Class B glassware and doubling the mass of potassium hydrogenphthalate used have been mentioned as have means of reducing systematic errors by rinsing glassware and preserving a colour standard to titrate to. In this case the low value may be because the citric acid was for culinary purposes and may not be 100% citric acid. This means that the mass of citric acid was actually less than the mass of solid weighed out hence the value determined for the molar mass would be greater than the true value as was found.

## SYLLABUS RELEVANCE: TOPIC 1.3 SKILL

Obtaining and using experimental values to calculate the molar mass of a gas from the ideal gas equation.

## Apparatus required

## Per group

- Plastic drink bottle (1 to 2 dm<sup>3</sup> PET carbonated drink bottles are fine)
- Measuring cylinder of volume slightly greater than drink bottle
- Stopped 100 cm<sup>3</sup> volumetric flask

## General

- Balance capable of weighing to at least 0.001 g
- Thermometer, preferably accurate to 0.1°C
- Barometer

## Chemicals required

- Gas from laboratory gas taps
- “methylated spirits” (~5 cm<sup>3</sup> per group)

## Notes

Probable timing—45 minutes laboratory time

## Sample results

## Gaseous fuel

Sample	Mass /g
Weighing one (air)	47.832
Weighing two (gas)	47.146
Weighing three (gas)	47.046
Weighing four (gas)	47.044
Weighing five (gas)	47.044

Uncertainty of weighings =  $\pm 0.0005$  g

Volume of bottle =  $1585 \pm 5$  cm<sup>3</sup>

Room temperature =  $23.7 \pm 0.1$  °C

Room pressure =  $103.2 \pm 0.2$  kPa

## Liquid fuel

Mass of empty flask =  $138.624 \pm 0.0005$  g

Mass of flask + liquid =  $138.792 \pm 0.0005$  g

Mass of flask + water =  $256.813 \pm 0.0005$  g

Temperature of water bath =  $98.8 \pm 0.1$  °C

Room pressure =  $103.2 \pm 0.2$  kPa



## Data Analysis

## Gaseous fuel

$$\text{a) Density of air under experimental conditions} = 1.275 \times \frac{273.1}{(273.1 + 23.7)} \times \frac{103.2}{100} = 1.211 \text{ g dm}^{-3}$$

$$\text{Mass of air} = 1.585 \times 1.211 = 1.919 \text{ g}$$

$$\text{Mass of empty bottle} = 47.832 - 1.919 = 45.913 \text{ g}$$

$$\text{Uncertainty of mass of air} = \left( \frac{0.1}{296.8} + \frac{0.2}{103.2} + \frac{5}{1585} \right) \times 100 = \pm 0.542\%$$

$$= 1.919 \times \frac{0.542}{100} = \pm 0.0104 \text{ g}$$

$$\text{Uncertainty of mass of bottle} = 0.0005 + 0.0104 = \pm 0.0109 \text{ g}$$

$$\text{b) Mass of gaseous fuel} = 47.044 - 45.913 = 1.131 \text{ g}$$

$$\text{Uncertainty} = 0.0005 + 0.0109 = \pm 0.0114 \text{ g}$$

c)

$$\text{Amount of gas} = \frac{P.V}{R.T} = \frac{103.2 \times 1.585}{8.31 \times (273.1 + 23.7)} = 0.0632 \text{ mol}$$

$$\text{Uncertainty of amount of gas} = \left( \frac{0.1}{296.8} + \frac{0.2}{103.2} + \frac{5}{1585} \right) \times 100 = \pm 0.542\%$$

$$\text{Molar mass of gas} = \frac{1.131}{0.0632} = 17.05 \text{ g mol}^{-1}$$

$$\text{Uncertainty of molar mass} = \left( \frac{0.0114}{1.131} \times 100 \right) + 0.542 = \pm 1.55\%$$

$$= 17.05 \times \frac{1.55}{100} = \pm 0.264 \text{ g mol}^{-1}$$

$$\text{Molar mass of gaseous fuel} = 17.1 \pm 0.3 \text{ g mol}^{-1}$$

## Liquid fuel

$$\text{d) Volume of flask} = 256.813 - 138.624 = 118.189 \pm 0.001 \text{ cm}^3$$

$$\text{Mass of vapour} = 138.792 - 138.624 = 0.168 \pm 0.001 \text{ g}$$

$$\text{e) Amount of vapour in flask} = \frac{P.V}{R.T} = \frac{103.2 \times 0.1182}{8.31 \times (273.1 + 98.8)} = 0.003947 \text{ mol}$$

$$\text{Uncertainty of amount of gas} = \left( \frac{0.1}{371.9} + \frac{0.2}{103.2} + \frac{0.001}{118.2} \right) \times 100 = \pm 0.221\%$$

$$\text{Molar mass of gas} = \frac{0.168}{0.003947} = 42.57 \text{ g mol}^{-1}$$

$$\text{Uncertainty of molar mass} = \left( \frac{0.001}{0.168} \times 100 \right) + 0.221 = \pm 0.816\%$$

$$= 42.57 \times \frac{0.816}{100} = \pm 0.347 \text{ g mol}^{-1}$$

$$\text{Molar mass of liquid fuel} = 42.6 \pm 0.3 \text{ g mol}^{-1}$$

## Evaluation

### Gaseous fuel

- Methane.
- The accuracy of the value is quite poor with an error of  $+2 \text{ g mol}^{-1}$  (+12.5%), ten times greater than the precision of  $\pm 0.2 \text{ g mol}^{-1}$ .
- The measurements of P, V and T all have uncertainties of a similar order of magnitude ( $\sim 0.03$ – $0.3\%$ ). The precision of the weighings seems much greater ( $\sim 0.001\%$ ) but because of the small difference between the weighings this small uncertainty becomes the greatest single factor in calculating the final uncertainty ( $\sim 0.5\%$ ), approximately equal in magnitude to the combination of all the other uncertainties.
- One source of systematic error might be some air remaining in the plastic bottle. This would mean that the molar mass determined would be nearer to that of air (that is too large for a gas with a lower molar mass and too small for a gas with a higher molar mass). A second, source of systematic error might be in the correction made for the mass of air displaced from the bottle (the buoyancy effect). The calculation of the molar mass is very dependent on the density of air because of the small difference between the weighings. The value given applies to dry air, but the presence of water vapour would, because of its lower molar mass (18 rather than  $\sim 29$ ), slightly reduce the density of the air, hence the mass of gas calculated is greater than the true mass, giving a molar mass slightly higher than the true value.
- Generally the reproducibility of the method is well in excess of the calculated uncertainty of each individual determination. This can really only be put down to human error and the fact that the values determined are critically dependent on a very small difference between two quite large weighings.
- The systematic error is probably quite small provided the bottle is weighed and refilled sufficient times and probably less than the  $\sim 1\%$  uncertainty in the values calculated, hence random errors are probably dominant.
- The method is critically dependent on weighings and the use of a balance reading to 4 dp would be a significant improvement. Looking at the other uncertainties, the volume of the bottle is probable the next highest ( $\sim 0.3\%$ ) and this could probably be significantly improved by weighing the bottle full of water, rather than using a measuring cylinder, and assuming the density of water as  $1 \text{ kg dm}^{-3}$ . A more precise determination of the pressure ( $\sim 0.2\%$ ) would also be an improvement. The uncertainty in the temperature determination, though it seems quite large ( $0.1 \text{ }^\circ\text{C}$  in  $23.7 \text{ }^\circ\text{C}$ ) is greatly reduced by the conversion of the temperature to Kelvin.
- The molar mass is slightly greater, so it is likely that traces of ethane, and possibly propane and butane, are present in the natural gas.
- Natural gas, which is mainly methane, has a lower density than air so it will collect in the top of an inverted bottle. Conversely bottled gas, which is mainly propane, has a higher density than air and will collect in the bottom of a bottle in the normal orientation.

### Liquid fuel

- Let the mol% ethanol =  $y$ , then the mol% methanol is  $(100-y)$ . The mean molar mass is therefore given by:  

$$46y + 32(100 - y) = 42.6 \times 100$$
 which on solving gives a value of  $y = 75.7\%$ . Hence methylated spirits would appear to be  $\sim 75\%$  ethanol.
- Pure ethanol is not used because it is the “alcohol” in alcoholic drinks. Governments tax alcoholic drinks and so the price of ethanol if it were taxed would be prohibitively high for its use as a fuel. Ethanol intended for use as a fuel must therefore be rendered unfit for consumption and this is usually done by adding methanol, which is toxic. Often pyridine, which has an unpleasant smell, and a coloured dye are also added. Pure methanol is not used because its price is significantly higher than that of ethanol.
- The heating period is critical. If it is not heated long enough and a small amount of liquid still remains then, because of its much greater density, it can have a significant effect on the result, increasing the mass of vapour and hence the result for the molar mass. If it is left for too long, some air might enter the flask, displacing vaporised liquid. Vaporised liquid will be lost and hence its mass, and consequently the molar mass, will be less than the true value. This will also occur if there is not sufficient vaporised liquid to displace all the air from the flask. The magnitude of these systematic errors is probably significantly greater than the experimental uncertainty of  $\sim 1\%$ .

- m) The systematic errors can only be really addressed by careful experimentation. The problem from still having unvaporised liquid present is much greater than that from air displacing vaporised liquid, so heating for a longer period (perhaps 5 minutes after all the liquid appears to be vaporised) is perhaps the safer option. In addition quite a large excess of liquid should be taken so as to ensure all air is flushed from the flask by its vapour. The uncertainty mainly arises from the determination of the mass of the condensed liquid so it could be significantly improved by using a more accurate balance, or a larger volumetric flask.

### Comparing fuels

- n) Assuming that your gaseous fuel comprises only the major alkane and that the liquid fuel is pure ethanol, use data from Section 13 of the IB Data Booklet, and elsewhere, to calculate the relative amount of heat energy that could be obtained from these fuels by amount (per mol), mass (per g), volume (per dm<sup>3</sup>) and price (per \$, or whatever the unit of currency is in your country). Comment on the possible advantages and disadvantages of the two fuels on these various bases of comparison.

Basis of comparison	Gaseous fuel	Liquid fuel
Amount (kJ mol <sup>-1</sup> )	891	1367
Mass (kJ g <sup>-1</sup> )	55.7	29.7
Volume (kJ dm <sup>-3</sup> )	36	23,450
Cost (kJ \$ <sup>-1</sup> )	90,000	4,690

**Per mol** – the value for ethanol is significantly greater than that for methane, and hence on this basis it is the better fuel, because it contains more C-C and C-H bonds that can generate energy by being converted to C-O and H-O bonds. Note that the ethanol value is significantly less than the equivalent alkane (ethane -1561 kJ mol<sup>-1</sup>) because this conversion has already started as a result of the O-H bond.

**Per gram** – Here the extra number of bonds is reflected in the mass of the atoms involved, so the values for similar types of molecules should be a similar order of magnitude (ethane is 52 kJ g<sup>-1</sup>). In the case of ethanol the mass of the oxygen, and the C-O-H bonds, contributes nothing to the enthalpy of combustion, hence the value is significantly lower. On a per weight basis therefore methane is the better fuel as you get 4 useful bonds for just 16 g, whereas with ethanol you get just 8 bonds for 46 g and two of these are useless!

**Per litre** – The density of the two states is the dominant factor here. A mole of gas occupies about 24 dm<sup>3</sup> at room temperature and pressure, whereas a mole of ethanol occupies a volume of ~60 cm<sup>3</sup>; about 400 times more. On a per volume basis, ethanol is by far the better fuel, which is obviously the reason liquid fuels are the major energy source for types of transport, such as planes and cars, that have to carry their own fuel.

**Per \$ (or other currency unit)** – The numbers in the table are based on the price of natural gas being \$0.4 m<sup>-3</sup> and methylated spirit \$5 dm<sup>-3</sup>. Obviously these vary from country to country and with time and often government taxation affecting matters. The general pattern however is that, in many countries, the price of natural gas as an energy source is significantly lower than liquid fuels, hence it is often used for large scale static energy consumption processes, such as electricity generation.

## SYLLABUS RELEVANCE: TOPIC 1.3

Emission spectra could be observed using discharge tubes of different gases and a spectroscope. Flame tests could be used to study spectra.

## Apparatus required

### Per group

- Hand held spectroscope
- 2 × watch glass
- Nichrome wire
- Bunsen burner

### General

Gas discharge tubes (sodium, neon, argon, mercury, hydrogen etc.)

## Chemicals required

About 10g in total of each of the following solids

- sodium chloride
- potassium chloride
- calcium chloride
- barium chloride
- copper(II) chloride
- lithium chloride
- strontium chloride
- Dilute hydrochloric acid (~10 cm<sup>3</sup> per group)

## Notes

The laboratory will need to be blacked out for this practical to be really successful.

*Probable timing – about 60 minutes laboratory time*

This is a qualitative look at emission spectra from various sources. The Data Analysis part of this is a little questionable as it refers more to background theory than to the interpretation of the results obtained, so you may feel more comfortable limiting it to just Data Collection.

If you have a few more capable students, you could ask them to further research the results they obtain for fluorescent lights as a little investigation.

Also, if the Physics department has a calibrated spectroscope that allows measurement of the wavelength of lines, then you could add a quantitative exercise to the end of this practical.

If you do not have hand held spectroscopes you can make your own from old CDs – see

<http://www.euhou.net/index.php/exercises-mainmenu-13/classroom-experiments-and-activities-mainmenu-186/178-a-home-made-spectroscope>



## Sample Data

### 1) Daylight

This is the familiar “rainbow” spectrum:

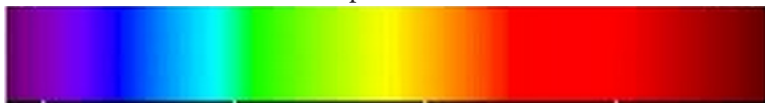


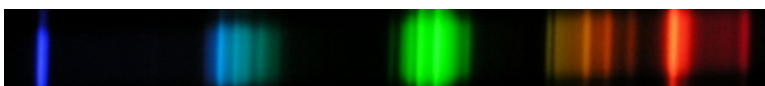
Image from- <http://cfialabioassignment.wikispaces.com/>

### 2) Incandescent (filament) and fluorescent lights

Filament lights also give the familiar “rainbow” spectrum, whereas with fluorescent lights this rainbow (from the coating of the tube) is superimposed on a line spectrum (from the discharge of the gas the tube is filled with):



Modern fluorescents have less of the background rainbow and more “fuzzier” lines:



Images from- <http://www.euhou.net/index.php/exercises-mainmenu-13/classroom-experiments-and-activities-mainmenu-186/178-a-home-made-spectroscope>.

### 3) Discharge tubes

These should give reasonable line spectra:



Hydrogen



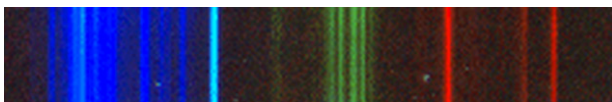
Helium



Neon



Sodium



Argon



Mercury

Images (other than Ar & Na) from - <http://www.uranmaschine.de/45520.Spektrallinien/Vergleichsbilder/index2.php?PHPSESSID=88c256b458e0f7029faaea165060acea>

Ar from- <http://ircamera.as.arizona.edu/NatSci102/NatSci102/lectures/spectroscopy.htm>

Na from- [http://www.phys.ufl.edu/~avery/course/3400/light/element\\_75.gif](http://www.phys.ufl.edu/~avery/course/3400/light/element_75.gif)

Often you can get quite reasonable sodium and mercury spectra from appropriate street lights.

#### 4) Flame tests

Sodium chloride – intense yellow

Potassium chloride – lilac

Calcium chloride – orange-red

Barium chloride – light green

Copper(II) chloride – blue-green

Lithium chloride – pink-red

Strontium chloride – red

### Data Analysis

- (a) The greater frequency ( $\nu$ ), and the shorter the wavelength ( $\lambda$ ), the greater the energy ( $E$ ) carried by each photon. These are related by the expression:

$$E = h \cdot \nu = h \cdot \frac{c}{\lambda}$$

where  $h$  is Planck's constant and  $c$  is the velocity of light.

- (b) Some of the spectra, such as the spectrum from daylight and incandescent light bulbs, are continuous spectra and others, such as those from discharge tubes and flame tests, are line spectra. Continuous spectra means that any amount of energy can be lost and emitted in the form of light. Line spectra means that the species involved can only emit very specific amounts of energy in the form of light.
- (c) Electrons in the atoms are excited from the ground state to higher energy levels through electrical or thermal energy. They then lose energy in the form of light by emitting light corresponding to the difference in energy of the orbitals the electron moves from and to. The colour of the light emitted is related to this energy difference through the formula given in exercise a).
- (d) What would be observed would be a continuation of the spectral emission into both the infrared and ultraviolet regions. Sunlight would have a greater intensity in the ultraviolet and incandescent bulbs in the infrared. With line spectra the patterns of lines would also continue into these two regions with series of lines being observed in each. In many cases a series of lines would converge towards the high frequency end where they would eventually merge into a short continuum.
- (e) The energy of the light emitted in the atomic emission spectrum of an element corresponds to the difference in energy of two electron orbitals in that atom. By studying these the allowed electron energy levels in the various atoms may be deduced.
- (f) When white light (containing all frequencies) is shone through an element in its gaseous state, light of certain wavelengths is absorbed by atoms/molecules of the gas and this appears as black lines superimposed on the "rainbow" spectrum. Absorption spectra are generally simpler than emission spectra because the electron must start from the ground state, whereas there are many different excited states in which the electrons involved in emission spectra can start.

## SYLLABUS RELEVANCE: TOPIC 3.2

Experiment with chemical trends directly in the laboratory or through the use of teacher demonstrations.

## Apparatus required

### Per group:

- 6 × test tube
- 3 × boiling tube
- watch glass

## Chemicals required

### About 10 cm<sup>3</sup> per student of:

Aqueous sodium hydroxide (~1 mol dm<sup>-3</sup>)

- Dilute sulfuric acid (~1 mol dm<sup>-3</sup>)
- Chlorine water
- Bromine water
- Aqueous lead nitrate (~0.1 mol dm<sup>-3</sup>)
- Aqueous silver nitrate (~0.01 mol dm<sup>-3</sup>)
- Iodine in aqueous potassium iodide (~0.1 mol dm<sup>-3</sup>) labelled "Iodine solution"
- Ethanol
- Hexane

### About 50 cm<sup>3</sup> per student of:

- Aqueous sodium chloride (~0.1 mol dm<sup>-3</sup>)
- Aqueous sodium bromide (~0.1 mol dm<sup>-3</sup>)
- Aqueous sodium (or potassium) iodide (~0.1 mol dm<sup>-3</sup>)

### Other:

- Iodine (about 1 g per student):
- Blue litmus paper

## Notes

*Probable timing—90 minutes laboratory time*

A few simple test tube reactions to investigate some properties of the halogens that it would be useful for students to be aware of. Iodine is expensive, so if you prefer, Part 1 could easily be done as a demonstration. Parts 2 and 3 rather involve the concept of equilibrium, so be warned if you have not yet introduced it, you may be better delaying this Investigation until the students have met it. In Part 4 a good test of the thinking student is whether they can explain why the non-aqueous solute is added. Don't forget to relate Part 5 to black and white photography. I have omitted the differential solubility of the silver halides in ammonia as the syllabus now excludes it, but you may want to add it in for fun. The solubility of the lead salts (Part 6) is not really necessary, but the iodide is very pretty as it recrystallises and the fact that the bright yellow iodide surprisingly produces a totally colourless solution is a good test of observation. Perhaps ask the good students why?

## Data Analysis and Evaluation

- 1) **Water**–Iodine is almost insoluble in water – the only indication of solubility is that the water becomes a pale ‘straw’ colour.

**Ethanol**–Iodine is slightly soluble in ethanol and gives a brown coloured solution.

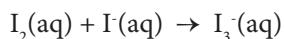
**Hexane** – Iodine dissolves readily in hexane to give a purple coloured solution.

**Sodium iodide** – Iodine dissolves readily in aqueous sodium iodide to give a brown solution.

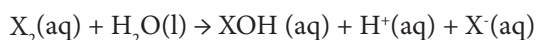
Iodine is most soluble in hexane (c). This is because hexane and iodine both have dispersion forces between their molecules and hence the bonds broken in the pure substances can be replaced by similar bonds in the solution.

Water molecules have strong hydrogen bonds between them and so only substances that can replace these bonds with interactions of a similar strength (other hydrogen bonds or the hydration of ions) will dissolve.

Iodine is much more soluble in water if iodide ions are present in solution. This is because the iodine reacts with the iodide ion to establish an equilibrium with the tri-iodide ion, which lies well to the right:

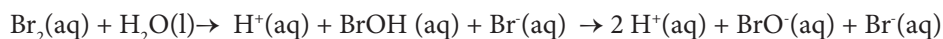


- 2) With chlorine water the blue litmus initially goes red and then is slowly bleached to colourless. With bromine water the reaction is similar though a little slower and the colour changes are slightly masked by the colour of the bromine. With the iodine solution the intensity of the colour often masks everything, except maybe the initial change to red.



Chlorine is used commercially as a bleach because it oxidizes many coloured compounds, such as litmus, to colourless products.

- 3) As the aqueous sodium hydroxide is added the brown colour of the bromine gradually fades and eventually the solution becomes colourless. When the acid is added the brown colour of the solution is gradually restored.



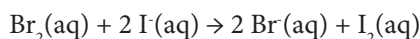
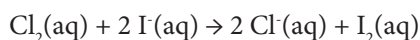
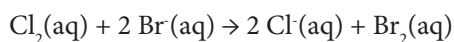
When the alkali is added it reacts with the hydrogen ions and the equilibria above are displaced to the right, so that the concentration of the coloured component ( $Br_2$ ) decreases. Upon adding acid the equilibria are displaced back to the left, restoring the brown colour of the bromine, though a little more dilute.



4)

Halogen	Sodium salt		
	Sodium chloride	Sodium bromide	Sodium iodide
<b>Chlorine water</b>	Initial reaction No reaction, remains clear and colourless After hexane added No change, upper layer remains colourless	Initial reaction Solution changes colour from colourless to orange-brown After hexane added Upper layer turns brown and colour in aqueous layer fades	Initial reaction Solution changes colour from colourless to brown After hexane added Upper layer turns purple and colour in aqueous layer fades
<b>Bromine water</b>	Initial reaction Colourless solution dilutes the colour of the brown solution After hexane added Upper layer turns brown and colour in aqueous layer fades	Initial reaction Colourless solution dilutes the colour of the brown solution After hexane added Upper layer turns brown and colour in aqueous layer fades	Initial reaction Brown and colourless solutions react to give a slightly different shade of brown After hexane added Upper layer turns purple and colour in aqueous layer fades
<b>Iodine solution</b>	Initial reaction Colourless solution dilutes the colour of the brown solution After hexane added Upper layer turns purple and the brown colour in aqueous layer fades	Initial reaction Colourless solution dilutes the colour of the brown solution After hexane added Upper layer turns purple and the brown colour in aqueous layer fades	Initial reaction Colourless solution dilutes the colour of the brown solution After hexane added Upper layer turns purple and the brown colour in aqueous layer fades

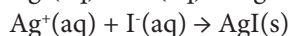
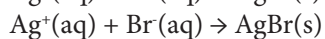
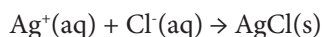
In the cases where there was a reaction (new product formed – white squares above) the reaction is between a halogen higher in group 17 and the halide ion of a lower halogen.



These are redox reactions and they show that going down group 17 the halogens become weaker oxidizing agents.

5)

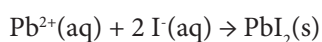
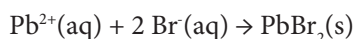
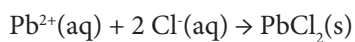
	Sodium chloride	Sodium bromide	Sodium iodide
<b>With aqueous silver nitrate</b>	Colourless solutions react to form a white precipitate	Colourless solutions react to form a cream coloured precipitate	Colourless solutions react to form a pale yellow precipitate
<b>Effect of sunlight</b>	Darkens through purple and grey to black	Very slowly darkens	Little if any effect



The silver halides undergo photo-reduction to produce silver metal which is a black solid, though initially the finely divided silver gives a purple-grey shading to the product.

6)

	Sodium chloride	Sodium bromide	Sodium iodide
With aqueous lead(II) nitrate	Colourless solutions react to form a white precipitate	Colourless solutions react to form a white precipitate	Colourless solutions react to form a bright yellow precipitate
Effect of heating and cooling	White solid dissolves on heating to form a colourless solution. On cooling white crystals separate out	White solid dissolves on heating to form a colourless solution. On cooling white crystals separate out	Yellow solid dissolves on heating to form a colourless solution. On cooling yellow crystals separate out



The lead(II) halides are all significantly more soluble in hot water than in cold water, so on heating they dissolve up, but when the solution is cooled again they precipitate out.

Usually when solids dissolve the colour of the solution they form is similar to the colour of the solid. Lead(II) iodide is unusual in that even though it is a bright yellow colour, the solution it forms is colourless. This implies that the yellow colour results from the interaction of the lead(II) ions and the iodide ions within the lead(II) iodide crystal.

## SYLLABUS RELEVANCE: TOPIC 4.1

Students could investigate compounds based on their bond type and properties.

## Apparatus required

### Per group

- 4 × ignition tube
- 8 × test tube
- 2 × 10 cm<sup>3</sup> measuring cylinder
- Accurate thermometer (0-50°C, by 0.2°C divisions if possible)
- Stirring rod

### Generally available

Three long, sealed tubes (0.5 m?) almost filled with liquid, but containing a small air bubble. The liquids should be hexane, paraffin & propan-1,2,3-triol (glycerol). The tubes should be labelled with the liquid they contain.

Five burettes in a fume cupboard, containing water, cyclohexane, propanone (acetone), tetrachloromethane (carbon tetrachloride) and trichloromethane (chloroform). There should be five large beakers for the liquid from the burettes to run into, as well as supplies of the liquid to top up the burettes.

A number of dry electrostatics rods, and cloths for charging them, will also be required.

## Chemicals required

### About 2 g per group of:

- Sodium chloride
- Urea
- 1,4-dichlorobenzene
- Silicon dioxide

### About 5 cm<sup>3</sup> per group of:

- Ethanol (clear meths)
- Ethyl ethanoate (ethyl acetate)
- Propanone (acetone)
- Trichloromethane (chloroform)

### Hexene

~50 cm<sup>3</sup> of hexane

## Notes

*Probable timing—60 minutes laboratory time*

This practical provides a chance to see whether students are capable of applying the concepts of forces between particles to explain some simple observations. Part 1 (melting of solids) may be better demonstrated because the temperatures may be quite high. For Part 4, it is probably best to have one set of burettes and liquids already set up in the fume cupboard and devise a roster for the students to use them.

## Sample Data

1)

Solid	Melting point
Sodium chloride	High (may not be able to melt it in a Bunsen flame)
Urea	Moderately high (above the boiling point of water)
1,4-dichlorobenzene	Quite low (below the boiling point of water)
Silicon dioxide	Very high (will not melt it in a Bunsen flame!)

Sodium chloride comprises a lattice of anions and cations with very strong electrostatic forces, so a high temperature is required to disrupt these.

Urea has a molecular covalent structure, but there are quite strong hydrogen bonds between its molecules, hence its melting point (133°C) is quite high for a molecule with a relative small molar mass (60 – similar to butane, which is a gas at room T & P).

1,4-dichlorobenzene has quite a low melting point (~53°C) for a substance with quite a high molar mass (~147) because it is slightly polar (symmetrical), so there are only weak dispersion forces between its molecules.

Silicon dioxide has strong covalent bonds that extend in three-dimensions holding all the silicon and oxygen atoms together, so a very large amount of energy would be required to break down these bonds.

2)

Solute	Solvent	
	Hexane	Water
Sodium chloride	Does not dissolve	Quite soluble
Urea	Does not dissolve	Quite soluble
1,4-dichlorobenzene	Quite soluble	Does not dissolve
Silicon dioxide	Does not dissolve	Does not dissolve

Sodium chloride does not dissolve in hexane because hexane, as a non-polar molecule, only has weak attractive forces to the ions it is comprised of and these cannot compensate for the breaking of the strong electrostatic forces in the ionic lattice.

Sodium chloride is quite soluble in water because water is a very polar molecule and hence there are quite strong ion-dipole forces between it and the ions sodium chloride is comprised of, so these compensate for the breaking of the strong electrostatic forces in the ionic lattice.

Urea is not soluble in hexane because, even though it is molecular covalent, it has quite strong hydrogen bonds between its molecules and the weak dispersion forces between urea and hexane molecules cannot compensate for the breaking of these bonds.

Urea is quite soluble in water because quite strong hydrogen bonds form between the two molecules to compensate for the hydrogen bonds that have to be broken in both pure substances.

1,4-dichlorobenzene is quite soluble in hexane because the weak dispersion forces between the two molecules compensate for those in the pure substances.

1,4-dichlorobenzene is insoluble in water because it cannot form hydrogen bonds to water molecules to compensate for the hydrogen bonds between water molecules that would have to be disrupted if it were to dissolve.



Silicon dioxide is insoluble in hexane because it has a giant covalent structure, hence there are no small particles that it could split into if it dissolved, and the forces that might exist between solvent and solute particles are far too weak to compensate for the breaking of covalent bonds.

Silicon dioxide is also insoluble in water because it has a giant covalent structure, hence there are no small particles that it could split into if it dissolved, and the forces that might exist between solvent and solute atoms are far too weak to compensate for the breaking of covalent bonds.

3) **Fastest** → hexane paraffin glycerol → **Slowest**

In hexane there are only weak dispersion forces between the molecules and, as these are very easily disrupted, it has a low viscosity so the air bubble passes quickly. Paraffin has longer, straight chain hydrocarbon molecules ( $M_r$  typically  $\sim 350$ ,  $C_{20}$ - $C_{30}$ ), hence the dispersion forces are stronger leading to a greater viscosity and slower movement of the bubble. Glycerol has quite strong hydrogen bonds between its molecules and, as these have to be broken and re-made when the molecules move relative to each other, this greatly increases the viscosity causing the bubble to move quite slowly.

4)

Liquid A	Liquid B	Miscibility	Volume /cm <sup>3</sup>	Temp. change /°C
Ethyl ethanoate	Trichloromethane	Miscible	9.8	+4.8
Propanone	Water	Miscible	9.5	+4.4
Water	Hexane	Immiscible	10.0	+0.2
Ethanol	Hexane	Miscible	9.6	-1.4
Hexane	Hexene	Miscible	10.0	0.0

Room temperature = 17 °C

Even though neither pure liquid can form hydrogen bonds between its molecules, ethyl ethanoate and trichloromethane can form hydrogen bonds to each other. These involve the very electropositive hydrogen on the trichloromethane (one of very few instances when a hydrogen not bonded to N, O or F H-bonds, but three Cl atoms have a major effect) and probably the carbonyl oxygen on the ester, hence the liquids are miscible. The molecules are more closely bonded in the mixture so that the volume decreases and, as bond formation is exothermic, the temperature of the system increases.

Even though propanone cannot form hydrogen bonds to itself the carbonyl oxygen allows it to form hydrogen bonds to the hydrogens of water and as a result the liquids are miscible. The molecules are more closely bonded in the mixture so that the volume decreases and, as bond formation is exothermic, the temperature of the system increases.

Water has very strong hydrogen bonds between its molecules, whereas hexane molecules are only attracted to each other by dispersion forces and, unlike propanone, hexane has no atoms through which it can participate in hydrogen bonding. If the two liquids were to mix, the presence of hexane molecules would result in the breaking of hydrogen bonds in the water making it a very endothermic process. As a result the liquids do not mix so there are no significant changes in bonding and the volume and temperature remain virtually unaltered.

Pure ethanol has hydrogen bonds between its molecules, whereas hexane molecules are only attracted to each other by dispersion forces. The hydrogen bonds in ethanol are however weaker than those in water and it has a short hydrocarbon chain on which dispersion forces can operate, hence unlike water and hexane, ethanol and hexane are miscible, with an increase in entropy being the driving force of the change. It does however result in a net weakening of the bonding in the system, hence it is an endothermic change. It might be expected that the volume would increase, but this does not seem to occur.

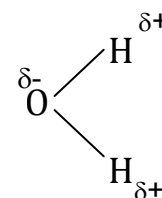
Hexane and hexene both have dispersion forces between their molecules so that bonding between the two compounds is similar to that in the pure substances, so they are readily miscible. The bonds involved are weak so any differences are very small and do not result in observable changes in volume or temperature.

5) Stream of liquid deviates—water, trichloroethane, propanone

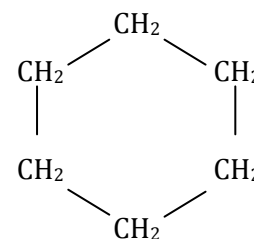
Stream of liquid does not deviate—cyclohexane, tetrachloromethane

Molecules that have a permanent dipole will orientate themselves in the electric field so that the negative end of the dipole is closer to the positively charged rod than the positive end of the dipole. As a result the force of attraction is greater than the force of repulsion and the stream of liquid will be deflected.

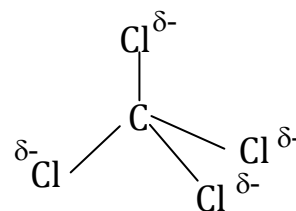
In the case of water, oxygen is much more electronegative than hydrogen, giving rise to polar bonds and, as the molecule is non-linear, this results in it having a permanent dipole.



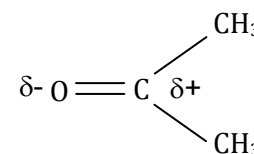
In the case of cyclohexane, not only are carbon and hydrogen very similar in electronegativity, giving rise to bonds of low polarity, the molecule is very symmetrical ensuring that it is non-polar.



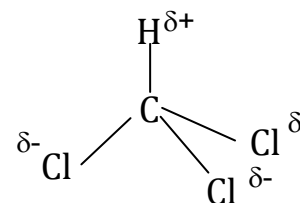
In the case of tetrachloromethane, the carbon-chlorine bonds are quite polar owing to their significant difference in electronegativity, but the molecule is very symmetrical so that these polar bonds cancel, resulting in a non-polar molecule.



In the case of propanone, the carbon-oxygen bond is quite polar and as a result of a lack of molecular symmetry this results in the molecule having a significant overall dipole.



In the case of trichloromethane, the carbon-chlorine bonds are quite polar owing to their significant difference in electronegativity and the molecule is not symmetrical enough for these polar bonds to cancel, so trichloromethane is a polar molecule.



## SYLLABUS RELEVANCE: TOPIC 5.1

A calorimetry experiment for an enthalpy of reaction should be covered and the results evaluated.

Experiments could include calculating enthalpy changes from given experimental data (energy content of food, enthalpy of melting of ice or the enthalpy change of simple reactions in aqueous solution).

## Apparatus required

## Per group

- Thermometer (0–110°C)
- Stop watch
- 100 cm<sup>3</sup> measuring cylinder
- Weighing bottle
- Polystyrene cup
- Electric stirrer

## Generally available

- Balance capable of weighing to at least 0.01 g
- Paper towels
- Kettle(s)

## Chemicals required

- Ice (~25 g per group)
- Aqueous 2 mol dm<sup>-3</sup> hydrogen peroxide (~50 cm<sup>3</sup> per group)
- Powdered manganese(IV) oxide (manganese dioxide, ~1 g per group)

## Notes

*Probable timing–60 minutes laboratory time*

A fairly straightforward thermochemistry practical that gives reasonably good results, though the latent heat generally gives better results than the enthalpy of reaction and there are less embarrassing questions about whether one should take into account the specific heat of manganese(IV) oxide.

## Part A

Mass of ice, filter paper and water =  $31.104 \pm 0.0005$  g

Mass of filter paper and water =  $8.135 \pm 0.0005$  g

Initial temperature of water =  $66.8 \pm 0.1$  °C

Final temperature of water =  $37.4 \pm 0.1$  °C

Volume of water =  $100 \pm 0.5$  cm<sup>3</sup>

## Relevant Qualitative Data

When drying the ice the water absorbed by the towel tends to drip off. Before the ice is added steam is visible rising from the surface of the hot water. When the ice is added to the water the size of the lumps of ice gradually decreases and eventually disappear.

- a)  $Q = m \cdot c \cdot \Delta T = 100 \times 4.18 \times (66.8 - 37.4) = 12289.2 \text{ J} = 12.29 \text{ kJ}$
- b)  $Q = m \cdot c \cdot \Delta T = (31.104 - 8.135) \times 4.18 \times (37.4 - 0) = 3590.8 \text{ J} = 3.59 \text{ kJ}$
- c) Heat lost by water = Heat required to melt ice + Heat required to heat water after melting  
 $12.29 = x + 3.59$   
 $x = 12.29 - 3.59 = 8.70 \text{ kJ}$
- d)  $22.969 (=31.104 - 8.135) \text{ g}$  of ice required  $8.70 \text{ kJ}$  to melt so  $1 \text{ mole}$  ( $18.02 \text{ g}$ ) would require:  
 $8.70 \times \frac{18.02}{22.969} = 6.83 \text{ kJ mol}^{-1}$
- e) Use your values for the precision of the readings to calculate the precision of this value

Quantity	Value	Absolute uncertainty	Percentage uncertainty
Volume of water	100	0.5	0.500
Decrease in water temperature	29.4	0.2	0.680
Heat lost by water	12.29	0.145	1.180
Mass of ice	22.969	0.001	0.004
Increase in ice temperature	37.4	0.1	0.267
Heat gained by molten ice	3.59	0.010	0.271
Heat required to melt ice	8.70	0.155	1.782
Molar enthalpy of fusion	6.83	0.122	1.786

Molar enthalpy of fusion of water =  $6.8 \pm 0.1 \text{ kJ mol}^{-1}$

## Part B

Time	Temperature	Time	Temperature	Time	Temperature
/s	/°C	/s	/°C	/s	/°C
0	19.0	210	69.0	420	58.5
30	19.0	240	67.0	450	57.5
60	19.0	270	65.0	480	56.0
90	19.0	300	63.5	510	55.0
120	19.0	330	62.0	540	54.5
150	33.0	360	61.0	570	53.0
180	64.0	390	60.0	600	52.5

Precision of time measurements =  $\pm 1 \text{ s}$

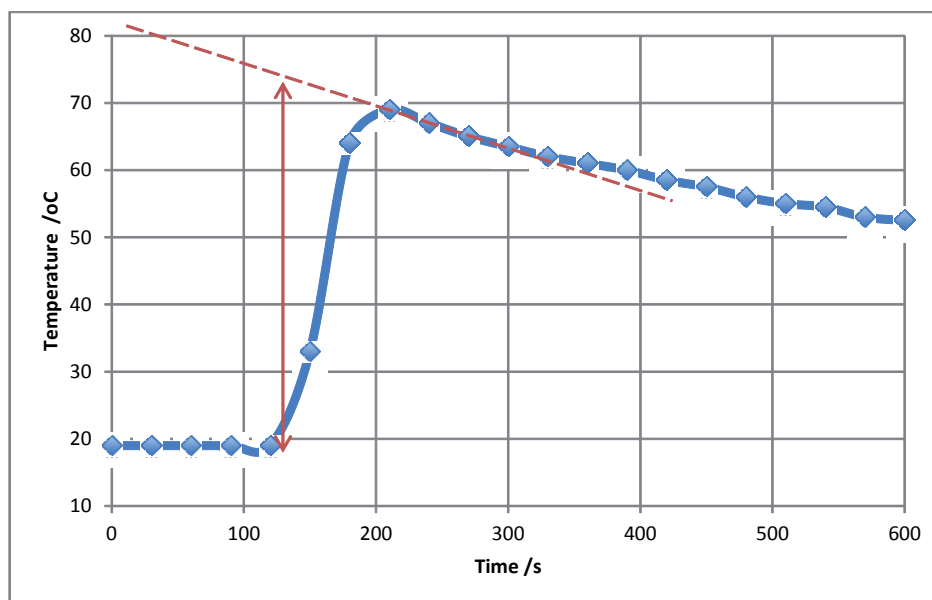
Precision of temperature measurements =  $\pm 0.25 \text{ }^\circ\text{C}$

Volume of aqueous hydrogen peroxide =  $50 \pm 0.5 \text{ cm}^3$



**Relevant qualitative data**

Initial very rapid reaction with evolution of gas and a little splashing out of a few droplets. After about a minute this subsided to leave a colourless liquid with black powder in the bottom and adhering to the sides of the container.

**Data Analysis**

- a) Rise in temperature if the reaction was instantaneous and the rate of heat loss was the same as in the initial stages of cooling, is shown on the graph above. It gives a value of:

$$\Delta T = 74 - 19 = 55 \pm 1 \text{ } ^\circ\text{C} \text{ (uncertainty estimated as accuracy of reading graph)}$$

- b) Heat to raise water temp = heat produced by reaction

$$Q = m.c.\Delta T = 50 \times 4.18 \times 55 = 11,495 \text{ J} = 11.495 \text{ kJ}$$

$$\text{Uncertainty in mass} = \text{uncertainty in volume} = \pm 1\%$$

$$\text{Uncertainty in temperature change} = 1.8\%$$

$$\text{Total uncertainty in } Q = \pm 2.8\%$$

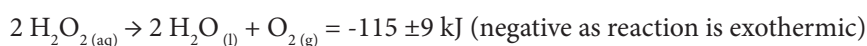
- c) Amount of  $\text{H}_2\text{O}_2 = n = c.V = 1.0 \times 0.050 = 0.050$

$$\Delta H = \frac{Q}{n} = \frac{11.495}{0.05} = 229.9 \text{ kJ mol}^{-1}$$

$$\text{Uncertainty in } n = \text{uncertainty in } V = \pm 1\%$$

$$\text{Total uncertainty in } \Delta H = 3.8\% = \pm 8.7 \text{ kJ}$$

Enthalpy change of reaction:



## Conclusion & Evaluation

- a) The accepted value for the enthalpy of fusion of ice is  $6.01 \text{ kJ mol}^{-1}$ . This value is less than the values determined (13% lower) and lies well outside the uncertainty of the experimentally determined value, implying that the procedure involves significant systematic errors.
- b)  $\Delta H = \Sigma\Delta H_f(\text{products}) - \Sigma\Delta H_f(\text{reactants}) = (2 \times 285.5) - (2 \times 187.8) = -195.4 \text{ kJ mol}^{-1}$   
(Remember  $\Delta H_f$  of oxygen = 0, like all elements in their standard states)
- c) In the reaction, two O-O single bonds are being replaced by a O=O double bond; the O-H bonds remain the same. Hence  
 $\Delta H = (2 \times 144) - (498) = -210 \text{ kJ mol}^{-1}$
- d) The value derived from standard enthalpies of formation should be the more accurate, the only source of error being that the reaction carried out involved aqueous hydrogen peroxide rather than the pure compound, so enthalpies of solution were neglected. In the case of the bond enthalpies the value for the O-O bond is an average value of all compounds that contain this bond and it may differ from the precise value in hydrogen peroxide. It also assumes that the bond enthalpies of the O-H bonds remain unchanged and this is probably not correct as the electronegativity of the atom joined on to the second bond of oxygen will affect its electronegativity and hence the strength of the O-H bond. Finally bond enthalpy data is only really valid for reactions taking place in the gas phase and this was in aqueous solution. For all these reasons, the bond enthalpy value is probably less accurate.
- e) As may be expected from a thermochemistry determination in simple apparatus, the experimental value for "uppercase delta"H is considerably less than the theoretical one:  $115 \text{ kJ mol}^{-1}$  compared to  $195 \text{ kJ mol}^{-1}$  (~41% too small). The most probable explanations for this is that the graphical extrapolation of the temperature underestimates the heat lost to the surroundings, because during the period of cooling no hot gas is being evolved, a process that was occurring during the reaction.
- f) Like all calorimetric techniques these methods both assume that there is no gain or loss of heat to the surroundings. Heat losses are often significant and could easily explain deviations from literature values of the order of magnitude observed. In addition the hydrogen peroxide involves the loss of gas from the apparatus and this would carry heat away.

This hydrogen peroxide experiment also assumes that the density and specific heat capacity of the aqueous hydrogen peroxide is equal to that of water. In practice the density of the aqueous solution is greater than that of water (~10% higher) and the specific heat capacity of the pure liquid is less ( $2.62$  rather than  $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ ) so at least the direction of the errors cancel, but the actual values of these two quantities for the solution used should be determined.

- g) If heat was lost to the surroundings the final temperature ( $37.4^\circ\text{C}$ ) would be below the true value so the heat lost by the water ( $12.29 \text{ kJ}$ ) would be greater than the true value and the heat gained by the molten ice ( $3.59 \text{ kJ}$ ) would be less than the true value. Therefore the heat required to melt the ice, and the enthalpy of fusion, would have been overestimated, as was indeed found.

A second significant source of error in this is that the mass is assumed to be that of ice and no water was transferred to the calorimeter. In practice the ice is always wet, so the true mass of ice is less than the measured mass ( $22.969 \text{ g}$ ). This would lead to the value determined for the enthalpy of fusion being smaller than the value determined, which was not what was found, hence it would appear that errors resulting from heat losses are greater than those resulting from the ice being wet.

A third potential source of error is that if the ice has been obtained fresh from the freezer then the centre of the ice will not be at 0°C, but will be at a lower temperature. As a result the heat needed to raise the temperature of the ice to its melting point needs to be added to the equation. This would mean the enthalpy of fusion was greater than the true value as was observed.

- h) The loss of heat to the surroundings could be reduced by putting the polystyrene cup inside a second polystyrene cup, so as to provide additional insulation and, perhaps even more importantly, a polystyrene lid with a hole for the thermometer could be fitted to the cup.

The dryness of the ice could be improved by ensuring that there is adequate paper towel to absorb water from the surface and by minimising the surface area of the ice.

Finally to control the starting temperature the ice to be used could be stored in a beaker immersed in an ice-water bath for sufficient time for the ice to be at 0°C.

Inaccuracies associated with the assumptions about the density and specific heat capacity of aqueous hydrogen peroxide could be removed by actually determining these values experimentally.

## SYLLABUS RELEVANCE; TOPIC 5.2

A calorimetry experiment for an enthalpy of reaction should be covered and the results evaluated.

Experiments could include Hess's Law labs.

## Apparatus required

## Per group

- Thermometer (preferably 0–50°C by 0.1°C intervals)
- Stop watch
- 100 cm<sup>3</sup> measuring cylinder
- Weighing bottle
- Polystyrene cup (at least 250 cm<sup>3</sup> capacity)

## General

Balance reading to 0.01 g

## Chemicals required

- 2 mol dm<sup>-3</sup> hydrochloric acid (~250 cm<sup>3</sup> per group)
- Solid sodium hydrogencarbonate (bicarbonate) (~15 g per group)
- Solid anhydrous sodium carbonate (~10 g per group)

## Notes

Probable timing – 60 minutes laboratory time

## Sample data

Sodium hydrogencarbonate	
Initial mass	14.307 ± 0.0005 g
Final mass	1.088 ± 0.0005 g

Sodium carbonate	
Initial mass	9.331 ± 0.0005 g
Final mass	1.104 ± 0.0005 g

Sodium hydrogencarbonate			
Time (s)	Temp (°C)	Time (s)	Temp (°C)
0	16.0	330	7.0
30	16.0	360	7.2
60	16.0	390	7.2
90	16.0	420	7.2
120	16.0	450	7.4
150	9.8	480	7.4
180	6.8	510	7.6
210	6.6	540	7.6
240	6.6	570	7.6
270	6.8	600	7.8
300	7.0	630	7.8

Sodium carbonate			
Time (s)	Temp (°C)	Time (s)	Temp (°C)
0	15.6	330	21.8
30	15.6	360	21.8
60	15.6	390	21.8
90	15.6	420	21.8
120	15.6	450	21.8
150	20.2	480	21.6
180	21.8	510	21.6
210	22.0	540	21.6
240	22.0	570	21.6
270	22.0	600	21.4
300	22.0	630	21.4

Uncertainties: Time =  $\pm 1$  s      Temp =  $\pm 0.2$  °C

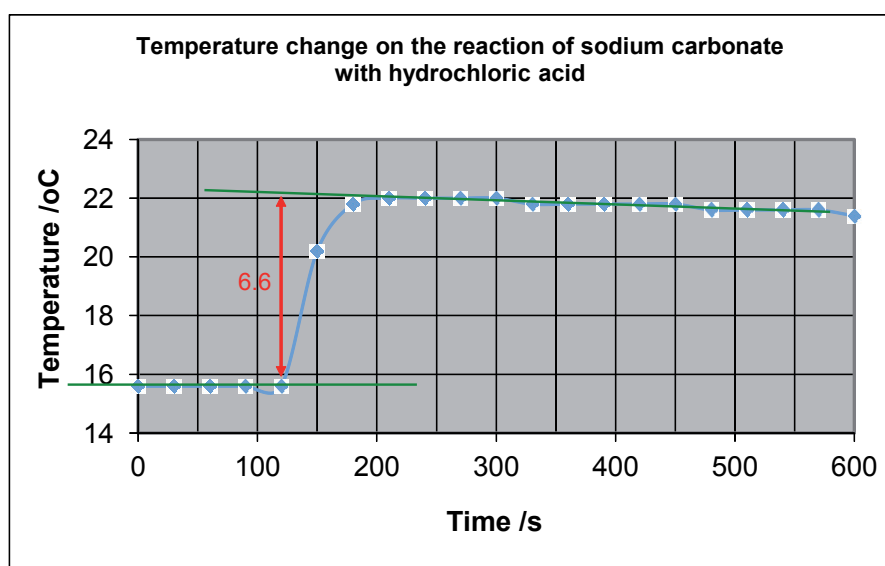
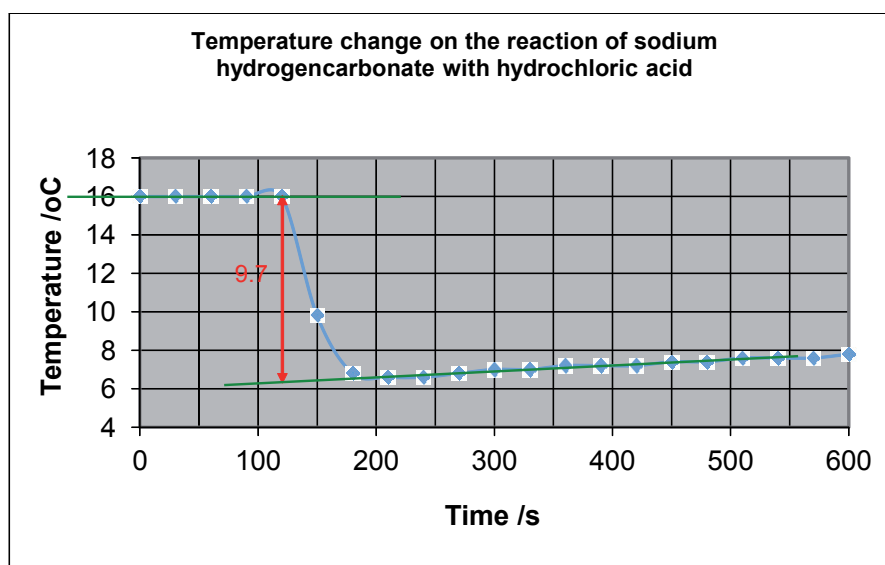
Volume of 2 mol dm<sup>-3</sup> HCl for both =  $100 \pm 0.5$  cm<sup>3</sup>

### Relevant qualitative observations

In both cases there was very rapid effervescence as the white powder is added to the colourless solution, so much so that it had to be added a little at a time over the first half minute to prevent the liquid frothing over the lip of the cup. Eventually all of the powder dissolved to leave a clear colourless solution.

### Data Analysis

a)



Uncertainty in both values estimated as  $\pm 0.1$  °C



- b)  $Q = m \cdot c \cdot \Delta T = 0.100 \times 4.18 \times 9.7 = 4.055 \text{ kJ}$   
(assuming density and specific heat capacity of  $2 \text{ mol dm}^{-3}$  HCl is the same as that of water)

$$n = \frac{14.307 - 1.088}{84.01} = 0.1574 \text{ mol}$$

$$\Delta H = \frac{4.055}{0.1574} = +25.77 \text{ kJ} \quad (\text{positive sign as endothermic})$$

$$\text{Uncertainties: } m = \frac{0.5}{100} \times 100 = 0.50\% \quad T = \frac{0.1}{9.7} \times 100 = 1.03\%$$

$$\text{Uncertainty in } \Delta H = 0.50 + 1.03 = 1.53\% = 25.77 \times \frac{1.53}{100} = 0.395$$

$$\Delta H = +25.8 \pm 0.4 \text{ kJ}$$

- c)  $Q = m \cdot s \cdot \Delta T = 0.100 \times 4.18 \times 6.6 = 2.759 \text{ kJ}$

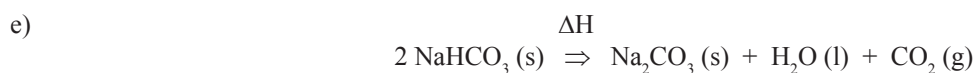
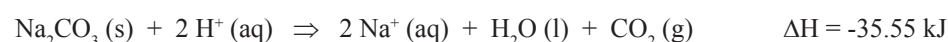
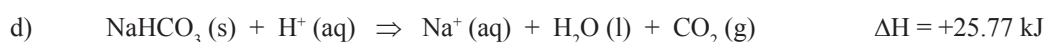
$$n = \frac{9.331 - 1.104}{105.99} = 0.07762 \text{ mol}$$

$$\Delta H = \frac{4.055}{0.1574} = -35.55 \text{ kJ} \quad (\text{negative sign as exothermic})$$

$$\text{Uncertainties: } m = \frac{0.5}{100} \times 100 = 0.50\% \quad T = \frac{0.1}{6.6} \times 100 = 1.52\%$$

$$\text{Uncertainty in } \Delta H = 0.50 + 1.52 = 2.02\% = 35.55 \times \frac{2.02}{100} = 0.718$$

$$\Delta H = -35.6 \pm 0.7 \text{ kJ}$$



$$\Delta H = 2 \times +25.77 \text{ kJ mol}^{-1}$$

$$\Delta H = -35.55 \text{ kJ mol}^{-1}$$



- f)  $\Delta H = (2 \times +25.77) - (-35.55) = +87.09 \text{ kJ}$

$$\text{Uncertainty} = (2 \times 0.395) + 0.718 = 1.508$$

$$\Delta H = +87.1 \pm 1.5 \text{ kJ}$$

## Evaluation

- (a) The value obtained is greater than the accepted value even taking into account the uncertainty. The experiment has however yielded a most acceptable result as the agreement is within  $\sim 2\frac{1}{2}$  % of the accepted value. The estimated uncertainty of  $\sim 1.7\%$  is also quite good. If the temperature changes had not been corrected for heat losses the value obtained would have been  $+84.5$  kJ. This suggests that the temperature correction has over-compensated for the heat losses.
- (b) In most thermochemistry determinations heat exchange with the surroundings is the major source of error and in this case, because the reactions evolve a gas, it may be expected to be worse than in some other cases. Heat exchange always leads to a smaller temperature change, irrespective of whether the reaction is exothermic or endothermic, and hence leads to smaller values for the enthalpy change being determined. In this case the heat losses appear to be quite small, perhaps because the temperature changes are quite modest ( $<10$  °C) and the agreement without compensating for them is within about  $\frac{1}{2}$  % of the accepted value. Other sources of systematic error would be ignoring the heat capacity of the polystyrene cup (which would also lead to a lower temperature change and hence a lower value for  $\Delta H$ ), and the assumption that the density and the specific heat capacity of the HCl are the same as those of water (internet sources give them as  $1.04$  g cm<sup>-3</sup> and  $4.04$  J g<sup>-1</sup> K<sup>-1</sup> respectively. If these are correct the two deviations would conveniently just about cancel each other! With regard to uncertainties the major contributor is the measurement of the temperature ( $\pm 0.2$  °C, hence  $\pm 0.4$  °C for  $\Delta T$ , about 5 %, though a lower value was estimated for the extrapolated data on the graph). This is about 10 times greater than the uncertainty in the measurement of the volume of acid.
- (c) The uncertainty could be significantly reduced by using a thermometer that reads to a greater precision. Many electronic digital thermometers can be read to 2 dp, so reducing the uncertainty in the measurement of  $\Delta T$  to a similar order of magnitude to the measurement of the mass of HCl. This could itself be easily improved by weighing the polystyrene cup before (hence giving a value for its heat capacity if compensating for this is deemed worthwhile) and after adding the acid. In the absence of a better thermometer some improvement could be made by using a greater mass of the solids along with a higher [HCl] to produce a greater temperature rise, though greater heat exchange might soon offset any improvement. With regard to the assumptions made, the density and the specific heat capacity of the acid used could have been measured as part of the investigation. The method used to compensate for heat exchange seems to over-compensate pointing to the need to adopt a more sophisticated theoretical model. If the solids were finely powdered and the volume reduced so there was little if any chance of the reagents bubbling over if it was all added at once, then perhaps the reaction could be considered instantaneous.
- (d) The reaction only occurs when the solid is heated. It is very difficult to make allowance for the contribution of the enthalpy of reaction in the way the temperature changes as this is usually much less than the heat introduced to raise the temperature to a level where the reaction would occur. Even then the reaction would be far from instantaneous giving rise to problems compensating for temperature exchange with the surroundings which would be very high at the temperatures required. The reverse reaction of solid sodium carbonate with water and carbon dioxide should be spontaneous and exothermic at room temperature, but the amount of water would have to be accurately controlled to prevent a solution occurring and again the reaction rate would be low, giving problems with heat exchange and knowing when the reaction was complete.

## SYLLABUS RELEVANCE: TOPIC 6.1

Investigation of rates of reaction experimentally and evaluation of the results.

Experiments could include investigating rates by changing concentration of a reactant or temperature

## Technique A

### Apparatus required

- 250 cm<sup>3</sup> conical flask fitted with a bung connected to a 100 cm<sup>3</sup> gas syringe
- 50 cm<sup>3</sup> measuring cylinder
- Stop watch
- Balance reading to at least 0.01 g

### Chemicals required

- 1.0 mol dm<sup>-3</sup> hydrochloric acid (~50 cm<sup>3</sup> per group)
- Magnesium ribbon (~4 cm per group)

## Technique B

### Apparatus required

- 250 cm<sup>3</sup> conical flask
- 100 cm<sup>3</sup> measuring cylinder
- Filter paper
- Stop watch
- Balance reading to at least 0.01 g

### Chemicals required

- 0.5 mol dm<sup>-3</sup> hydrogen peroxide (~50 cm<sup>3</sup> per group)
- Manganese(IV) oxide (manganese dioxide, ~1 g per group)

## Technique C

### Apparatus required

- Burette
- 10 cm<sup>3</sup> pipette and pipette filler
- 250 cm<sup>3</sup> conical flask
- 100 cm<sup>3</sup> conical flask
- 50 cm<sup>3</sup> measuring cylinder
- 25 cm<sup>3</sup> measuring cylinder
- Stop watch

### Chemicals required

- 0.0025 mol dm<sup>-3</sup> aqueous sodium thiosulfate (~250 cm<sup>3</sup> per group)
- 0.01 mol dm<sup>-3</sup> iodine solution
- 2 mol dm<sup>-3</sup> hydrochloric acid (~60 cm<sup>3</sup> per group)
- 0.2 mol dm<sup>-3</sup> aqueous propanone (~50 cm<sup>3</sup> per group)
- Solid sodium hydrogen carbonate (~25 g per group)
- Starch indicator

## Technique D

### Apparatus required

- Spectrophotometer or colorimeter
- 100 cm<sup>3</sup> conical flask
- 25 cm<sup>3</sup> measuring cylinder
- 10 cm<sup>3</sup> measuring cylinder
- Stop watch

### Chemicals required

- 0.02 mol dm<sup>-3</sup> aqueous sodium thiosulfate (~20 cm<sup>3</sup> per group)
- 2 mol dm<sup>-3</sup> hydrochloric acid (~5 cm<sup>3</sup> per group)

### Notes

*Probable timing–120 minutes laboratory time*

This practical is designed to allow students to become familiar with a variety of techniques that can be used for monitoring the rate of a chemical reaction as well as encountering equipment with which they have had little previous experience, such as the gas syringe and spectrophotometer/colorimeter. It will also allow them to gain practice with various IT supports, such as data logging equipment and graph plotting programmes

## SAMPLE DATA

### Technique A–Volume of evolved gas

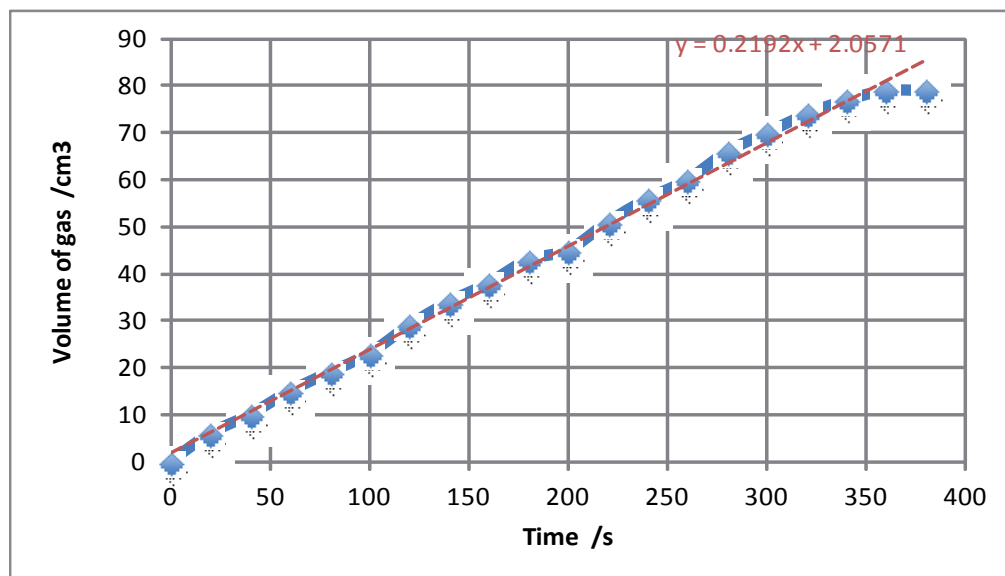
Time /s	Gas volume /cm <sup>3</sup>	Time /s	Gas volume /cm <sup>3</sup>
0	0	200	45
20	6	220	51
40	10	240	56
60	15	260	60
80	19	280	66
100	13	300	70
120	29	320	74
140	34	340	77
160	38	360	79
180	43	380	79

Precision of time measurements = ± 1 s      Precision of volume measurements = ± 1 cm<sup>3</sup>

### Relevant qualitative data

There was a steady evolution of gas on the surface of the magnesium ribbon and this continued throughout the reaction with the piece of magnesium gradually decreasing in size. Eventually the ribbon dissolved completely leaving a clear colourless solution. There was also a noticeable increase in the temperature of the flask and its contents.

## Data Analysis



Initial rate of evolution of gas =  $0.22 \text{ cm}^3 \text{ s}^{-1}$

## Conclusion & Evaluation

- Can only be used for reactions that evolve a gaseous product. If it is collected over water, rather than in a syringe, the gas should not react with, or be particularly soluble in water.
- Very simple apparatus and easy to employ.
- Gas syringes usually have quite low precision. If the gas is alternatively collected over water then the gaseous product should not react with, or be soluble in, water (if very soluble then this can be a problem even with a gas syringe). There are also problems with gas escaping when the reaction is started. It does not give the number of moles of product, and hence the change in concentration, but, if the pressure and temperature are known, the amount can be calculated.
- The loss of gas when initiating the reaction can be overcome by a variety of techniques that keep the reactants separate and can be overcome without removing the bung of the flask. The acid could, for example, be placed in a test tube that can be tipped over by tilting the flask.



## Technique B Decrease in mass

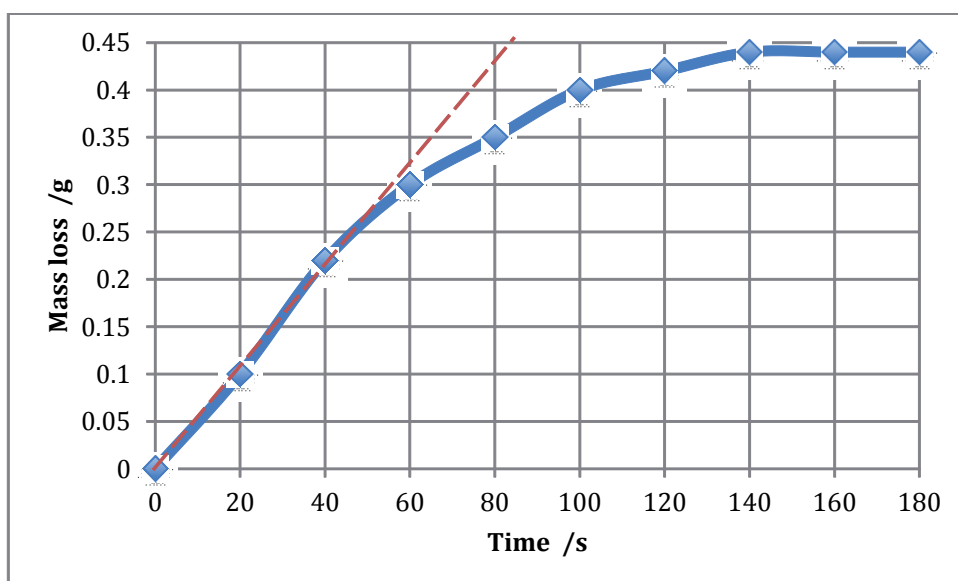
Time /s	System mass /g
0	157.98
20	157.88
40	157.76
60	157.68
80	157.63
100	157.58
120	157.56
140	157.54
160	157.54
180	157.54

Precision of time measurements =  $\pm 1$  s      Precision of mass measurements =  $\pm 0.005$  g

## Relevant qualitative data

When the black powder was added to the clear, colourless solution in the flask there was a rapid effervescence, so vigorous that the liquid almost overflowed from the container. The rate of gas evolution gradually subsided and at the end a clear, colourless solution remained with black powder on the bottom and sides of the beaker. There was a significant increase in temperature during the course of the reaction.

## Data Analysis



Initial rate of mass loss =  $0.0055 \text{ g s}^{-1}$

## Conclusion & Evaluation

- Again, can only be used for reactions that evolve a gaseous product and it needs to have quite a high molar mass otherwise the mass loss is very small (not good for  $H_2$ ).
- Probably the simplest possible apparatus and can be easily connected to data-logging programmes for direct recording of the results.
- It does not give the number of moles of product, and hence the change in concentration, directly, but knowing the molar mass of the gas this is easily compensated for. As the reactions usually involve the reaction between a solid and a liquid, keeping the surface area constant can be a challenge.
- The only way to compensate for variable surface area is to have a very finely divided powder, which should average out variations between samples, or to have a number of replicate experiments, which should have a similar effect.

## Technique C–Titrating Samples

Time /min	Titre of 0.0025 M $Na_2S_2O_3$ /cm <sup>3</sup>
0	11.0
2	10.0
5	9.5
10	9.0
15	7.5
20	6.5
25	5.5
30	4.5
35	3.8
40	2.5

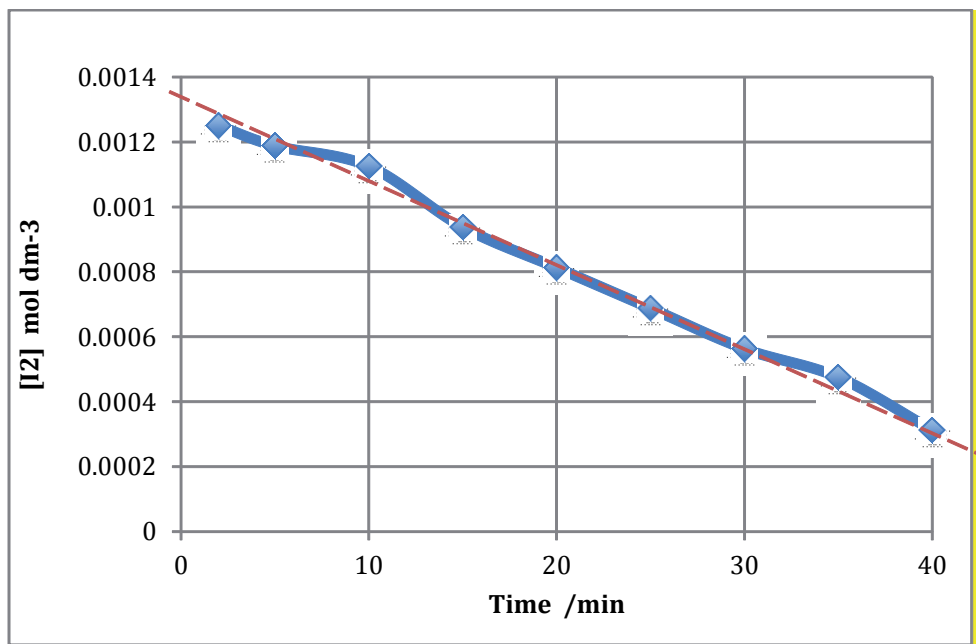
Precision of time measurements  $\pm 0.02$  min

Precision of burette readings  $\pm 0.1$  cm<sup>3</sup>

### Relevant qualitative data

The iodine solution turned the colourless acidified propanone a pale yellow colour and as the reaction progressed the intensity of this colour gradually diminished. When the sample was pipetted out, reaction with the hydrogencarbonate caused a vigorous effervescence. Addition of thiosulfate again decreased the intensity of the yellow colour. When starch was added the mixture turned a blue-black but the change to colourless at the end point was somewhat indistinct.

## Data Analysis



Initial rate of change in iodine concentration =  $4.3 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$

## Conclusion & Evaluation

- Can only be used for quite slow reactions, even if the samples are quenched when removed. Slow and quite time consuming.
- Very simple apparatus and can be applied to almost all reactions by choosing a suitable titration reaction.
- All of the usual problems accompanying titrations, such as difficulties determining the end-point, apply but the precision is often quite high and the results directly give the change in concentration. The major disadvantage is that the technique is quite time consuming.
- If time allows, precision could be improved by taking replicate samples. Little can be done about the time taken apart from honing titration techniques.

## Technique D – Light absorption

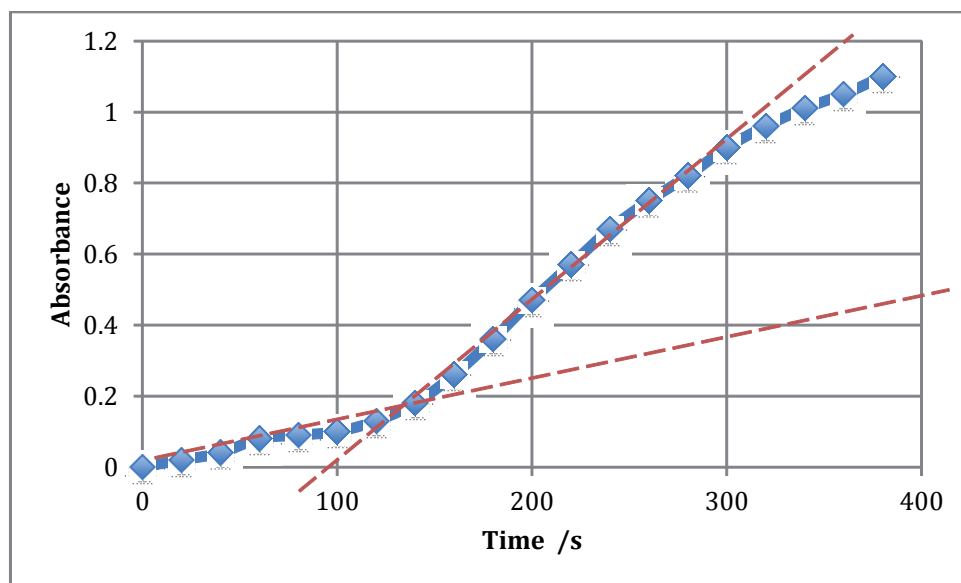
Time /s	Absorbance	Time /s	Absorbance
0	0.00	200	0.47
20	0.02	220	0.57
40	0.04	240	0.67
60	0.08	260	0.75
80	0.09	280	0.82
100	0.10	300	0.90
120	0.13	320	0.96
140	0.18	340	1.01
160	0.26	360	1.05
180	0.36	380	1.10

Precision of time measurements =  $\pm 1$  s    Precision of absorbance measurements  $\pm 0.005$

## Relevant qualitative data

When the two colourless solutions were mixed there initially appeared to be no reaction occurring, but slowly the solution became a cloudy yellow and increasingly opaque as the reaction proceeded.

## Data Analysis



Initial rate of change in absorbance =  $0.0012 \text{ s}^{-1}$ , but soon increases to  $\sim 0.0045 \text{ s}^{-1}$

## Conclusion & Evaluation

- a) Can only be used for reactions involving coloured reactants and/or products, though occasionally UV absorption differences will work. Requires a spectrophotometer or colorimeter.

In this case the graph is non-linear, probably because it involves the scattering of light by a precipitate. In reactions involving the formation or loss of a coloured species in solution there is almost always a simple linear dependence on concentration.

- b) Very simple to use and can easily be linked to data-logging systems for the continuous recording of results.
- c) There is usually a time delay in transferring samples to the cuvette and the results do not directly give the change in concentration, though the absorption may be calibrated to permit this.
- d) Sometimes samples can be removed at regular intervals and the concentration of an appropriate reactant or product may be determined by absorption, if a reagent that produces a coloured product is added to the reaction mixture.



### SYLLABUS RELEVANCE; TOPIC 6.1

Investigation of rates of reaction experimentally and evaluation of the results.

Experiments could include investigating rates by changing concentration of a reactant or temperature

### Apparatus required (per group)

- 250 cm<sup>3</sup> conical flask
- 50 cm<sup>3</sup> measuring cylinder
- 0–110°C thermometer
- Stop watch
- Balance reading to at least 0.1 g

### Chemicals required

- 5 mol dm<sup>-3</sup> hydrochloric acid (~400 cm<sup>3</sup> per group)
- Small lumps of calcium carbonate (~25 g per group)
- Large lumps of calcium carbonate (one ~5 g lump per group)

### Notes

*Probable timing–120 minutes laboratory time (can be reduced if Parts allocated)*

A fairly straightforward practical that looks at the effect of most variables, except the presence of a catalyst, on the rate of reaction. If the students do all the parts of it themselves it would take a long time, so perhaps ask them all to do Part A (just so they can see how varied the results are!) and then assign them one of the other parts and they can share results at the end.

As the students do not look at the effect of a catalyst here, I often do a demonstration of the effect of a catalyst either during the practical or another lesson close to it. The “pink foam” is always fun:

Put a couple of spatulas full of “red lead” into the bottom of a 500 cm<sup>3</sup> conical flask and add a good squirt of detergent and about an equal volume of water, then swirl it around the inside of the flask. Support the flask on a tripod over a sink (for easy cleaning up!), tip in about 25 cm<sup>3</sup> of the 100-Volume hydrogen peroxide and stand back. You should get a pink foam serpent erupting out of the top of the flask. It does work with manganese(IV) oxide, but I prefer the pretty pink produced by the “red lead”.

**Warning–this involves 100-volume hydrogen peroxide, which is a very corrosive liquid, blistering the skin easily. Keep the students well back, do not allow them to touch the foam and wear gloves on your hands, especially when cleaning up. Note too that “red lead” (Pb<sub>3</sub>O<sub>4</sub>), like all lead compounds, is quite toxic.**



My favourite however, although it prompts a lot of difficult-to-answer questions, is the catalysis of the reaction between sodium potassium tartrate (Rochelle’s salt) and hydrogen peroxide as described below.

Take about 4 spatulas of the tartrate and dissolve it in about 20 cm<sup>3</sup> of 20-volume hydrogen peroxide, then divide the solution equally between two boiling tubes. Heat the first one and note that it has to be almost boiling before there is any sign of reaction. Add a couple of crystals of cobalt(II) chloride to the second, swirl until these dissolve and then warm gently. Note that gas starts to be evolved when it is still cool enough to hold. The colour changes, showing that the cobalt is involved in the reaction, but changes back to the original pink at the end, showing that it has not undergone any permanent change.

## Quantitative Data

Time /s	Total mass /g					
	A	B	C	D	E	F
0	58.65	161.65	57.58	67.03	61.48	67.53
30	58.01	161.27	57.12	66.84	61.47	65.99
60	57.43	160.79	56.83	66.61	61.47	65.42
90	57.09	160.41	56.52	66.38	61.47	65.23
120	56.93	160.18	56.32	66.24	61.46	65.17
150	56.77	160.02	56.20	66.14	61.46	65.14
180	56.72	159.92	56.10	66.05	61.46	65.12
210	56.69	159.85	55.98	66.02	61.45	65.10
240	56.67	159.81	55.90	66.00	61.45	65.08
270	56.66	159.77	55.83	65.99	61.45	65.06
300	56.65	159.75	55.76	65.98	61.44	65.05
Mass CaCO <sub>3</sub> /g	5.01	5.02	5.06	2.51	5.06 (4 lumps)	5.02

## Relevant qualitative observations

A-D produced rapid effervescence which gradually subsided and eventually all of the white solid dissolved to leave a colourless solution. With E, very slow bubbling at start and solid remained at end of the timed reaction. In F the reaction was very vigorous with the bubbles almost causing the contents to overflow.

## Data Analysis



b) Amount of  $\text{CaCO}_3 = \frac{m}{M_r} = \frac{5}{100} = 0.05 \text{ mol}$

Amount of HCl =  $c \times V = 5 \times 0.050 = 0.25 \text{ mol}$

As 0.1 mol HCl would be required to react with the 0.05 mol of  $\text{CaCO}_3$ , HCl is in excess and the limiting reagent is therefore  $\text{CaCO}_3$ . In Part C the amount of acid is halved (0.125 mol), but even so the acid will still remain in excess.

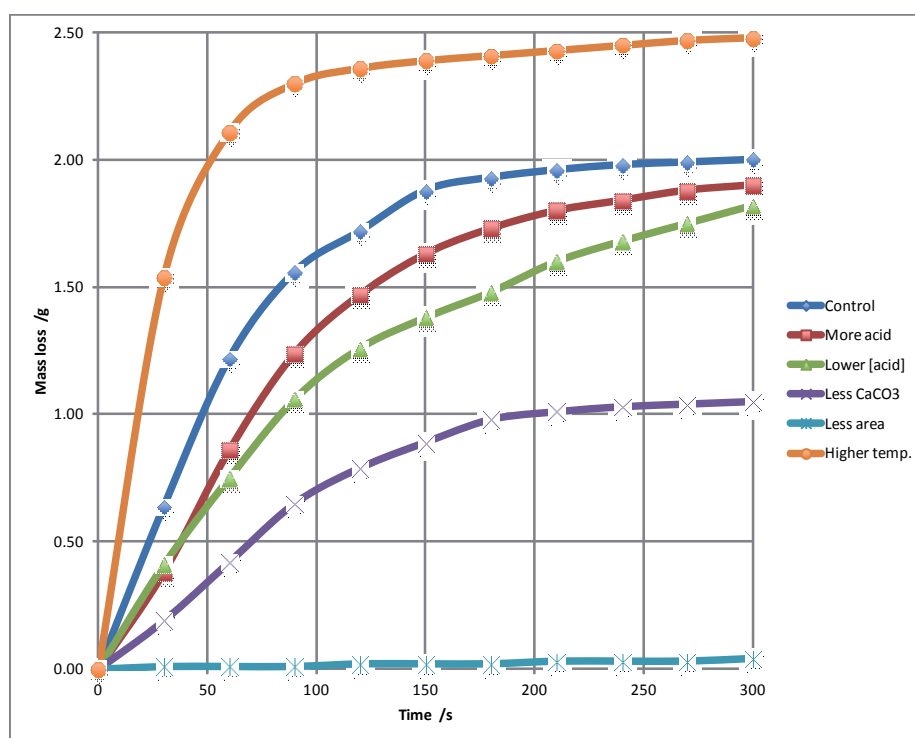
d)  $0.25 - 0.10 = 0.15 \text{ mol}$  (or 60%) of the HCl will remain in excess.

e) Amount of  $\text{CaCO}_3 = \frac{m}{M_r} = \frac{5.01}{100.09} = 0.0501 \text{ mol}$

Mass of  $\text{CO}_2 = n \times M_r = 0.0501 \times 44.01 = 2.20 \text{ g}$

e) continued

Time /s	Mass loss /g					
	Control	More acid	Lower [acid]	Less CaCO <sub>3</sub>	Less area	Higher temp.
0	0.00	0.00	0.00	0.00	0.00	0.00
30	0.64	0.38	0.41	0.19	0.01	1.54
60	1.22	0.86	0.75	0.42	0.01	2.11
90	1.56	1.24	1.06	0.65	0.01	2.30
120	1.72	1.47	1.26	0.79	0.02	2.36
150	1.88	1.63	1.38	0.89	0.02	2.39
180	1.93	1.73	1.48	0.98	0.02	2.41
210	1.96	1.80	1.60	1.01	0.03	2.43
240	1.98	1.84	1.68	1.03	0.03	2.45
270	1.99	1.88	1.75	1.04	0.03	2.47
300	2.00	1.90	1.82	1.05	0.04	2.48



f)

Part	Initial rate /g s <sup>-1</sup>
A	0.0217
B	0.0152
C	0.0125
D	0.00877
E	0.000013
F	0.0581

$$g) \quad 0.0217 \text{ g s}^{-1} = \frac{0.0217}{44.01} = 0.000493 \text{ mol s}^{-1}$$

$$h) \quad \text{Each CO}_2 \text{ formed requires two HCl, so rate of change of amount of HCl} = 0.000986 \text{ mol s}^{-1}$$

$$\text{Rate of change of concentration} = \frac{\text{Rate in mol s}^{-1}}{\text{Volume}} = \frac{0.000986}{0.050} = 0.0197 \text{ mol dm}^{-3} \text{ s}^{-1}$$

## Conclusion & Evaluation

- a) The mass of  $\text{CO}_2$  lost in Part A is significantly less than the theoretical mass loss – 2.00 compared to 2.20 g. This is probably explained by the solubility of carbon dioxide in water or carbon dioxide displacing air from the flask.
- b) Part A was only carried out once, but Part B should have the same initial rate and both this and Part C should have the same final weight loss, so looking at these data gives some idea of reproducibility. It can be seen that the rate of Part B is significantly less than that of Part A, but all three of these experiments look as if they will give a final weight loss of ~2 g.
- c) One major problem is the variation of the surface area between different  $\text{CaCO}_3$  samples. This would be greatly improved by using powder, but this would result in a much higher reaction rate. Reducing the concentration of acid to remedy this would result in it not being in excess and hence a smaller total mass loss.
- d) **Part A** was a control experiment, providing a value that the reaction rates under other conditions could be compared to.
- e) **Part B**–There should be no significant change in the initial rate of reaction, but it appears to have decreased by ~30%. This can only be attributed to experimental error because collisions only take place at the surface of the calcium carbonate and there is no change in this, as this is controlled by the concentration of the acid, not by the total amount present.

**Part C**–The initial rate of reaction should be approximately halved because halving the concentration of the acid halves the number of collisions between the acid and the surface of the carbonate. The results are approximately in accord with this, though slightly on the high side (0.0125 rather than 0.0109).

**Part D**–The initial rate of reaction should be approximately halved because halving the mass of carbonate halves the surface area and hence halves the rate of collision with the acid. It can be seen that the results are approximately in accordance with this, though slightly on the low side (0.0088 rather than 0.0109). It should be noted that the final mass is also halved indicating that the  $\text{CaCO}_3$  is, as predicted, the limiting reagent.

**Part E**–The initial rate is greatly reduced. The large lumps have a much smaller surface area than a much larger number of smaller lumps of the same mass, hence the rate of collision with the acid is much less. The experimental results corroborate this.

**Part F**–The initial rate is greatly increased because at a higher temperature the particles have more kinetic energy. The particles move faster so there is a slight increase in the collision rate, but a much greater effect comes from the increase in the proportion of collisions which have an energy greater than the activation energy. The result, with the rate more than doubling, fits in with this prediction. It should be noted that, perhaps slightly unexpectedly, the total loss of mass is about 10% greater and this may be attributed to the lower solubility of  $\text{CO}_2$  in warm water.

- f) The effect of a catalyst on the rate of reaction has not been investigated. Reactions in which this could be easily investigated practically include:
  - i) The catalysis of the decomposition of hydrogen peroxide by manganese(IV) oxide
  - ii) The catalysis of the reaction of hydrogen peroxide with sodium potassium tartrate by cobalt(II) chloride
  - iii) The catalysis of the reaction of hydrogen peroxide with iodide ions by iron(II) or copper(II) salts

### SYLLABUS RELEVANCE: TOPIC 6.1

Investigation of rates of reaction experimentally and evaluation of the results.

Experiments could include investigating rates by changing concentration of a reactant or temperature

### Apparatus and chemicals required

As with any student planned practical, it is difficult to be precise about the requirements. If the students have recently completed the practical on “Techniques for Measuring Reaction Rates” then it is probable that their requirements will be quite similar to those for that Investigation.

### Notes

*Probable timing - 60 minutes planning, 90 minutes laboratory time*

After Investigation 6A it is a good idea to follow up with either 6B or 6C, probably not both. Students often tend to choose one of the reactions investigated in 6A and all the apparatus is still out. It is also a good introduction to independently planning an investigation, something they will need to be very familiar with before embarking on the Internal Assessment project. An example of the sort of investigation a student might come up with is shown below.

### (Sample) Design

#### Research problem

A study of the way in which the initial rate of carbon dioxide evolution from the reaction of dilute hydrochloric acid and marble chips depends upon the proportion of glycerol (propan-1.2.3-triol), by volume, present in the solvent.

**Independent variable** the proportion of glycerol, by volume, in the solvent

**Dependent variable** the rate of reaction as measured by the rate of evolution of carbon dioxide gas

#### Controlled variables

- the concentration of hydrochloric acid
- the volume of hydrochloric acid
- the mass of marble chips
- the surface area of the marble chips
- the temperature of the reaction mixture

*What technique will you use to measure the rate of reaction? Explain why you have chosen this particular technique.*

The loss of mass from the system was chosen for its simplicity and the fact that the gas being produced has a relatively high molar mass. Alternatives could have been the volume of gas evolved or the increase in pressure of the system, but both are slightly more complex and display no obvious advantages.

*Discuss how your method will seek to keep the controlled variables constant, or at least monitor that they remain unchanged.*

**the concentration of hydrochloric acid** – The same acid will be used to prepare all of the solutions and as the sum of the volumes of the reagents is constant, the concentration of acid in the reacting system will be constant neglecting any volume changes on mixing.

**the volume of hydrochloric acid** - The sum of the volumes of the reagents is constant, so the volume of acid in the reacting system will be constant neglecting any volume changes on mixing.

**the mass of marble chips** – Marble chips with an approximately constant mass will be selected and the actual mass of each will be recorded so any variations may be allowed for.

**the surface area of the marble chips** – An assumption is made that marble chips of a given mass have an approximately equal surface area.



**the temperature of the reaction mixture** – The room is thermostatically controlled, so it is assumed that the temperature will remain constant.

*What other difficulties could you encounter and what precautions may you need to take?*

Some of the gas will remain dissolved in the water and in the flask, so there will be a time lag before the loss becomes apparent. Quite concentrated acid is being used and so this must be treated with due care (gloves and goggles).

*Describe specifically what data will you intend to collect.*

- The mass of each marble chip
- The mass of the system at regular intervals to produce a mass-time graph

*Make a quantitative prediction of the way in which you expect the dependent variable to change as you alter your independent variable.*

It is expected that, because of its greater viscosity, the rate of reaction will decrease in a linear manner as the mole fraction of propan-1.2.3-triol in the mixture increases.

*How will you use the results to test this prediction?*

Graphs will be drawn of the loss in mass against time and the rate of loss in mass (in  $\text{g s}^{-1}$ ) determined from the gradients. A graph of rate of mass loss against the mole fraction of propan-1.2.3-triol in the mixture will be drawn to examine the relationship between the variables.

### (Sample) Method

1. Select and weigh a marble chip with a mass of approximately 1 g. Record the mass.
2. Using a 25  $\text{cm}^3$  measuring cylinder add 20  $\text{cm}^3$  of water to a 100  $\text{cm}^3$  conical flask.
3. Using a 10  $\text{cm}^3$  measuring cylinder measure out 5  $\text{cm}^3$  of 5  $\text{mol dm}^{-3}$  hydrochloric acid into the flask and mix thoroughly.
4. Place the flask on a balance and place the marble chip next to it on the balance pan. Record the initial mass.
5. Add the marble chip to the acid and start the stop watch. Record the mass of the flask and reagents at appropriate intervals – every minute at for the first five minutes, then every 5 minutes until 30 minutes has elapsed.
6. Repeat parts 2 – 6, but at stage 2 instead of adding 20  $\text{cm}^3$  of water add 5  $\text{cm}^3$  of propan-1.2.3-triol and 15  $\text{cm}^3$  of water, then 10 : 10 and finally 15 : 5.

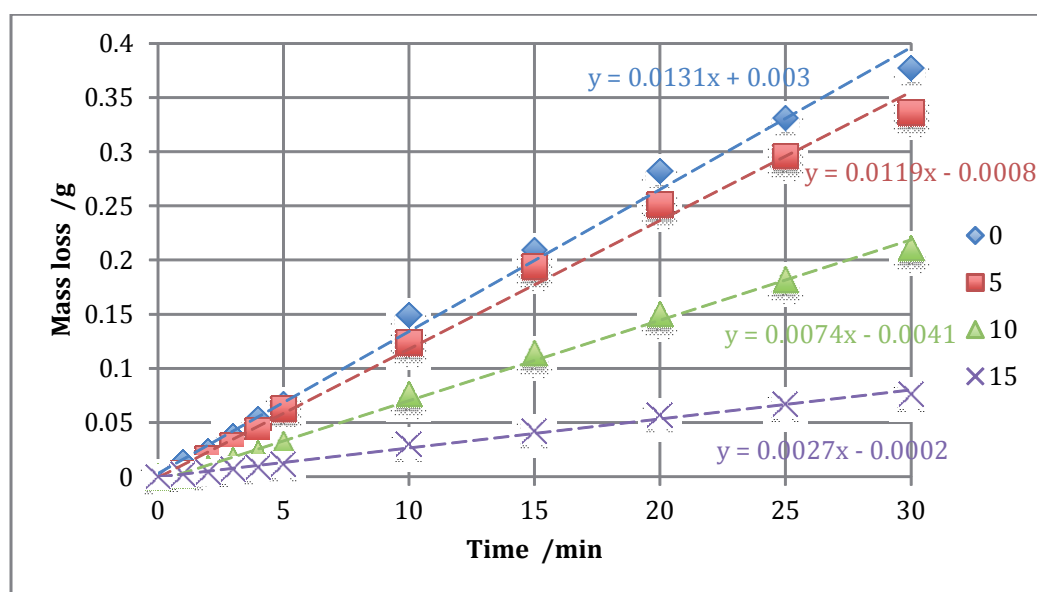
### (Sample) Data Collection

Volume propan-1.2.3-triol / $\text{cm}^3$	0	5	10	15
Mass of chip /g	1.094	1.148	1.056	1.113
Time /min	Total mass /g			
0	99.497	112.755	106.936	95.611
1	99.484	112.752	106.934	95.609
2	99.474	112.738	106.928	95.607
3	99.460	112.726	106.921	95.604
4	99.444	112.712	106.915	95.602
5	99.430	112.692	106.906	95.599
10	99.348	112.631	106.860	95.581
15	99.288	112.561	106.822	95.569
20	99.215	112.504	106.786	95.554
25	99.166	112.459	106.754	95.544
30	99.120	112.419	106.725	95.535

### (Sample) Data Analysis

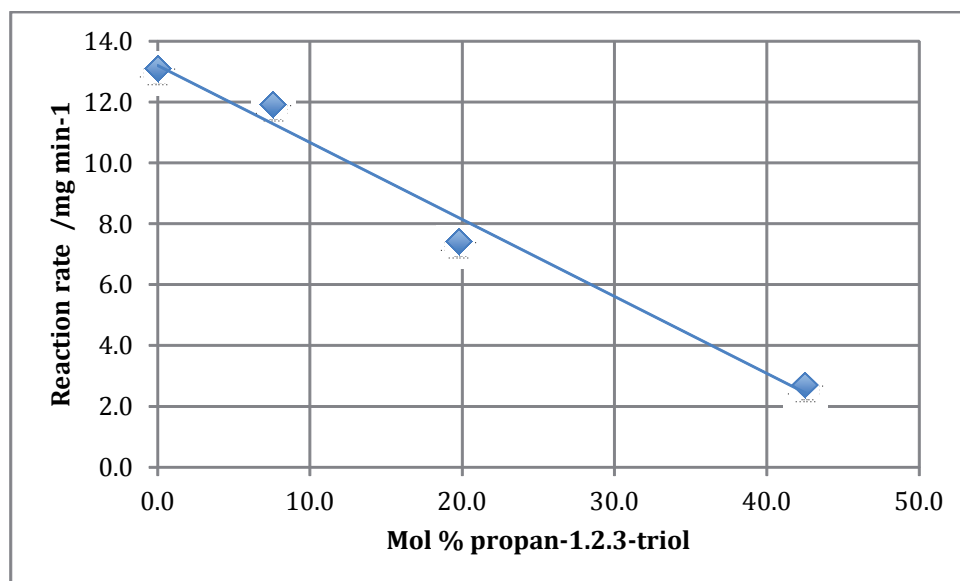
Calculating the loss in mass and plotting a graph:

Time /min	Vol triol /cm <sup>3</sup>			
	0	5	10	15
0	0	0	0	0
1	0.013	0.003	0.002	0.002
2	0.023	0.017	0.008	0.004
3	0.037	0.029	0.015	0.007
4	0.053	0.043	0.021	0.009
5	0.067	0.063	0.03	0.012
10	0.149	0.124	0.076	0.03
15	0.209	0.194	0.114	0.042
20	0.282	0.251	0.15	0.057
25	0.331	0.296	0.182	0.067
30	0.377	0.336	0.211	0.076



Calculating the molar composition, taking the density of propan-1.2.3-triol as 1.26 g cm<sup>-3</sup>

Volume propan-1.2.3-triol /cm <sup>3</sup>	Mass propan-1.2.3-triol /g	Amount propan-1.2.3-triol /mol	Volume water / cm <sup>3</sup>	Mass water /g	Amount water / mol	Mol % propan-1.2.3-triol	Rate / mg min <sup>-1</sup>
0.0	0.0	0.00	20.0	20.0	1.11	0.0	13.1
5.0	6.3	0.07	15.0	15.0	0.83	7.6	11.9
10.0	12.6	0.14	10.0	10.0	0.55	19.8	7.4
15.0	18.9	0.21	5.0	5.0	0.28	42.5	2.7



### (Sample) Conclusion & Evaluation

- The conclusions appear to confirm the hypothesis of a linear relationship between molar composition and rate. The precision seems to be reasonable for the task, though there is some scatter of data points around the line.
- The addition of propan-1,2,3-triol increases the viscosity of the solvent and hence decreases the rate at which the particles diffuse through the liquid. As the rate of diffusion decreases, the collision rate between the reactants will decrease and hence the reaction rate will decrease.
- The results overall were quite satisfactory. The major problem encountered was the lack of sufficient data points, especially to test the hypothesis at high concentrations of glycerol. Other minor problems are that the graphs indicate a slight curvature at long times because the decrease in the concentration of acid may have been significant at these times and also the water in the hydrochloric acid has been ignored in the calculations. There may have also been some loss of droplets of liquid from the beaker as a result of spray from the effervescence. The assumptions that there was no volume change on mixing and that the surface area was constant must also remain open to question. Finally there was no temperature control, so a temperature variation may have affected the results.
- The investigation should be repeated but with a greater range of compositions. Changing the volume of propan-1,2,3-triol by 2cm<sup>3</sup> each time in the liquid added to the acid and including a point for pure propan-1,2,3-triol would be a distinct improvement. In addition carrying out the reaction in a conical flask, perhaps with cotton wool in the neck, would eliminate any loss of mass from spray. The volume of the mixture of acid and solvent should be measured so that any volume changes in mixing can be seen and additional water:propan-1,2,3-triol mixture added to keep the total volume at 25 cm<sup>3</sup>. Finally carrying out the reactions in a thermostatically controlled water bath would eliminate any doubt surrounding the temperature of the system.

The results would be more reliable if only the early points, where the acid concentration can be assumed constant, were used to calculate the rate (though the uncertainty in mass loss would be greater) and also the water in the acid should be taken into account in calculating the solvent composition. Both of these could indeed be done with the current data.

## SYLLABUS RELEVANCE: TOPIC 7.1

The characteristics of chemical and physical systems in a state of equilibrium.

Physical and chemical systems should be covered.

## Apparatus required (per group)

- 100 cm<sup>3</sup> measuring cylinder
- 10 cm<sup>3</sup> measuring cylinder
- 4 × 100 cm<sup>3</sup> beaker

## Chemicals required

- 0.02 mol dm<sup>-3</sup> aqueous potassium thiocyanate (~100 cm<sup>3</sup> per group)
- 1.0 mol dm<sup>-3</sup> aqueous potassium thiocyanate (~2 cm<sup>3</sup> per group)
- 0.01 mol dm<sup>-3</sup> aqueous iron(III) nitrate (~20 cm<sup>3</sup> per group)
- ~1 mol dm<sup>-3</sup> aqueous sodium fluoride (~20 cm<sup>3</sup> in a shared bottle with a dropper)

## Notes

*Probable timing—30 minutes laboratory time*

Consider doing this as a demonstration by putting the four beakers on top of the overhead projector (if you can find one!), or putting the beakers on a white surface with a visualiser directly above, so that the colours are easy to compare. In that way you can promote some relevant discussion and ensure that the students fill in each section before going on to the next. Students usually think it is a normal reaction in which the iron(III) is the limiting reagent and become rather agitated when their prediction, that adding extra thiocyanate will have no effect, proves to be incorrect!

**A The reaction between iron(III) ions and thiocyanate ions**

When the very pale straw coloured solution was added to the colourless solution in the measuring cylinder, a clear, but intensely 'blood-red' coloured solution was formed.

**B Increasing the concentration of iron(III) ions**

- The colour of the solution became a much more intense blood-red colour.
- More of the coloured complex ion has been formed, implying that the iron(III) ions were the limiting reagent and that thiocyanate is in excess.
- If the iron(III) ions are the limiting reagent and the thiocyanate is in excess, then adding more thiocyanate should have no effect.

**C Increasing the concentration of thiocyanate ions**

- The colour of the solution again became more intense, but less so than in Part B.
- Adding the thiocyanate, like adding iron(III) ions, has increased the amount of the complex ion.
- The reaction cannot be one that goes to completion otherwise the amount of product would be controlled by the limiting reagent and so only one of the reactants could have affected the amount of complex ion formed.

**D Adding fluoride ions**

- The blood red colour of the solution dispersed as the mixture was swirled, leaving a straw coloured solution. The fluoride ions, once they had mixed, removed all traces of the complex ion.
- The concentration of the complex ion has been reduced to almost zero.
- The fact that fluoride ions, which react with the iron(III) ions, remove the complex ion indicates that the reaction by which it is formed must be reversible.

## SYLLABUS RELEVANCE; TOPIC 7.1

The characteristics of chemical and physical systems in a state of equilibrium.

Physical and chemical systems should be covered.

**Apparatus required (per group)**

- Data logger with pressure sensor linked to fit onto flasks
- 5 small Buchner flasks (or multi-neck Quickfit flasks)
- 1 large Buchner flask (or multi-neck Quickfit flask)
- $2 \times 5 \text{ cm}^3$  syringe with long tube attached
- Water bath at  $\sim 40^\circ\text{C}$

**Chemicals required**

- Propanone ( $\sim 10 \text{ cm}^3$  per group)
- Propan-2-ol ( $\sim 2 \text{ cm}^3$  per group)

**Notes**

*Probable timing—90 minutes laboratory time*

This introduces students to the concept of vapour pressure and some of the factors that do and, perhaps more importantly, do not affect it. It is quite a fine balance choosing the correct temperature so as to get a reasonable vapour pressure that builds up at a slow enough rate. It is useful to discuss both the rate at which the vapour pressure increases as well as the final saturated vapour pressure.

This Investigation can be easily extended to give students an opportunity to plan a more detailed quantitative exploration into how some variable affects vapour pressure – again excellent preparation for the Internal Assessment.

**Part A – Observing vapour pressure**

- Molecules of propanone in the liquid phase escape from the surface into the vapour phase, increasing the total pressure.
- Molecules of propanone in the vapour phase can also enter the surface and return to the liquid phase. At first this only occurs at a very slow rate, but this increases as the pressure of the vapour increases. Eventually the rate of return equals that at which molecules escape into the vapour phase and equilibrium is established.

**Part B – The effect of intermolecular forces**

- The pressure–time graph for propan-2-ol has a smaller gradient and reaches a lower final level than that for propanone.
- Molecules of propan-2-ol have hydrogen bonds between them, in addition to the dipole-dipole and dispersion forces also found in propanone. The intermolecular forces in propan-2-ol are therefore significantly greater than in propanone. The energy needed for a molecule to break free from the surface in propan-2-ol is therefore significantly greater and hence this occurs at a slower rate. As a result the gradient of the pressure–time is lower and the pressure required for the rate of escape to equal the rate of return (unaffected by the nature of the particles) is lower.



### Part C – The effect of the volume of liquid

- Doubling the volume of the liquid has no effect on the pressure–time graph.
- Vapour pressure is a surface phenomenon so, provided the surface area is not affected and there is sufficient liquid to saturate the vapour in the container, the volume of liquid will not affect the vapour pressure.

### Part D – The effect of temperature

- At a lower temperature, the gradient of the pressure–time graph is smaller and it reaches a lower final pressure.
- Molecules require a certain minimum energy to escape from the liquid surface into the vapour phase (similar to an activation energy, hence an exponential dependence). At lower temperatures a smaller proportion of the molecules have the required energy, hence the rate of escape is reduced. The dependence of the return rate on pressure ( $P.V = n.R.T$ , so concentration is proportional to absolute temperature) is much less affected by a reduction in temperature, hence a lower vapour pressure is required for the rate of return to equal the rate of escape.

### Part E – The effect of surface area

- With a reduced surface area the gradient of the pressure–time graph is smaller but it still reaches the same final value.
- Vapour pressure is a surface phenomenon (only molecules on the surface can escape) so a decrease in the surface area decreases the rate of escape, hence the gradient of the pressure–time graph is less. The molecules can only return to the liquid surface so a reduction in the surface area reduces the rate of return by the same factor, hence the pressure required for the two rates to be equal is unaffected.

### Part F – The effect of container volume

- With a larger container the gradient of the pressure–time graph is smaller but it still reaches the same final level.
- When molecules escape into the vapour phase they exert a pressure. This pressure will depend on the volume of the container ( $P.V = n.R.T$ ) so the larger the container the lower the pressure that a given number of molecules (the number that escape the surface in a given time) will exert. The rate of return (unaffected by the container volume) will not equal the rate of escape (also unaffected by the container volume) until the pressure is equal to the vapour pressure. As a result the equilibrium pressure is unaffected, but the greater volume means it takes longer to reach this pressure, because it requires more molecules in the vapour phase.

## SYLLABUS RELEVANCE; TOPIC 7.1

Le Châtelier's principle can be investigated qualitatively by looking at pressure, concentration and temperature changes on different equilibrium systems.

## Apparatus required (per group)

- Boiling tubes
- Test tubes

## Apparatus required (shared)

- Gas syringes (as below)

## Chemicals required

- 0.1 mol dm<sup>-3</sup> aqueous potassium dichromate(VI) (~10 cm<sup>3</sup> per group)
- 1 mol dm<sup>-3</sup> aqueous sodium hydroxide (~10 cm<sup>3</sup> per group)
- 1 mol dm<sup>-3</sup> sulfuric acid (~10 cm<sup>3</sup> per group)
- 0.1 mol dm<sup>-3</sup> aqueous cobalt(II) chloride (~10 cm<sup>3</sup> per group)
- Concentrated hydrochloric acid (~10 cm<sup>3</sup> per group)
- 1 mol dm<sup>-3</sup> aqueous magnesium sulfate (~10 cm<sup>3</sup> per group)
- 5 mol dm<sup>-3</sup> aqueous ammonia (~10 cm<sup>3</sup> per group)
- Solid ammonium chloride (~2 g per group)
- Fresh lime water (~10 cm<sup>3</sup> per group)
- Carbon dioxide cylinder or generator
- 2 gas syringes  $\frac{3}{4}$  filled with nitrogen dioxide gas and sealed

(Note – if students have problems differentiating between the initial colour change, caused by the change in concentration, and the second change, caused by the equilibrium shift, then storing the syringes in an iced water bath will slow the latter process.)

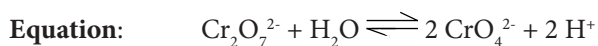
## Notes

*Probable timing–90 minutes laboratory time*

This investigation allows students to observe visible changes to systems in equilibrium and then analyse the changes they observe in terms of the underlying theory.

## Part A–The Effect of pH

- 1) The solution is an orange colour.
- 2) The solution turns to a yellow colour.
- 3) The orange colour is restored.

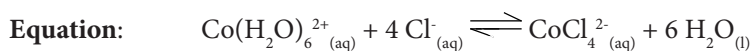


**Prediction from Le Châtelier's Principle:** Increasing the pH by adding sodium hydroxide, would decrease  $[\text{H}^+]$ , so the position of equilibrium would shift to the right to produce more  $\text{H}^+$ , so converting orange  $\text{Cr}_2\text{O}_7^{2-}$  to yellow  $\text{CrO}_4^{2-}$ . Decreasing the pH, by adding sulfuric acid, would increase  $[\text{H}^+]$ , so the equilibrium would try to decrease it again by shifting to the left.

**Reaction rate explanation:** Increasing the pH would reduce  $[\text{H}^+]$  and so reduce the rate of the reverse reaction, leaving the forward one unchanged. The position of equilibrium therefore shifts to the right until the increase in the  $[\text{H}^+]$  &  $[\text{CrO}_4^{2-}]$  and the decrease in  $[\text{Cr}_2\text{O}_7^{2-}]$  cause the rates of forward and reverse reactions to once again become equal. Similarly, if the  $[\text{H}^+]$  is increased again, the reverse reaction rate increases, shifting the equilibrium to the left until the changes in concentrations of the species cause the forward and reverse rates to once again become equal.

## Part B – The Effect of Temperature

- 1) The solution is a pink colour.
- 2) The solution turns through purple to a blue colour.
- 3) The pink colour is restored when water is added drop by drop, but when the solution is heated the colour becomes blue again.
- 4) The pink colour is gradually restored as the solution cools.



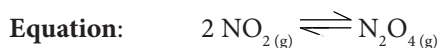
**Deduction from Le Châtelier's Principle:** As an increase in temperature drives the equilibrium to the right, the forward reaction must be endothermic.

**Reaction rate explanation:** The endothermic reaction will always have a greater activation energy than the exothermic reaction and hence it will be more affected by changes in temperature. When the temperature is increased the rate of both reactions will increase, but the rate of the forward reaction (endothermic) will increase by more than that of the reverse reaction (exothermic), hence the equilibrium shifts to the right until the increased concentration of  $[\text{CoCl}_4^{2-}]$  and decreased concentration of  $[\text{Co}(\text{H}_2\text{O})_6^{2+}]$  &  $[\text{Cl}^-]$  cause the rates to once again become equal. These changes reverse when the solution is cooled.

## Part C – The Effect of Pressure

- 1) The gas is a light brown colour.
- 2) The gas initially becomes a darker brown colour and then over a second or two the colour becomes slightly paler again.
- 3) The gas initially becomes a lighter brown colour and then over a second or two the colour becomes slightly darker again.

The initial change is caused by the change in volume and the resultant change in concentration of the gas. The slower change results from the change in the position of the equilibrium caused by the pressure change.

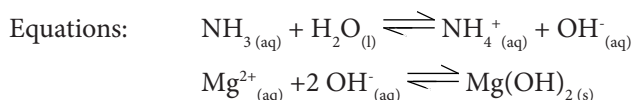


**Prediction from Le Châtelier's principle:** Increasing the pressure will shift the equilibrium to the side with the least number of moles of gas, hence the equilibrium will shift to the right. This turns brown nitrogen dioxide into colourless dinitrogen tetroxide, causing the colour to fade. Reducing the pressure causes the opposite shift.

**Reaction rate explanation:** Increasing the pressure will affect the rate of the forward reaction {proportional to  $p(\text{NO}_2)^2$ } more than the reverse reaction {proportional to  $p(\text{N}_2\text{O}_4)$ } so the equilibrium will shift to the right until the greater  $[\text{N}_2\text{O}_4]$  and lower  $[\text{NO}_2]$  cause the rates to once again become equal. Reducing the pressure has the opposite effect.

## Part D – The Common Ion Effect

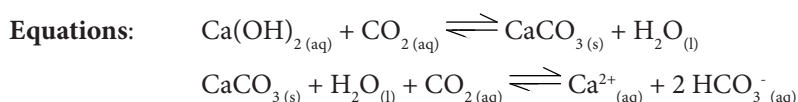
- 1) A white precipitate forms causing the solution to become cloudy.
- 2) The ammonium chloride dissolves to form a clear colourless solution and it remains clear and colourless when the aqueous ammonia is added; no white precipitate forms.



**Explanation:** When aqueous ammonia is added to aqueous  $\text{MgSO}_4$  the hydroxide ions, in equilibrium with the ammonia in the first equilibrium, displace the second equilibrium to the right and solid  $\text{Mg}(\text{OH})_2$  is precipitated. If  $\text{NH}_4\text{Cl}$  is dissolved in the solution however the  $\text{NH}_4^+$  ions cause the first equilibrium to shift to the left so that the concentration of hydroxide ions is no longer great enough to shift the second equilibrium far enough to cause  $\text{Mg}(\text{OH})_2$  to be precipitated.

## Part E – The Effect of Concentration

- 1) The clear solution becomes milky owing to the formation of a white precipitate.
- 2) As the white precipitate redissolves, the milky solution clears to leave a colourless solution.
- 3) As the solution is heated the white precipitate is gradually reformed.



**Explanation:** When carbon dioxide is initially passed through aqueous  $\text{Ca}(\text{OH})_2$  the first equilibrium is displaced to the right, causing a precipitate of  $\text{CaCO}_3$ . When excess carbon dioxide is passed the second equilibrium is displaced to the right, causing the precipitate to redissolve. When the solution is heated the solubility of  $\text{CO}_2$  decreases and its concentration falls so the position of the second equilibrium shifts to the left reforming solid  $\text{CaCO}_3$ . The concentration of  $\text{CO}_2$  however remains high enough for the position of the first equilibrium to remain to the right.

## SYLLABUS RELEVANCE; TOPIC 8.2

Candidates should have experience of acid-base titrations with different Indicators.

The evidence for these properties could be based on a student's experimental experiences.

## Apparatus required

### Per group

- 250 cm<sup>3</sup> beaker
- 100 cm<sup>3</sup> conical flask
- Burette and burette funnel
- 20 cm<sup>3</sup> pipette and pipette fillers

## Chemicals required

- Ethanedioic acid dihydrate (~20 g per group)
- 1 mol dm<sup>-3</sup> aqueous sodium hydroxide (~200 cm<sup>3</sup> per group)
- Phenolphthalein indicator

### Apparatus required for student method

As with all student planned practicals, it is not possible to precisely predict the apparatus required, but the following are likely to be requested.

### Apparatus required

- Burette and burette funnel
- Pipettes of various sizes and pipette fillers
- Volumetric flasks of various sizes
- Weighing bottles
- Conical flasks
- Beakers
- Filter funnels and filter papers
- Top pan balance reading to 0.01 g

### Chemicals required

Ethanedioic acid dihydrate (~20 g per group)

Students are also likely to request solutions of aqueous calcium chloride and aqueous potassium manganate(VII). As the concentrations requested may vary, it will most likely be simplest to have quite concentrated solutions available that students can then dilute as required.

## Notes

*Probable timing – 40 minutes laboratory time for given method and 60 minutes laboratory time for second method*

This is a fairly straightforward revision exercise in carrying out titrations (it may have been some time ago when they did the Stoichiometric Relationships section) and also allows them to plan a method of their own, which is excellent preparation for their IA investigation. Either part may be carried out on its own.



## Data Collection

Titration No.	1	2	3	4
Final reading (cm <sup>3</sup> )	28.20	44.30	30.50	45.70
Initial reading (cm <sup>3</sup> )	0.00	14.30	0.70	15.60
Titre (cm <sup>3</sup> )	28.20	30.00	29.80	30.10

Precision of burette readings =  $\pm 0.05 \text{ cm}^3$

Volume of acid solution taken =  $20.00 \pm 0.06 \text{ cm}^3$

### Relevant qualitative observations

When the white crystalline acid was initially added to the water the amount present noticeably diminished as it dissolved to form a colourless solution. As time passed the rate at which the solid dissolved decreased and it became quite difficult to tell when no further solid was dissolving. There was no noticeable change in temperature of the solution when it dissolved. In the titration the indicator in the colourless solution gave pink “flashes” as the alkali was added that disappeared on swirling, but eventually the addition of one drop led to a permanent pink colouration, but as this was quite faint it was sometimes difficult to observe.

## Data Analysis

a) Mean titre =  $\frac{1}{3} (30.00 + 29.80 + 30.10) = 29.97 \text{ cm}^3$

Amount of alkali consumed =  $c \cdot V = 1.00 \times 0.02997 = 0.02997 \text{ mol}$

Amount of acid this reacts with =  $\frac{1}{2} \times 0.02997 = 0.01498 \text{ mol}$  (as acid dibasic)

Concentration of solution =  $\frac{n}{v} = \frac{0.01498}{0.0200} = 0.749 \text{ mol dm}^{-3}$

Uncertainty in average titre =  $\pm 0.29\% \left( \text{Using } \Delta X = \pm \frac{X_{\max} - X_{\min}}{2\sqrt{N}} = \pm 0.087 \text{ cm}^3 \right)$

So uncertainty in amount of alkali =  $\pm 0.29\%$  (ignoring uncertainty in concentration)

Uncertainty in volume of acid =  $\pm 0.30\%$

Uncertainty in concentration of acid =  $\pm 0.59\% = \pm 0.004$

Concentration of acid =  $0.749 \pm 0.004 \text{ mol dm}^{-3}$

b) Molar mass =  $126.08 \text{ g mol}^{-1}$  (as the acid is a dihydrate,  $\text{C}_2\text{O}_4\text{H}_2 \cdot 2 \text{H}_2\text{O}$ )

In  $100 \text{ cm}^3$  there will be  $0.0749 \text{ mol} = 0.0749 \times 126.4 = 9.44 \text{ g}$

### Alternative method

1. Measure out  $100 \text{ cm}^3$  of water using a  $100 \text{ cm}^3$  measuring cylinder and add it to a  $250 \text{ cm}^3$  beaker.
2. Weigh out accurately about  $20 \text{ g}$  of solid ethanedioic acid and record the mass.
3. Add the solid acid to the water and stir until no more solid will dissolve.
4. Weigh a filter paper and, after folding, use it to filter off the excess solid.
5. When all the solution has drained through, leave the filter paper and residue to dry overnight at room temperature.
6. Weigh the filter paper and residue.

## Data Collection

Initial mass of solid	= 20.06 ± 0.005 g
Mass of filter paper	= 1.06 ± 0.005 g
Mass of filter paper and residue	= 11.73 ± 0.005 g
Volume of water used	= 100 ± 1 cm <sup>3</sup>

## Relevant qualitative observations

When the white crystalline acid was initially added to the water the amount present noticeably diminished as it dissolved to form a colourless solution. As time passed the rate at which the solid dissolved decreased and it became quite difficult to tell when no further solid was dissolving. There was no noticeable change in temperature of the solution when it dissolved. On filtration the crystals appeared to retain a considerable volume of water and the filter paper, after drying, was quite stiff owing to the solid that crystallised from the solution it had absorbed.

## Data Analysis

Mass of solid remaining in filter paper = 11.73 – 1.06 = 10.67 ± 0.01 g

Mass of solid dissolved in 100 cm<sup>3</sup> solution = 20.06 – 10.67 = 9.39 ± 0.015 g

Concentration of saturated solution =  $10 \times \frac{9.39}{126.08} = 0.745 \pm 0.001 \text{ mol dm}^{-3}$

## Conclusion & Evaluation

- a) The two values obtained for the solubility  $0.749 \pm 0.004 \text{ mol dm}^{-3}$  and  $0.743 \pm 0.001 \text{ mol dm}^{-3}$ , or 9.47 and 9.39 g/100 cm<sup>3</sup>, are in surprisingly good agreement. The solubility of ethanedioic acid dihydrate seems to increase quite a lot with temperature. The literature values found were 13.8 g/100 cm<sup>3</sup> at 20°C, and 14.3 g/100 cm<sup>3</sup> at 25°C, both are considerably higher than the solubility determined in this experiment.. It is not surprising that both methods give values that are less than the literature value because the solution does not have time to become fully saturated.

There is no temperature control in the given experiment and student methods probably share this deficiency. Titration methods can give high values if students are careless and pipette up some solid. Methods that involve filtering off undissolved solid frequently lead to low values for solubility as the dissolved solid in the solution trapped in the filter paper will increase the apparent mass of undissolved solid.

Methods that involve evaporating a saturated solution have problems because the temperature of drying can affect whether the hydrate or the anhydrous acid is produced. Also, as with any organic solid, prolonged heating at high temperatures can lead to loss of solid through evaporation, even if charring does not take place.

If any students try the calcium oxalate method the precipitate is very fine and often passes through the filter paper, giving a low value, though often failure to wash the precipitate and/or thoroughly dry the filter paper can compensate!

- b) As mentioned above all methods will probably suffer from lack of time to ensure saturation and lack of temperature control.

Gravimetric methods generally appear to have smaller uncertainties than volumetric methods (balances are often very precise), but various potential systematic errors may more than compensate for this if the method is not well designed and applied

- c) Leaving the solution for longer to allow it to become saturated is one obvious improvement. Even better would be to carry out the determination twice, one day after making the solution and two days after mixing the solid and water. Obtaining the same value on both days would indicate it was saturated (if not then it could be repeated daily until successive values were equal).

All of the methods really need proper temperature control for producing the solutions – the ideal would be to have the mixtures of the solid acid and water immersed in a thermostatically controlled water bath.

## SYLLABUS RELEVANCE; TOPIC 8.2

Candidates should have experience of acid-base titrations with different Indicators.

The evidence for these properties could be based on a student's experimental experiences.

**Apparatus required (per group)**

- Burette
- Burette funnel
- 25 cm<sup>3</sup> pipette
- 10 cm<sup>3</sup> pipette
- Pipette filler
- Weighing bottle
- 250 cm<sup>3</sup> conical flask
- 100 cm<sup>3</sup> conical flask
- Wash bottle of distilled water

**Also generally available**

- Top pan balance reading to at least 0.01 g

**Chemicals required**

- Standardised 1 mol dm<sup>-3</sup> hydrochloric acid (~300 cm<sup>3</sup> per group, give concentration and uncertainty on the container)
- *Approximately* 2 mol dm<sup>-3</sup> aqueous sodium hydroxide (~200 cm<sup>3</sup> per group)
- Solid ammonium sulfate, labelled "Fertiliser" (~10 g per group)
- Bromothymol blue indicator (2-3 cm<sup>3</sup> per group)
- Red litmus paper (~10 pieces per group)

**Notes**

*Probable timing—120 minutes laboratory time*

This Investigation introduces the technique of back titration. Being a rather more complicated procedure it leaves rather more scope for student error, hence it is excellent for assessing their technique, considering both their final result and the variation between different determinations. The better students will have the sense to save time by doing the standardisation titrations whilst waiting for the ammonia to boil off.

## Sample Data

### Back titration

Sample	A	B	C
Mass of weighing bottle & fertiliser (g)	3.242	3.125	3.199
Mass of weighing bottle after emptying (g)	1.182	1.180	1.181
Mass of fertiliser (g)	2.060	1.945	2.018
Final reading (cm <sup>3</sup> )	22.0	41.4	45.3
Initial reading (cm <sup>3</sup> )	4.5	22.0	27.5
Titre (cm <sup>3</sup> )	17.5	19.4	17.8

Precision of balance =  $\pm 0.0005$  g

Volume of aqueous sodium hydroxide taken =  $25 \pm 0.06$  cm<sup>3</sup>

Precision of burette =  $\pm 0.05$  cm<sup>3</sup>

### Relevant qualitative observations

The solid sample dissolved readily in the aqueous alkali to give a colourless solution. The solution has a sharp smell of ammonia and as it is heated the intensity of the smell initially increases and then decreases again. The liquid in the flask required occasional topping up with distilled water to prevent it boiling dry. When initially the steam was tested with moist red litmus paper it rapidly turned blue but eventually the paper was unaffected. During the titration the indicator gave a clear blue to yellow change at the end point.

### Standardisation

Titration No.	1	2	3	4
Final reading (cm <sup>3</sup> )	43.7	25.5	45.1	23.4
Initial reading (cm <sup>3</sup> )	22.9	5.8	25.5	3.7
Titre of HCl (cm <sup>3</sup> )	20.8	19.7	19.6	19.7

Concentration of hydrochloric acid =  $1.00 \pm 0.005$  mol dm<sup>-3</sup>

Volume of aqueous sodium hydroxide taken =  $10.00 \pm 0.04$  cm<sup>3</sup>

Precision of burette =  $\pm 0.05$  cm<sup>3</sup>

### Relevant qualitative observations

The indicator was initially a blue colour. As the acid was added yellow flashes appeared in the solution, but these disappeared on swirling. Eventually the addition of one drop of acid caused a permanent change to yellow.

## Data Analysis

- a) Mean titre:
- $19.67 \text{ cm}^3$
- (Rough titre omitted)

As it is a 1:1 reaction:  $c_1 \cdot V_1 = c_2 \cdot V_2$ Substituting:  $1.00 \times 19.67 = c_2 \times 10.0$ 

$$c_2 = 1.967 \text{ mol dm}^{-3}$$

Uncertainty of concentration of HCl =  $\pm 0.5\%$ 

Uncertainty of titre =  $\pm \frac{\text{Range}}{2\sqrt{n}} = \pm \frac{0.1}{2\sqrt{3}} = \pm 0.03 \text{ cm}^3 = \pm 0.15\%$

Uncertainty of volume of NaOH =  $\pm 0.4\%$ 

Uncertainty of concentration of NaOH =  $0.5 + 0.15 + 0.4 = \pm 1.05\%$

- b) Amount of NaOH added =
- $1.967 \times 0.025 = 0.0492 \text{ mol}$

Uncertainty of volume of NaOH added =  $\pm 0.6\%$ 

Uncertainty of amount of NaOH added =  $1.05 + 0.6 = \pm 1.65\% = 0.00081$

- c) Amount of HCl added =
- $1.00 \times 0.0175 = 0.0175 \text{ mol}$

Amount of NaOH neutralised by fertiliser =  $0.0492 - 0.0175 = 0.0317 \text{ mol}$ Uncertainty of concentration of HCl =  $\pm 0.5\%$ Uncertainty of volume of HCl  $0.1 \text{ cm}^3 = \pm 0.571\%$ Uncertainty of amount of HCl =  $0.5 + 0.571 = \pm 1.07\% = 0.00019$ Uncertainty of amount of NaOH neutralised by fertiliser =  $0.00081 + 0.00019 = 0.001 = 3.15\%$ 

- d) Equation:
- $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$

Amount of N =  $0.0317 \text{ mol}$ Mass of N =  $14.01 \times 0.0317 = 0.444 \text{ g}$ 

Percentage of N =  $\frac{0.444}{2.060} \times 100 = 21.55\%$

Uncertainty of amount of NaOH neutralised by fertiliser =  $3.15\%$ 

Uncertainty of mass of fertiliser =  $\frac{0.001}{2.060} \times 100 = 0.05\%$

Uncertainty of percentage of N =  $3.15 + 0.05 = \pm 3.2\% = \pm 0.69$



**Sample B**

Amount of NaOH neutralised by fertiliser =  $0.0492 - 0.0194 = 0.0298$  mol

Mass of N =  $14.01 \times 0.0298 = 0.417$  g

Percentage of N =  $\frac{0.417}{1.945} \times 100 = 21.47\%$

**Sample C**

Amount of NaOH neutralised by fertiliser =  $0.0492 - 0.0178 = 0.0314$  mol

Mass of N =  $14.01 \times 0.0314 = 0.440$  g

Percentage of N =  $\frac{0.440}{2.018} \times 100 = 21.80\%$

Mean percentage of N =  $\frac{21.55 + 21.47 + 21.80}{3} = 21.61\%$

Uncertainty =  $\pm \frac{\text{Range}}{2\sqrt{n}} = \pm \frac{0.33}{2\sqrt{3}} = \pm 0.095$

Percentage of N =  $21.6 \pm 0.1$

**Conclusion & Evaluation**

- The result obtained of 21.6 is ~2% greater than the accepted value of 21.2. The discrepancy is greater than the uncertainty of  $\pm 0.1$  calculated from replicate determinations. It is however well within the instrumental uncertainty of each value  $\pm 0.7$ . The replicate values are in very good agreement and the fact that they are much closer than the instrumental uncertainty may be because the same apparatus was used so any errors in apparatus will be the same for all the replicates.
- The uncertainty of the standardised HCl (0.5%) is actually a significant source of uncertainty, of a similar order of magnitude to the uncertainties in the pipettes and burette. The good agreement between replicate values implies that the random errors were quite small, or constant between the replicates. It also appears that the most probable source of systematic error (not boiling for long enough to remove all the ammonia, which would have given a low value) was not significant.
- A more precise value for the concentration of the standardised HCl provided would most likely be the single greatest improvement. This could be done by accurate standardisation of the HCl against sodium carbonate. In addition, using A-grade rather than B-grade volumetric apparatus would have significantly improved the precision of this determination.

## SYLLABUS RELEVANCE; TOPIC 8.4

Students should be familiar with the use of a pH meter and universal indicator.

Students should have experimental experience of working qualitatively with both strong and weak acids and bases. Examples to include:  $\text{H}_2\text{SO}_4$  (aq),  $\text{HCl}$  (aq),  $\text{HNO}_3$  (aq),  $\text{NaOH}$  (aq),  $\text{NH}_3$  (aq).

**Apparatus (per group)**

- 6 × Test tubes
- 4 × Boiling tubes
- 10 cm<sup>3</sup> measuring cylinder
- 100 cm<sup>3</sup> conical flask
- Burette and funnel

**also generally available**

- Conductivity apparatus

**Chemicals required**

- 1 mol dm<sup>-3</sup> hydrochloric acid (~100 cm<sup>3</sup> per group)
- 1 mol dm<sup>-3</sup> sulfuric acid (~100 cm<sup>3</sup> per group)
- 1 mol dm<sup>-3</sup> nitric acid (~100 cm<sup>3</sup> per group)
- 1 mol dm<sup>-3</sup> ethanoic acid (~100 cm<sup>3</sup> per group)
- 0.1 mol dm<sup>-3</sup> hydrochloric acid (~100 cm<sup>3</sup> per group)
- 0.01 mol dm<sup>-3</sup> hydrochloric acid (~100 cm<sup>3</sup> per group)
- 1 mol dm<sup>-3</sup> aqueous sodium hydroxide (~100 cm<sup>3</sup> per group)
- 0.1 mol dm<sup>-3</sup> aqueous sodium hydroxide (~20 cm<sup>3</sup> per group)
- 0.01 mol dm<sup>-3</sup> aqueous sodium hydroxide (~20 cm<sup>3</sup> per group)
- 1 mol dm<sup>-3</sup> aqueous ammonia (~20 cm<sup>3</sup> per group)
- 1 mol dm<sup>-3</sup> aqueous ammonium chloride (~20 cm<sup>3</sup> per group)
- 1 mol dm<sup>-3</sup> aqueous potassium hydroxide (~2 cm<sup>3</sup> per group)
- Marble chips (~6 per group)
- Magnesium ribbon (~6 x 2 cm lengths per group)
- Copper(II) oxide (~2 g per group)
- Calcium hydroxide (~2 g per group)
- Magnesium hydroxide (~2 g per group)
- Narrow range pH paper (a selection to cover pH 0 to pH 14)
- Red litmus paper (~5 pieces per group)
- Phenolphthalein indicator

## Notes

*Probable timing–120 minutes laboratory time*

This is a rather lengthy practical as it combines an investigation of the properties that all acids have in common with the differences between strong and weak acids and bases. As conductivity equipment varies I have not included specific instructions, so you will probably have to demonstrate the use of the apparatus available to the students before they start. In parts 1 I specify the use of narrow range pH paper rather than a pH meter, because for the purpose required I find it just as accurate and simpler, not to mention the fact that glass electrodes may not perform accurately with concentrated alkali. A pH meter could however be used, if you prefer it.

## Sample results

1) & 2)

Solution	pH	Conductivity /Sm <sup>-1</sup>
Distilled water	6.5	0.05
0.01 mol dm <sup>-3</sup> hydrochloric acid	2.0	0.49
0.1 mol dm <sup>-3</sup> hydrochloric acid	1.0	4.0
1 mol dm <sup>-3</sup> hydrochloric acid	0.5	36
1 mol dm <sup>-3</sup> ethanoic acid	2.5	0.89
0.01 mol dm <sup>-3</sup> aqueous sodium hydroxide	12.0	0.22
0.1 mol dm <sup>-3</sup> aqueous sodium hydroxide	13.0	2.0
1 mol dm <sup>-3</sup> aqueous sodium hydroxide	13.5	20
1 mol dm <sup>-3</sup> aqueous ammonia	12.0	0.10

- The pH increased with decreasing concentration as it is a measure of the concentration of H<sup>+</sup> ions and this decreases as the acid is diluted. In theory the increase should be 1 pH unit for each dilution by a factor of 10 as the pH is dependent on the logarithm of [H<sup>+</sup>]. This is reflected between 0.1 and 0.01 mol dm<sup>-3</sup> HCl, but the value for the 1 mol dm<sup>-3</sup> solution is higher than expected.
- The pH of CH<sub>3</sub>COOH is the highest of all the acids, indicating the lowest concentration of hydrogen ions. It is 2 units greater than HCl of the same concentration because the acid is only partially dissociated. It is slightly greater than the pH of 0.01 mol dm<sup>-3</sup> HCl so, if HCl is fully dissociated, less than 1% of the CH<sub>3</sub>COOH is dissociated.
- The conductivity of the acid depends on the movement of H<sup>+</sup> ions so the greater the concentration of these, the greater the conductivity. As the conductivity of pure water is negligible, the conductivity should be proportional to the concentration and even though the values do not reflect this precisely they are of the correct order of magnitude.
- The conductivity of CH<sub>3</sub>COOH is much less than HCl again showing that, because of its partial dissociation, the concentration of ions in the solution is much lower. Again it is of a similar order of magnitude to the 0.01 mol dm<sup>-3</sup> HCl indicating about 1% dissociation.
- NaOH is a strong base and hence fully dissociated into ions. The greater the concentration of OH<sup>-</sup> the greater the pH (increased [OH<sup>-</sup>] means decreased [H<sup>+</sup>]) and the greater the conductivity of the solution, but once again the pH of the 1 mol dm<sup>-3</sup> is slightly different to the expected value. Ammonia is a weak base and in aqueous solution it is only partially dissociated.

3)

Acid	Observations
1 mol dm <sup>-3</sup> hydrochloric acid	Rapid effervescence of a colourless gas. The size of the marble chip gradually decreases.
1 mol dm <sup>-3</sup> sulfuric acid	Initial rapid effervescence of a colourless gas, but quickly the reaction slows and almost totally ceases. The size of the marble chip does not noticeably decrease.
1 mol dm <sup>-3</sup> nitric acid	Rapid effervescence of a colourless gas. The size of the marble chip gradually decreases.
1 mol dm <sup>-3</sup> ethanoic acid	Slow effervescence of a colourless gas. The decrease in size of the marble chip is hardly perceptible.
0.1 mol dm <sup>-3</sup> hydrochloric acid	Steady effervescence of a colourless gas. The decrease in size of the marble chip is just visible.
0.01 mol dm <sup>-3</sup> hydrochloric acid	Very slow effervescence of a colourless gas. No noticeable decrease in size of the marble chip.

- f) Initially the rate of reaction for HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> are very similar, though the latter rapidly ceases to react. The rate of reaction of HCl decreases with concentration as less H<sup>+</sup> ions are present in the solution. The ethanoic acid reacts much more slowly than the other 1 mol dm<sup>-3</sup> acids showing that the concentration of hydrogen ions is much less.
- g)  $\text{CaCO}_3 + 2 \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2$
- h) The reaction quickly slowed and ceased. This is because the product, CaSO<sub>4</sub>, is only sparingly soluble in water hence it forms an insoluble layer on the surface of the marble chip, preventing further reaction.

4)

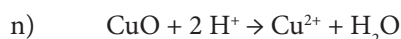
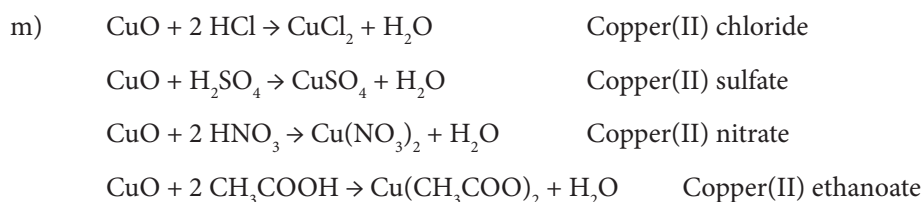
Acid	Observations
1 mol dm <sup>-3</sup> hydrochloric acid	Rapid effervescence of a colourless gas and the ribbon gradually dissolves to leave a colourless solution.
1 mol dm <sup>-3</sup> sulfuric acid	Rapid effervescence of a colourless gas and the ribbon gradually dissolves to leave a colourless solution.
1 mol dm <sup>-3</sup> nitric acid	Rapid effervescence of a colourless gas and the ribbon gradually dissolves to leave a colourless solution.
1 mol dm <sup>-3</sup> ethanoic acid	Slow effervescence of a colourless gas forming a colourless solution. The size of the ribbon only slowly decreases.

- i) Yes, except for the fact that the sulfuric acid reacted in an identical manner to the other strong acids.
- j)  $\text{Mg} + 2 \text{H}^+ \rightarrow \text{Mg}^{2+} + \text{H}_2$
- k) The CH<sub>3</sub>COOH reacted much more slowly than the other acids because it is only partially dissociated and hence the [H<sup>+</sup>] is much less than in the strong acids.

5)

Acid	Observations
1 mol dm <sup>-3</sup> hydrochloric acid	The black powder slowly dissolves to give a clear blue-green solution. No gas is evolved.
1 mol dm <sup>-3</sup> sulfuric acid	The black powder slowly dissolves to give a clear blue solution. No gas is evolved.
1 mol dm <sup>-3</sup> nitric acid	The black powder slowly dissolves to give a clear blue solution. No gas is evolved.
1 mol dm <sup>-3</sup> ethanoic acid	The solution slowly turns from colourless to a pale blue-green colour, but little change is noticed in the black powder. No gas is evolved.

l) The reactions all resulted in the solution turning a blue or blue-green colour and the black powder dissolving, but this was very slow in the case of CH<sub>3</sub>COOH.



6)

Base	Observations
Sodium hydroxide	A pungent smelling gas, which turns red litmus paper blue, is evolved.
Potassium hydroxide	A pungent smelling gas, which turns red litmus paper blue, is evolved.
Calcium hydroxide	The white solid dissolves slightly and a pungent smelling gas, which turns red litmus paper blue, is evolved.
Magnesium hydroxide	A pungent smelling gas, which turns red litmus paper blue, can just be detected. The white solid does not dissolve.

o) Ammonia.



q) Any ammonium salt would give the same result as it is a reaction of the ammonium ion and is independent of the anion present with it.



7)

Acid	Initial burette reading /cm <sup>3</sup>	Final burette reading /cm <sup>3</sup>	Volume of acid added /cm <sup>3</sup>
1 mol dm <sup>-3</sup> hydrochloric acid	0.0	10.8	10.8
1 mol dm <sup>-3</sup> sulfuric acid	11.0	31.4	20.4
1 mol dm <sup>-3</sup> nitric acid	31.5	42.9	11.4
1 mol dm <sup>-3</sup> ethanoic acid	20.0	29.8	9.8
0.1 mol dm <sup>-3</sup> hydrochloric acid	30.0	31.2	1.2
0.01 mol dm <sup>-3</sup> hydrochloric acid	32.0	32.1	0.1

- r) Hydrochloric, nitric and ethanoic acid all require about 10 cm<sup>3</sup> of alkali.
- s) Each sulfuric acid has two hydrogens that can react with the hydroxide ions, hence the titre would be expected to be double, which it approximately is.
- t) The volume of alkali depends on the amount of hydrogen ions present and hence the more dilute solutions need much less. The volumes are approximately the  $\frac{1}{10}$  and  $\frac{1}{100}$  values that would be predicted.
- u) As it depends only on the amount of H<sup>+</sup> that can be produced, there is no difference between CH<sub>3</sub>COOH and the other 1 mol dm<sup>-3</sup> acids. The reaction of the OH<sup>-</sup> with the H<sup>+</sup> causes the equilibrium in aqueous CH<sub>3</sub>COOH to be displaced to the right and this continues until all the CH<sub>3</sub>COOH has been converted to H<sup>+</sup> and CH<sub>3</sub>COO<sup>-</sup>.
- v)  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$

## Conclusions And Evaluation

- a) The reactions that are common to all acids are those with reactive metals, metal oxides and hydroxides, and metal carbonates and hydrogencarbonates. They have these reaction because they are reactions of the hydrogen ion and all acids form hydrogen ions in aqueous solution.
- b) A weak acid is one that is only partially dissociated into its ions, for example in aqueous ethanoic acid the equilibrium below lies well to the left:  $\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+$
- The lower [H<sup>+</sup>] affects the pH and conductivity of the solution (Parts 1 & 2) as well as the rate of chemical reaction (Parts 3, 4 & 5).
- c) Basicity refers to the number of hydrogen ions that each acid molecule can produce or, in the case of a base, the number of hydrogen ions that it can react with. This is most readily observed for properties that rely on the number of hydrogen ions, rather than their concentration, such as the titrations in Part 7.
- d) A base is a substance that can react with a hydrogen ion. In the reactions above; CO<sub>3</sub><sup>2-</sup>, the O<sup>2-</sup> in CuO and OH<sup>-</sup> accept hydrogen ions from the various acids and act as bases.
- e) The magnesium did not act as a base because there was no product formed in which a hydrogen from the acid is joined to the magnesium. The reaction is in fact a redox reaction in which the magnesium reduces hydrogen ions to hydrogen gas and is itself oxidised to the Mg<sup>2+</sup> ion

## SYLLABUS RELEVANCE; TOPIC 9.1

Experiments could include demonstrating the activity series, redox titrations and using the Winkler Method to measure BOD.

## Apparatus (per group)

- 6 × Test tubes
- 2 × Boiling tubes
- 2 × wooden splints

## Chemicals required

About 10 cm<sup>3</sup> of each of the following aqueous solutions per group:

- Aqueous iron(II) sulfate (Fresh solution)
- Aqueous copper(II) sulfate
- Aqueous sodium hydroxide
- Aqueous potassium iodide
- Aqueous iodine in potassium iodide
- Aqueous sodium thiosulfate
- Aqueous potassium dichromate(VI)
- Aqueous potassium manganate(VII)
- Aqueous ethanedioic (oxalic) acid
- Dilute hydrochloric acid
- Dilute sulfuric acid
- Hydrogen peroxide
- Aqueous chlorine
- Aqueous sulfur dioxide
- Limewater

(Concentrations are not too critical)

- Granulated zinc
- Magnesium ribbon
- Calcium metal

## Notes

*Probable timing—90 minutes laboratory time*

This is a simple series of reactions designed to familiarise students with a variety of oxidising and reducing agents. In the space for the equations I have left three lines so that the students can write the relevant half equations before combining them, though of course they could produce the balanced equation by other methods if you prefer.

If you like demonstrations, there are a number of fairly spectacular redox demonstrations such as the “Thermit” reaction (powdered Al & Fe<sub>2</sub>O<sub>3</sub>, ignited by a fuse of Mg ribbon), or the formation of aluminium iodide (powdered Al & I<sub>2</sub>, activated by a few drops of water)—both can be a bit hazardous so check out details in a book of demonstration reactions.

My favourite however, because of its simplicity is just to make a crater in a small mound of finely ground potassium manganate(VII) on a steel plate (porcelain or glassware may crack) and pour in a little propane-1,2,3-triol (glycerol). It takes a few seconds to start, but then there are lots of impressive lilac flames!

## Sample results

### 1) AQUEOUS IRON(II) IONS AND HYDROGEN PEROXIDE

#### Observations

During reaction the pale green colour of the iron(II) sulfate solution in the solution that has hydrogen peroxide added darkens to a yellow brown colour as the solution is warmed and some bubbles of gas are formed. When aqueous sodium hydroxide is added the untreated solution produces a murky green precipitate whereas the solution to which hydrogen peroxide was added forms a red-brown precipitate.

At the end of the session the murky green precipitate in the untreated test tube has darkened and brown patches have formed on its surface.

#### Analysis

The formation of a brown rather than a green precipitate when aqueous sodium hydroxide is added shows that reaction with the hydrogen peroxide has oxidised the iron(II) to iron(III). As the iron has been oxidised then the hydrogen peroxide must have been reduced presumably to water (the bubbles noted are probably oxygen from the thermal decomposition of the peroxide and unrelated to the reaction with iron ions).

Oxidised species – iron(II) ions    Reduced species – hydrogen peroxide

Oxidation half equation  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^{-}$

Reduction half equation  $\text{H}_2\text{O}_2 + 2 \text{H}^{+} + 2 \text{e}^{-} \rightarrow 2 \text{H}_2\text{O}$

Overall ionic equation  $2 \text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2 \text{H}^{+} \rightarrow 2 \text{Fe}^{3+} + 2 \text{H}_2\text{O}$

### 2) ZINC AND AQUEOUS COPPER(II) IONS

#### Observations

The surface of the zinc immediately darkens and then a loose red-brown solid forms gradually on its surface. The blue colour of the copper(II) sulfate gradually fades.

#### Analysis

The solid formed on the surface of the zinc looks like copper metal and this, coupled with the fading of the colour of the copper(II) ions implies that these are being reduced to the metal. The reaction occurring on the surface of the zinc metal seems to imply that this is the reducing agent, being converted to its ions.

Oxidised species–zinc    Reduced species – copper(II) ions

Oxidation half equation  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2 \text{e}^{-}$

Reduction half equation  $\text{Cu}^{2+} + 2 \text{e}^{-} \rightarrow \text{Cu}$

Overall ionic equation  $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$

### 3) AQUEOUS CHLORINE AND AQUEOUS IODIDE IONS

#### Observations

The colourless solution turns yellow and then brown. As an excess of chlorine is added then a black solid precipitates and eventually the solution loses its colour.

#### Analysis

The yellow-brown colour indicates that the iodide ions are being oxidised to iodine and this is confirmed by the eventual formation of the black precipitate (iodine is soluble in aqueous solutions containing iodide ions owing to the formation of the tri-iodide ion, but it is almost insoluble in water). Chlorine is a strong oxidising agent and is presumably reduced to the chloride ion.

Oxidised species – iodide ions    Reduced species–chlorine

Oxidation half equation  $2 \text{I}^{-} \rightarrow \text{I}_2 + 2 \text{e}^{-}$

Reduction half equation  $\text{Cl}_2 + 2 \text{e}^{-} \rightarrow 2 \text{Cl}^{-}$

Overall ionic equation  $2 \text{I}^{-} + \text{Cl}_2 \rightarrow \text{I}_2 + 2 \text{Cl}^{-}$

#### 4) IODINE AND AQUEOUS THIOSULFATE IONS

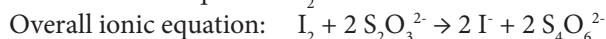
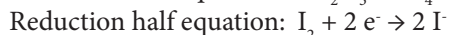
##### Observations

As the thiosulfate is added the brown colour of the iodine solution gradually fades to yellow and eventually it disappears completely to leave a colourless solution.

##### Analysis

The iodine is gradually reduced by the thiosulfate to the colourless iodide ion and the thiosulfate undergoes a reductive dimerization to form the tetrathionate ion.

Oxidised species – thiosulfate ion      Reduced species – iodine



#### 5) AQUEOUS THIOSULFATE IONS AND HYDROCHLORIC ACID

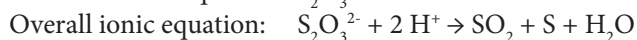
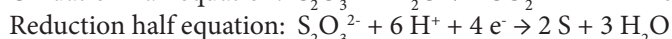
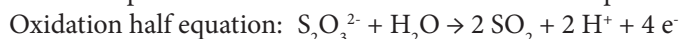
##### Observations

The mixture of thiosulfate and acid gradually becomes opaque and eventually a pale yellow precipitate forms. The odour of an acidic choking gas can be smelt and indeed tasted.

##### Analysis

The pale yellow precipitate is sulfur formed by the reduction of the thiosulfate ion. The acidic choking gas is sulfur dioxide, formed by the oxidation thiosulfate ion. Note that the thiosulfate ion is simultaneously oxidised and reduced; reactions of this type are known as disproportionation reactions.

Oxidised species – thiosulfate ion      Reduced species – thiosulfate ion



#### 6) AQUEOUS DICHROMATE(VI) IONS AND AQUEOUS SULFUR DIOXIDE

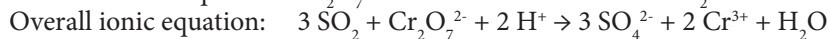
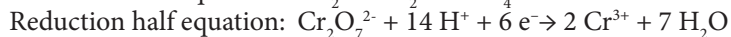
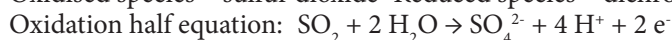
##### Observations

The orange solution gradually turns through blue-green to a dark green colour.

##### Analysis

The orange solution gradually turning green indicates that the dichromate(VI) ions are being reduced to chromium(III) ions. The sulfur dioxide must be acting as the reducing agent and is presumably being converted to the very stable sulfate ion.

Oxidised species – sulfur dioxide      Reduced species – dichromate(VI) ions



#### 7) MAGNESIUM AND HYDROCHLORIC ACID

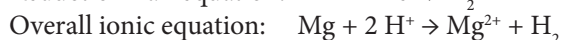
##### Observations

The ribbon reacts rapidly with the hydrochloric acid to produce bubbles of a colourless gas, which ignites with a squeaky pop when tested with a lighted splint. The magnesium ribbon gradually dissolves in the acid to leave a colourless solution.

##### Analysis

The gas is obviously hydrogen, presumably produced by reduction of the hydrogen ions in the acid. Magnesium is acting as the reducing agent, being oxidised to magnesium ions.

Oxidised species – magnesium      Reduced species – hydrogen ions



## 8) AQUEOUS MANGANATE(VII) IONS AND AQUEOUS ETHANEDIOIC ACID

**Observations**

As the solution is warmed, the purple colour of the manganate(VII) ion gradually fades to leave a colourless solution and a few bubbles of gas can be observed. The gas evolved turns the limewater slightly milky.

**Analysis**

The fading of the purple colour indicates the manganate(VII) ion is being reduced and as a colourless solution is formed the product is the manganese(II) ion rather than the manganate(VI) ion (green) or manganese(IV) oxide (brown-black solid). The formation of carbon dioxide would seem to indicate that this is the oxidation product of the ethanedioic acid.

Reduced species – manganate(VII) ion      Oxidised species – ethanedioic acid

Oxidation half equation:  $(\text{COOH})_2 \rightarrow 2 \text{CO}_2 + 2 \text{H}^+ + 2 \text{e}^-$

Reduction half equation:  $\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}$

Overall ionic equation:  $5 (\text{COOH})_2 + 2 \text{MnO}_4^- + 6 \text{H}^+ \rightarrow 10 \text{CO}_2 + 2 \text{Mn}^{2+} + 8 \text{H}_2\text{O}$

## 9) AQUEOUS MANGANATE(VII) IONS AND AQUEOUS HYDROGEN PEROXIDE

**Observations**

The purple colour of the manganate(VII) ion disappears to leave a colourless solution and bubbles of gas can be observed. The gas evolved caused the splint to glow more brightly.

**Analysis**

The fading of the purple colour to colourless indicates the manganate(VII) ion is being reduced to the manganese(II) ion. The gas, even though it did not relight the splint, would appear to be oxygen indicating that the hydrogen peroxide is being oxidised in this reaction, rather than reduced to water as it was in part 1.

Reduced species – manganate(VII) ion      Oxidised species – hydrogen peroxide

Oxidation half equation:  $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^-$

Reduction half equation:  $\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}$

Overall ionic equation:  $5 \text{H}_2\text{O}_2 + 2 \text{MnO}_4^- + 6 \text{H}^+ \rightarrow 5 \text{O}_2 + 2 \text{Mn}^{2+} + 8 \text{H}_2\text{O}$

## 10) CALCIUM AND WATER

**Observations**

The calcium reacts vigorously with the water and the mixture gets quite hot. The water turns to a white milky suspension and the reaction produces copious bubbles of a colourless gas, which ignites with a squeaky pop when tested with a lighted splint. The grey colour of the calcium metal gradually disappears.

**Analysis**

The gas is obviously hydrogen formed by the reduction of water. Calcium would appear to be acting as the reducing agent and the resulting calcium ions react with the hydroxide ions, produced by the reduction of water, to form calcium hydroxide.

Oxidised species – calcium      Reduced species – water

Oxidation half equation:  $\text{Ca} \rightarrow \text{Ca}^{2+} + 2 \text{e}^-$

Reduction half equation:  $2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-$

Overall ionic equation:  $\text{Ca} + 2 \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{H}_2$



## SYLLABUS RELEVANCE; TOPIC 9.1

Experiments could include demonstrating the activity series, redox titrations and using the Winkler Method to measure BOD.

## Apparatus (per group)

- Burette & funnel
- 3 × 1 cm<sup>3</sup> pipette
- 50 cm<sup>3</sup> pipette
- 10 cm<sup>3</sup> pipette
- Pipette filler
- 50 cm<sup>3</sup> measuring
- 100 cm<sup>3</sup> conical flask
- 250 cm<sup>3</sup> conical flask
- cylinder
- 2 × BOD bottle (~250 cm<sup>3</sup> with tight fitting ground glass stoppers)

## Chemicals required

- 0.0025 mol dm<sup>-3</sup> aqueous sodium thiosulfate (~250 cm<sup>3</sup> per group)
- 0.001 mol dm<sup>-3</sup> aqueous potassium manganate(VII) (permanganate, ~100 cm<sup>3</sup> per group)
- 1 mol dm<sup>-3</sup> sulfuric acid (~100 cm<sup>3</sup> per group)
- 2.5 mol dm<sup>-3</sup> aqueous manganese sulfate (~10 cm<sup>3</sup> per group)
- Alkaline iodide solution (50g NaOH & 13.5 g NaI in 100 cm<sup>3</sup>, ~10 cm<sup>3</sup> per group)
- Concentrated sulfuric acid (~10 cm<sup>3</sup> per group)
- Starch indicator
- Solid potassium iodide (~10g per group)

## NOTES

*Probable timing—~60 minutes laboratory time then a second session, 5 days later requiring ~40 minutes*

Rather than the more usual standardisation against potassium iodate, the thiosulfate is standardised against a potassium manganate(VII) solution. This is very irregular as potassium manganate(VII) solutions are too unstable to be used as a standard and it is only done to introduce manganate(VII) titrations. If you want accurate results it would be advisable to standardise the potassium manganate(VII) against ethanedioic acid and give the students the precise value. If you wanted to extend the investigation you could even include this standardisation as part of the student work.

Apart from this the practical is a fairly routine Winkler determination and the extension to determine the BOD can be omitted as it offers little in the way of new learning experiences.

## Sample results

### Standardisation

Titration No.	1	2	3
Final reading /cm <sup>3</sup>	18.60	37.10	41.60
Initial reading /cm <sup>3</sup>	0.00	18.60	23.20
Titre of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> /cm <sup>3</sup>	18.60	18.50	18.40

Mean titre = 18.50 cm<sup>3</sup>

Concentration of aqueous potassium manganate(VII) = 0.00100 ± 0.00001 mol dm<sup>-3</sup>

Volume of aqueous potassium manganate(VII) taken = 10.00 ± 0.06 cm<sup>3</sup>

Precision of burette = ± 0.05 cm<sup>3</sup>

### Relevant qualitative observations

The purple manganate(VII) solution turned yellow when the solid potassium iodide was added. The colour faded as it was titrated with the thiosulfate, but became blue when starch solution was added. The solution eventually became colourless at the end point but the endpoint lacked precision and the solution had a tendency to become pale blue again on standing after it had reached the end point.

### Oxygen concentration

Titration No.	1	2	3
Final reading /cm <sup>3</sup>	15.10	31.30	46.60
Initial reading /cm <sup>3</sup>	0.00	16.00	31.50
Titre of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> /cm <sup>3</sup>	15.10	15.30	15.30

Mean titre = 15.23 cm<sup>3</sup>

Volume of water sample taken = 50 ± 0.12 cm<sup>3</sup>

Precision of burette = ± 0.05 cm<sup>3</sup>

### Relevant qualitative observations

The water sample was slightly opaque with a few small particles of solid on the bottom. After adding the aqueous manganese(II) sulfate and alkaline iodide solution a pale brown precipitate formed, which gradually darkened. When the sulfuric acid was added this precipitate redissolved to form a pale yellow solution. The colour faded as it was titrated with the thiosulfate, but became blue when starch solution was added. The solution eventually became colourless at the end point but the endpoint lacked precision and the solution had a tendency to become pale blue again on standing after it had reached the end point.

## BOD determination

Titration No.	1	2	3
Final reading /cm <sup>3</sup>	10.80	21.50	32.20
Initial reading /cm <sup>3</sup>	0.00	10.80	21.50
Titre of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> /cm <sup>3</sup>	10.80	10.70	10.70

Mean titre = 10.73 cm<sup>3</sup>

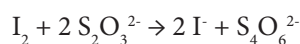
Volume of water sample taken = 50 ± 0.12 cm<sup>3</sup>

Precision of burette = ± 0.05 cm<sup>3</sup>

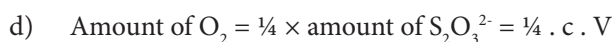
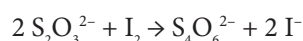
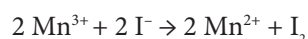
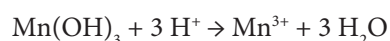
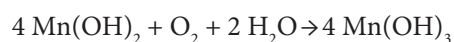
## Relevant qualitative observations

Again the sample had some solid particles on the bottom. Apart from that the changes observed it was almost identical to those recorded in the Winkler method above.

## Data Analysis



$$[\text{S}_2\text{O}_3^{2-}] = \frac{n}{V} = \frac{5 \times 10^{-5}}{0.0185} = 0.00270 \text{ mol dm}^{-3}$$



$$= \frac{1}{4} \times 0.0027 \times 0.01523 = 0.0000103 \text{ mol}$$

$$[\text{O}_2] = \frac{n}{V} = \frac{0.0000103}{0.050} = 0.000206 \text{ mol dm}^{-3}$$

$$\text{Mass of O}_2 = n \times M_r = 0.000206 \times 32.00 = 0.00658 \text{ g}$$

$$\text{Concentration in ppm} = \text{mg in } 1 \text{ dm}^3 = 6.58 \text{ ppm}$$

Just over 70% saturated taking saturated value as 9.1 ppm.

e) Amount of  $O_2 = \frac{1}{4} \times \text{amount of } S_2O_3^{2-} = \frac{1}{4} \cdot c \cdot V$

$$= \frac{1}{4} \times 0.0027 \times 0.01073 = 0.00000724 \text{ mol}$$

$$[O_2] = \frac{n}{V} = \frac{0.00000724}{0.050} = 0.000145 \text{ mol dm}^{-3}$$

$$\text{Mass of } O_2 = n \times M_r = 0.000145 \times 32.00 = 0.00464 \text{ g}$$

$$\text{Concentration in ppm} = \text{mg in } 1 \text{ dm}^3 = 4.64 \text{ ppm}$$

$$\text{BOD of sample} = 6.58 - 4.64 = 1.94 \text{ ppm}$$

As a BOD of >2 ppm is usually taken as moderately polluted, this value would indicate it is on the borderline between low and moderate pollution.

#### f) Standardisation

$$\text{Uncertainty in } [KMnO_4] = 1\%$$

$$\text{Uncertainty in volume of } KMnO_4 = 0.6\%$$

$$\text{Uncertainty in volume of } Na_2S_2O_3 = \frac{\text{Range}}{2\sqrt{N}} = \frac{0.2}{2\sqrt{3}} = \mathbf{0.0577} = 0.3\%$$

$$\text{Total uncertainty in } [Na_2S_2O_3] = 1 + 0.6 + 0.3 = 1.9\%$$

#### Initial dissolved oxygen determination

$$\text{Uncertainty in } [Na_2S_2O_3] = 1.9\%$$

$$\text{Uncertainty in volume of water} = 0.24\%$$

$$\text{Uncertainty in volume of } Na_2S_2O_3 = \frac{\text{Range}}{2\sqrt{N}} = \frac{0.2}{2\sqrt{3}} = \mathbf{0.0577} = 0.3\%$$

$$\text{Uncertainty in } [O_2] = 1.9 + 0.24 + 0.3 = 2.44\% = 0.161 \text{ ppm}$$

#### Final dissolved oxygen determination

$$\text{Uncertainty in } [Na_2S_2O_3] = 1.9\%$$

$$\text{Uncertainty in volume of water} = 0.24\%$$

$$\text{Uncertainty in volume of } Na_2S_2O_3 = \frac{\text{Range}}{2\sqrt{N}} = \frac{0.1}{2\sqrt{3}} = \mathbf{0.0289} = 0.3\%$$

$$\text{Uncertainty in } [O_2] = 1.9 + 0.24 + 0.3 = 2.44\% = 0.113 \text{ ppm}$$

#### BOD value

$$\text{Uncertainty in BOD} = 0.161 + 0.113 = 0.274 = 14.1\%$$

$$\text{Final BOD value} = 1.9 \pm 0.3 \text{ ppm}$$

## SYLLABUS RELEVANCE; TOPIC 9.2

Performance of laboratory experiments involving a typical voltaic cell using two metal/metal-ion half-cells.

**Apparatus (per group)**

- Petri dish
- Filter paper
- 3 × Test tubes
- 3 × 100 cm<sup>3</sup> beakers
- High resistance voltmeter
- Copper electrode
- Zinc electrode
- DC power supply
- 2 × graphite electrodes

**Chemicals required****Small pieces of:**

- Magnesium ribbon
- Iron sheet
- Lead sheet
- Silver foil

**About 10 cm<sup>3</sup> of each of the following ~0.1 mol dm<sup>-3</sup> aqueous solutions per group.**

- Aqueous iron(II) sulfate (Fresh solution)
- Aqueous magnesium sulfate
- Aqueous lead(II) nitrate
- Aqueous silver nitrate
- Saturated aqueous potassium nitrate

**About 100 cm<sup>3</sup> of each of the following ~0.1 mol dm<sup>-3</sup> aqueous solutions per group.**

- Aqueous copper(II) sulfate
- Aqueous zinc sulfate
- Aqueous copper(II) bromide

(Mix approximately equal volumes of sulfuric acid, sodium bromide and copper(II) sulfate – without the acid, copper hydroxide precipitates on the cathode)

**Notes**

*Probable timing–90 minutes laboratory time*

A chance for students to investigate some simple electrochemistry (both voltaic and electrolytic cells) and to link the concepts to redox and displacement reactions.



## Sample results

## 1) Metal Reactivity and Potential Difference

Metal pair	Potential difference /V	Positive metal
Iron-Lead	0.270	Lead
Iron-Silver	0.498	Silver
Iron-Magnesium	0.989	Iron
Lead - Silver	0.695	Silver
Lead-Magnesium	1.039	Lead
Silver-Magnesium	1.560	Silver

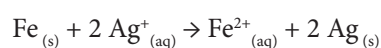
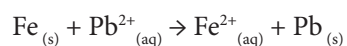
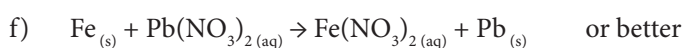
- a) The metal that forms the negative terminal loses its electrons to form its aqueous ions more easily than the metal that forms the positive terminal.
- b) The greater the difference in reactivity between the two metals, the greater the potential difference. (The values for silver-iron and silver-lead seem anomalous in this regard!)

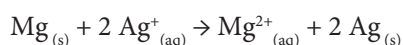
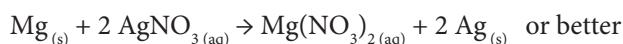
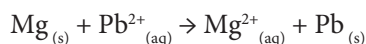
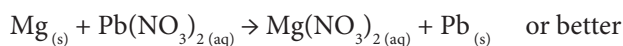
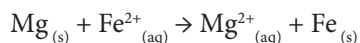
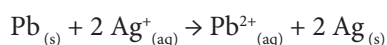
## 2) Displacement Reactions

- c) For any two metals are connected together the metal that is the negative terminal will displace the other metal from a solution of one of its salts, but the reverse reaction will not occur.
- d) See table below.

Aqueous salt	Iron(II) sulfate	Lead(II) nitrate	Magnesium sulfate	Silver nitrate
<b>Metal</b>				
Iron		✓ A dark coloured layer forms where the surface has been cleaned	X No change in metal or solution	✓ A dark coloured layer forms where the surface has been cleaned
Lead	X No change in metal or solution		X No change in metal or solution	✓ Loose silvery coloured coating forms on the surface
Magnesium	✓ Initial effervescence, but then a dark coloured layer forms on the surface	✓ Immediately forms a matt black layer on the surface		✓ Immediately forms a matt black layer on the surface
Silver	X No change in metal or solution	X No change in metal or solution	X No change in metal or solution	

- e) Experimental results matched the predictions, with more reactive metals displacing less reactive metals from solutions of their salts.





### 3) Voltaic Cells

Potential difference 1.008 V    Polarity copper is the positive electrode, zinc the negative

- g) The electrons flow from the zinc electrode to the copper electrode, that is from the more reactive metal to the less reactive.
- h) Half equation  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2 \text{e}^-$   
Oxidation/Reduction? Oxidation                      Anode/Cathode? Anode
- i) Half equation  $\text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}$   
Oxidation/Reduction? Reduction                      Anode/Cathode? Cathode
- j)  $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Zn}^{2+} + \text{Cu}$
- k) To allow the movement of ions between the two solutions, balancing out the flow of charge and completing the circuit.
- l) From the zinc electrode to the copper electrode as the reactions will result in too many cations in the zinc electrolyte and too few in the copper electrolyte.
- m) From the copper electrode to the zinc electrode as the reactions will result in too many anions in the copper electrolyte and too few in the zinc electrolyte.

### 4) Electrolytic Cells

**Positive electrode** –                      The solution near to the surface of the electrode turns a yellow-orange colour, especially the side facing the cathode. Eventually the yellow-orange colour diffuses into the solution.

**Negative electrode** –                      A red-brown solid is deposited on the surface of the graphite electrode, especially the side facing the anode.

**Solution** –                                      The colour of the solution slowly fades, plus it becomes more green as the yellow colour from the positive electrode diffuses into the bulk of the solution.

- n) Oxidation/Reduction? Oxidation    Anode/Cathode? Anode  
Half equation  $2 \text{Br}^- \rightarrow \text{Br}_2 + 2 \text{e}^-$
- o) Oxidation/Reduction? Reduction    Anode/Cathode? Cathode  
Half equation  $\text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}$

## SYLLABUS RELEVANCE; TOPIC 10.1

Construction of 3-D models (real or virtual) of organic molecules.

## Apparatus (per group)

A set of molecular models

## NOTES

*Probable timing--90 minutes, though a laboratory is not really necessary*

This is an exercise in some basic organic concepts that involves some use of molecular models. The use of these models can be replaced by 3-dimensional computer simulation programmes, especially those that allow rotation of the molecules. One of the simplest free resource is the "Molecular playground" developed by the University of Liverpool <<http://www.chemtube3d.com/playground/playground.html>> though there are many others available.

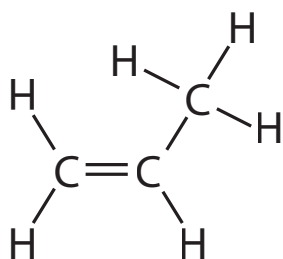
## Sample answers

## 1) 2- or 3-dimensions?

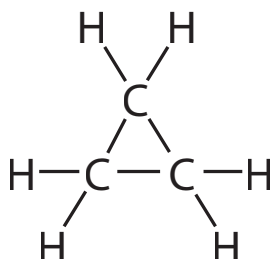
- a) When carbon has four single bonds these point to the corners of a tetrahedron and hence extend in three dimensions. This means that all of the positions are equivalent and hence structures that only differ in whether groups are at 90° or 180° to each other in a two-dimensional structure are in fact equivalent.

## 2) Hydrocarbons

- b) Two hydrogens can be eliminated from neighbouring carbon atoms and replaced by a double bond between these carbons (to give propene) or two hydrogens can be eliminated from the terminal carbon atoms and replaced by a single bond between these carbons (to give cyclopropane).

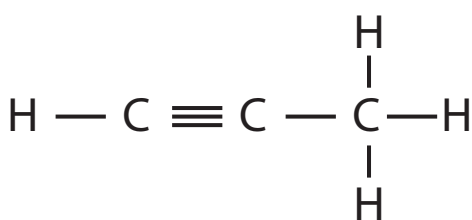


Propene

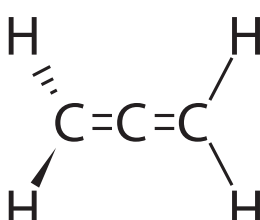


Cyclopropane

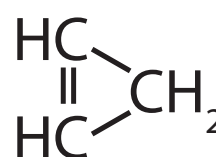
- c) There are three possibilities for losing two more hydrogens. Firstly the two carbons either side of the double bond in propene could lose hydrogens to form a triple bond (to give propyne), and secondly the two carbons either side of the single bond in propene could lose hydrogens to form a second double bond (to give propadiene), or thirdly two carbons in cyclopropane could lose hydrogens to form a double bond in the ring (to give cyclopropene).



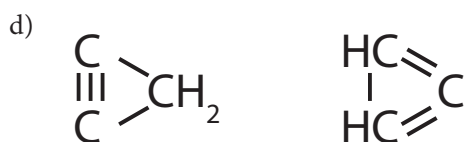
Propyne



Propadiene



Cyclopropene



Cyclopropyne

Cyclopropadiene

The only structure that has hydrogens on adjacent carbons is cyclopropene. This could produce either cyclopropyne or cyclopropadiene. Cyclopropane and cyclopropene suffer from severe repulsion between the bonding electron pairs and this would be even greater in the two possibilities given, hence the problems with their synthesis.

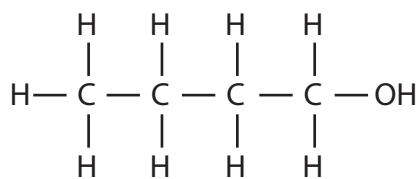
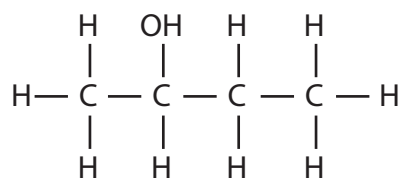
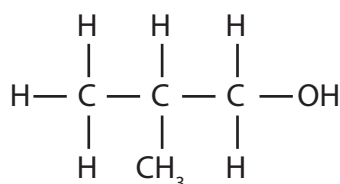
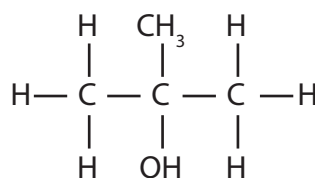
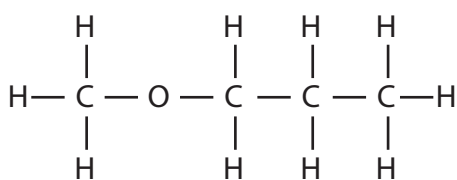
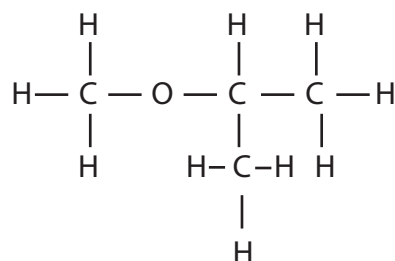
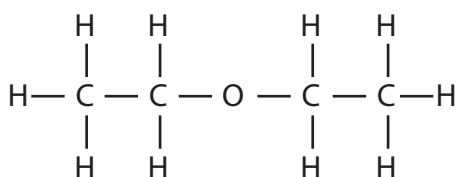
- e) Saturated means that the compound only contains single bonds so only propane and cyclopropane are saturated. Compounds that contain double or triple bonds are termed unsaturated so all the other compounds mentioned (propene, propyne, propadiene, cyclopropene, cyclopropyne and cyclopropadiene) are unsaturated.

### 3) Homologous series

- f) Molecular formula  $-C_2H_5OH$  Name *-ethanol*
- g) Molecular formula  $-C_3H_7OH$  Name *-propanol*
- h) Molecular formula  $-C_4H_9OH$  Name *-butanol*
- i) The boiling points would gradually increase as the number of carbon atoms increases. All of the alcohols contain an  $-OH$  group, so they will have similar ability to hydrogen bond, but as the number of C-atoms increases the strength of the dispersion forces will increase resulting in stronger intermolecular forces and hence a higher boiling point.
- j) i.)  $C_nH_{(2n+1)}OH$   
 ii.) Alcohols  
 iii.) Hydroxyl group  
 iv.) The names all end in *-anol*, following a prefix indicating the hydrocarbon chain length.
- k) The hydrocarbon part of a molecule is chemically rather inert, hence chemical reactivity is mainly a result of the functional groups present. In this case the molecules all have a primary hydroxyl group ( $-CH_2-OH$ ), hence they will have similar chemical reactions.

Class	Functional group	General formula
Halogenoalkanes	Halogen ( $-X$ ; $-F$ , $-Cl$ , $-Br$ , $-I$ )	$C_nH_{(2n+1)}-X$
Aldehydes	Carbonyl ( $-CO-$ ) / aldehyde ( $-CHO$ )	$C_nH_{(2n+1)}-CO-H$
Carboxylic acids	Carboxyl ( $-CO-OH$ )	$C_nH_{(2n+1)}-CO-OH$
Amines	Amine ( $-NH_2$ , for primary ones)	$C_nH_{(2n+1)}-NH_2$
Amides	Carboxamide ( $-CO-NH_2$ )	$C_nH_{(2n+1)}-CO-NH_2$

## 4) Structural isomers

*Butan-1-ol**Butan-2-ol (actually two enantiomers of this)**methylpropan-1-ol**methylpropan-2-ol**1-methoxypropane**2-methoxypropane**ethoxyethane*

Number of isomers = 7

The major difference is between the ethers (R-O-R) and the alcohols (R-O-H). The alcohols could also be divided into straight (butan-1-ol & butan-2-ol) or branched chain (methylpropan-1-ol & methylpropan-2-ol) skeletons. The ethers differ as to whether they are methoxy (CH<sub>3</sub>-O-) or ethoxy (C<sub>2</sub>H<sub>5</sub>-O-).

Class-Primary alcohol                      Name - butan-1-ol & methylpropane-1-ol

Class-Secondary alcohol                      Name - butan-2-ol

Class-Tertiary alcohol                      Name -methylpropane-2-ol

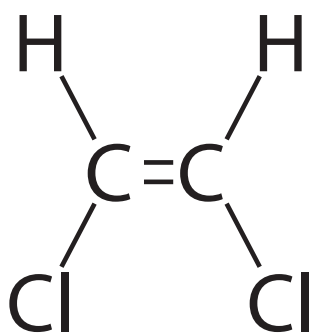
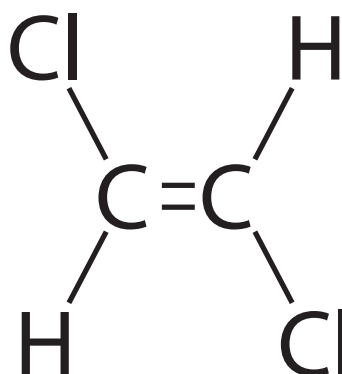


## HL Extension

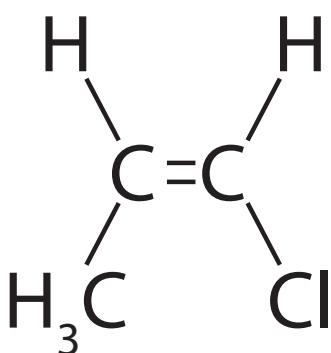
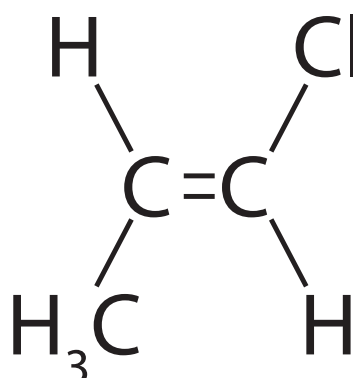
## 5) Cis/trans and E/Z isomers

- p) There are many possible configurations as the two ends of the molecule are free to rotate relative to each other around the carbon-carbon bond.
- q) In the case of 1,2-dichloroethene the molecule is not free to rotate around the carbon-carbon double bond as the second bond is a pi-bond and this involves two areas of interaction, above and below the sigma-bond. Rotation would involve breaking and then remaking the pi-bond interaction and hence would require a great deal of energy.

r)

*Cis-1,2-dichloroethene**Trans-1,2-dichloroethene*

s)

*Z-1-chloroprop-1-ene**E-1-chloroprop-1-ene*

The isomers in 1-chloroprop-1-ene are not cis/trans because they do not have identical substituents at either end of the double bond. In the E/Z system the atomic masses of the substituents are considered. If on the doubly bonded carbons the groups with the highest atomic masses are on the same side it is the Z- form (*Zusammen*), if on opposite sides the E-form (*Entgegen*).

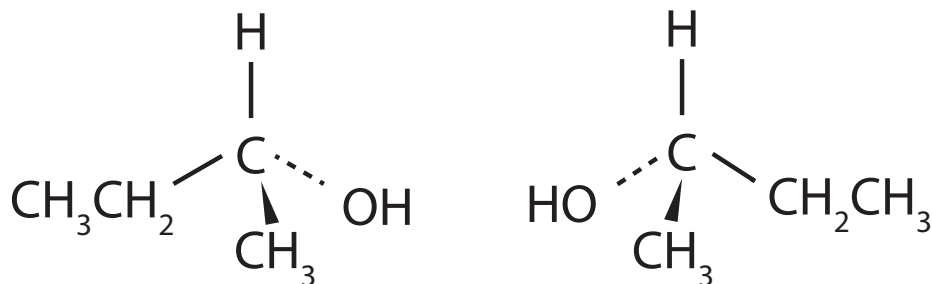
- t) There are eight possible geometric isomers of 1,2,3,4,5,6-hexachlorocyclohexane. Considering U to have the chlorine above the ring (considered planar, which it isn't, but the method is still valid!) and D below the ring, the following combinations are possible:

UUUUUU      DUUUUU      DDUUUU      DUDUUU

DUUDUU      DDDUUU      DDUDUU      DUDUDU

## 6) Optical isomers (Enantiomers)

u)



The two molecules are mirror images of each other.

- v) No longer would two distinct forms be possible. The requirement for different forms to exist is that there should be four different groups attached to a particular carbon atom.
- w) When plane-polarised light is shone through the two forms, one form will rotate the plane of polarisation in a clockwise direction and the other form will rotate it by an equal amount in an anticlockwise direction.
- x) i. Chiral carbon – means a carbon that has four different groups bonded to it, so that it is not identical to its mirror image.  
ii. Optically active – means that the substance will rotate the plane of polarisation of plane-polarised light.  
iii Racemic mixture – refers to a mixture that contains equal quantities of the two optical isomers so that their effects cancel out and it is not optically active.
- y) Substances produced synthetically are almost always racemic mixtures, whereas most naturally occurring products are a single pure enantiomer, because they are formed by enzyme catalysed reactions and enzymes are stereospecific, hence this can be used to tell the substances apart.

A polarimeter should be used and the synthetic product would not affect the plane of polarisation, but the natural product would rotate the plane of polarisation.

## SYLLABUS RELEVANCE; TOPIC 10.2

Experiments could include distinguishing between alkanes and alkenes.

**Apparatus (per group)**

- 6 × test tubes with corks/bungs
- watch glass or evaporating basin
- 2 × wooden splints

**Chemicals required (per group)**

- Hexane (~10 cm<sup>3</sup>)
- Cyclohexene (~10 cm<sup>3</sup>)
- Methylbenzene (toluene, ~10 cm<sup>3</sup> in total)
- Bromine water (Freshly prepared, ~5 cm<sup>3</sup>)
- Aqueous ammonia (~10 cm<sup>3</sup> in total)
- Aqueous acidified potassium manganate(VII) (~5 cm<sup>3</sup>) (dilute sulfuric acid with just enough manganate(VII) to make it purple).
- Unknown organic compounds, labelled with a letter—to be chosen by the teacher

*(suggestions would be gas from the cyclohexane, paraffin, hexene).*

**Note** – Hexane and cyclohexene have been chosen so that there is a significant difference in the names and students are less likely to get confused! It also helps a little bit with the C:H ratio in the combustion. Obviously the straight chain or cyclo version of either would work equally as well.

**Notes**

*Probable timing—40 minutes laboratory time*

A number of fairly simple reactions of hydrocarbons coupled with testing some unknowns for saturation. I include the reaction with manganate (VII) for two reasons—firstly because the colour remains in the aqueous layer as a contrast to bromine (revise intermolecular forces). Secondly it emphasises that both it and the bromine are reduced in the addition reactions and so the test for unsaturation would not be valid if other groups that act as reducing agents are present. There is actually quite limited chance of success with the testing for HBr as there is too much water around. You may wish to demonstrate it using pure bromine and hexane, or just scale up the student experiment, but separate out the non-aqueous layer (which will of course have extracted the bromine) before exposing the mixture to sunlight.

## Sample Data

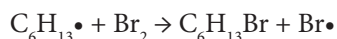
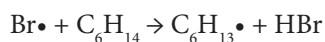
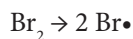
- 1) **Hexane** Ignites readily and burns with a blue flame tinged with yellow. Traces of soot are formed.  
**Cyclohexene** Ignites readily and burns with a blue flame tinged with rather more yellow than in the case of hexane. Traces of soot are formed.  
**Methylbenzene** Not easy to ignite and burns slowly with a yellow flame. Large quantities of soot are formed.
- 2) **Hexane** The hexane forms an immiscible upper layer and on shaking this becomes an orange-brown colour, leaving the aqueous layer a paler yellow-orange colour. On standing in the sunshine the orange colour of both layers slowly fades to leave two immiscible colourless layers, but no change observed with ammonia. The sample left in the dark does not undergo any change.  
**Cyclohexene** The cyclohexene reacts immediately with the bromine water, being decolourised from its initial orange-brown colour to leave two immiscible colourless layers. No further change is noted on further standing either in sunlight or in the dark. There is no reaction with ammonia solution.
- 3) **Hexane** The hexane forms an immiscible upper layer and on shaking this remains colourless above the purple aqueous.  
**Cyclohexene** The cyclohexene reacts immediately decolourising the manganate(VII) from its initial purple colour to leave two immiscible colourless layers.

## Data Analysis

- A) Hexane (C<sub>6</sub>H<sub>14</sub>) has a C:H ratio of 1:2.33  
 Cyclohexene (C<sub>6</sub>H<sub>10</sub>) has a C:H ratio of 1:1.67  
 Methylbenzene (C<sub>7</sub>H<sub>8</sub>) has a C:H ratio of 1:1.14 (The greater the proportion of hydrogen present the more flammable the liquid and the cleaner the flame.)
- b)  $C_6H_5-CH_3 + 9 O_2 \rightarrow 7 CO_2 + 4 H_2O$
- c) The combustion did not seem to be complete as the flame was yellow (an indicator of the presence of carbon particles) and quite large quantities of soot (carbon) were formed indicating incomplete combustion.
- d) Incomplete combustion results in the formation of carbon monoxide and carbon:  
 $C_6H_5-CH_3 + 6 O_2 \rightarrow 3 CO_2 + 2 CO + 2 C + 4 H_2O$
- e) The combustion products do have health implications; carbon monoxide is a toxic gas and soot can cause respiratory problems.
- f) More oxygen is required, so perhaps burning in pure oxygen rather than air would help, also vaporising the fuel, or atomising it into minute droplets would ensure more oxygen would be near to the fuel as it burns.
- g)  $C_6H_8 + Br_2 \rightarrow C_6H_8Br_2$  It is an addition reaction



- h) The bromine preferentially dissolves in the upper non-aqueous layer causing the colour of the aqueous layer to fade. This occurs because bromine does not have any appropriate groups (-OH or -NH) that could form H-bonds to water. As a result it is much more soluble in non-polar solvents, such as hexane, where the intermolecular forces are dispersion forces, similar to those in bromine.
- i) The reaction of bromine with alkanes occurs through the production of bromine atoms. Breaking the bromine-bromine bond requires a significant amount of energy and this is provided by UV radiation in the sunlight.



- j) Ammonia reacts with hydrogen bromide to form solid ammonium bromide, which may be detected as a white smoke.
- k)  $\text{C}_6\text{H}_{14} + \text{Br}_2 \rightarrow \text{C}_6\text{H}_{13}\text{Br} + \text{HBr}$       It is an substitution reaction
- l) Further substitution of hydrogen atoms in the product can occur, so that substances such as  $\text{C}_6\text{H}_{12}\text{Br}_2$  might be produced. With a large excess of bromine eventually all the hydrogen atoms could be substituted by bromine to give  $\text{C}_6\text{Br}_{14}$ . (though unlikely owing to stereochemical considerations!)
- m) Alkenes are far more reactive than alkanes, so that if one of these two compounds is to react it is far more likely to be the alkene; cyclohexene. The characteristic reactions of alkenes are addition reactions, so it is quite likely that the reaction with acidified manganate(VII) ions is an addition reaction.
- n) The purple colour in the aqueous manganate(VII) is due to the manganate(VII) ion ( $\text{MnO}_4^-$ ). Ions are much more soluble in polar liquids, such as water where the polar molecules can arrange themselves around the ion, producing strong attractive forces. Hexane is non-polar, hence it cannot solvate the ions and as a result the colour remains in the aqueous layer.

## SYLLABUS RELEVANCE: TOPIC 10.2

Experiments could include reflux and distillation.

## Apparatus (per group)

- 6 × Test tubes
- 2 × Boiling tubes
- Watch glass or evaporating basin
- Quickfit apparatus for reflux and distillation
- 2 x wooden splints

## Chemicals required

- Ethanol
- Methanol
- Propan-1-ol
- Propan-2-ol (isopropanol)
- Butan-1-ol
- Butan-2-ol (*sec.* butanol)
- 2-methylpropan-2-ol (*tert.* butanol)
- Aqueous potassium dichromate(VI)
- 'Concentrated acidified dichromate(VI)' (50 g  $K_2Cr_2O_7$  dissolved in 100cm<sup>3</sup> of dil  $H_2SO_4$ , then 20 cm<sup>3</sup> conc  $H_2SO_4$  carefully added)
- Ice
- Ethanoic acid (glacial)
- Concentrated sulfuric acid
- Solid sodium hydrogencarbonate
- 1-chlorobutane
- Aqueous silver nitrate
- Aqueous sodium chloride
- Aqueous sodium hydroxide
- Dilute nitric acid
- Blue litmus paper

## Notes

*Probable timing–90 minutes laboratory time*

A number of reactions that cover what students are expected to know about these two classes of organic compounds, with questions to see whether they understand the chemistry behind the observations.



## Sample results

### Alcohols

- 1) Ethanol ignites easily and burns with a blue flame, which is occasionally yellow at the tip. After the combustion dark smudges remain on the evaporating basin.
- 2) The orange colour of the dichromate(VI) darkens when the ethanol is added and as it is warmed the colour of the solution gradually changes to green and a faint smell of apples can be detected.
- 3)

Alcohol	Observation
Methanol	Methanol causes the orange dichromate to turn green
Propan-1-ol	Propan-1-ol causes the orange dichromate to turn green
Propan-2-ol	Propan-2-ol causes the orange dichromate to turn green
Butan-1-ol	Butan-1-ol causes the orange dichromate to turn green
Butan-2-ol	Butan-2-ol causes the orange dichromate to turn green
2-methylpropan-1-ol	2-methylpropan-1-ol causes the orange dichromate to turn green
2-methylpropan-2-ol	With 2-methylpropan-2-ol the dichromate remains orange

- 4) The orange colour of the dichromate(VI) darkens when the ethanol is added and when the mixture is refluxed a clear, colourless liquid can be seen condensing at the bottom of the condenser. Distillation produces a clear, colourless distillate which has a sharp odour with a tinge of fruitiness.
- 5) The mixture when heated remains clear and colourless with a sharp, but distinctly fruity odour. When it is poured into the beaker of water the fruity smell is more obvious. When the hydrogencarbonate is added there is a vigorous effervescence and the fruity smell is further enhanced.

### Halogenoalkanes

- 6) With sodium chloride a thick white precipitate is formed which rapidly darkens to purple. With 1-chlorobutane the halogenoalkane forms an immiscible layer, but there is no sign of reaction, even on standing.
- 7) When the 1-chlorobutane is added it forms an immiscible layer, but this disappears when the ethanol is added. After acidification and the addition of silver nitrate a white cloudiness is observed.

## Data Analysis

### Alcohols

- a)  $\text{C}_2\text{H}_5\text{OH} + 3 \text{O}_2 \rightarrow 2 \text{CO}_2 + 3 \text{H}_2\text{O}$
- b) The combustion appeared to be quite, but not totally, complete. The flame was blue, but some traces of yellow and deposits of carbon on the evaporating basin indicate that it was not totally complete.
- c) Ethanol would produce less heat than ethane as it has the same number of carbon atoms, but it is already partially oxidised.
- d) The colour change occurs because the orange dichromate(VI) ion, forming the green chromium(III) ion.
- e) The major organic product would be ethanal, hence the aroma of apples.

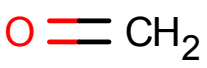
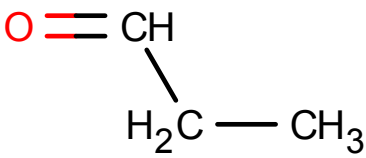
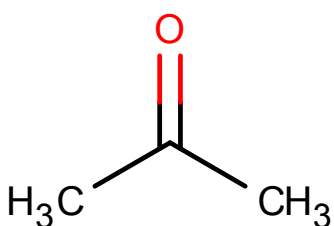
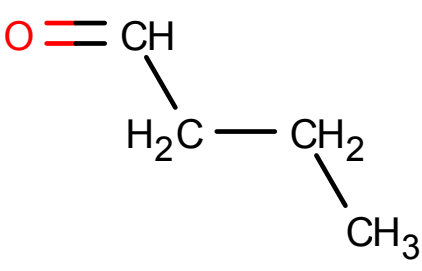
f) Reduction of the dichromate(VI) ion:  $\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$

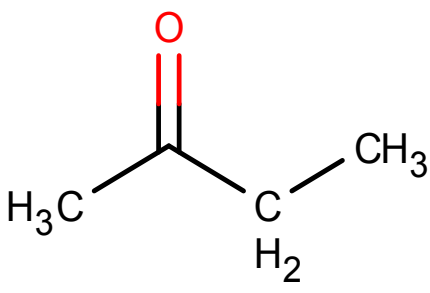
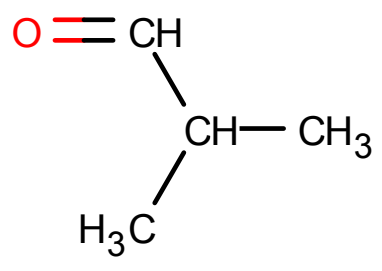
Oxidation of the ethanol:  $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{CHO} + 2 \text{H}^+ + 2 \text{e}^-$

Overall ionic equation:  $\text{Cr}_2\text{O}_7^{2-} + 8 \text{H}^+ + 3 \text{C}_2\text{H}_5\text{OH} \rightarrow 2 \text{Cr}^{3+} + 3 \text{CH}_3\text{CHO} + 7 \text{H}_2\text{O}$

g) 2-methylpropan-2-ol was the only alcohol that was not oxidised. This is because it is a tertiary alcohol and these are resistant to oxidation.

h)

Alcohol	Primary/ Secondary/ Tertiary	Structural formula of product
Methanol	Primary	
Propan-1-ol	Primary	
Propan-2-ol	Secondary	
Butan-1-ol	Primary	

Butan-2-ol	Secondary	
2-methylpropan-1-ol	Primary	
2-methylpropan-2-ol	Tertiary	Not easily oxidised

- i) Ethanoic acid was the major product but traces of ethyl ethanoate were present produced by the reaction of ethanol with the ethanoic acid.
- j)  $C_2H_5OH + 2 [O] \rightarrow CH_3COOH + H_2O$
- k) The other primary alcohols (methanol, propan-1-ol, butan-1-ol and 2m-methylpropan-1-ol) could all have been further oxidised to their corresponding carboxylic acids.
- l)  $C_2H_5OH + CH_3COOH \rightarrow CH_3COOC_2H_5 + H_2O$
- m) It is an addition-elimination reaction (also called a condensation reaction) and, as it produces an ester, it is an esterification reaction.
- n) The sulfuric acid acted as a catalyst in the reaction and it also reacted with the water produced driving the equilibrium to the right and increasing the yield of product.
- o) (i) *Why pour the mixture into water?* The ester is insoluble in water and so floats on the surface, separating it from the acid which dissolves in the water, and hence this enhances the fruity smell.  
(ii) *Why add sodium hydrogencarbonate?* This reacts with the acid, removing its smell entirely.

### Halogenoalkanes

- p)  $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$
- q) Because the chlorine is joined to the molecule by a covalent bond, so chloride ions are not present.
- r)  $\text{C}_4\text{H}_9\text{Cl} + \text{OH}^- \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{Cl}^-$

The formation of the white precipitate of silver chloride showed the presence of chloride ions and hence that a reaction had occurred.

- s) (i) *Why add ethanol to the reaction mixture?* This allowed the aqueous alkali and the halogenoalkane to become miscible and hence it increases the rate of reaction.
- (ii) *Why add nitric acid before adding aqueous silver nitrate?* If the mixture had not been acidified then the silver ions would have reacted with the alkali to form a brown precipitate of silver oxide.
- t) It is a nucleophilic substitution reaction and it is also a hydrolysis reaction.



## SYLLABUS REFERENCE: TOPIC 11.3

Deduction of information about the structural features of a compound from percentage composition data, MS,  $^1\text{H}$  NMR or IR.

## Apparatus &amp; Chemicals

As this Investigation is based on pre-recorded spectra, no apparatus or chemicals are required.

## Notes

*Probable timing - ~90 minutes, though a lot could be done as homework.*

This Investigation comprises two exercises that involve students in interpreting organic spectra, and other analytical data, then making deductions from these. As always with spectra there are far more details that could be drawn out of them and this is something that you may want to do when going through the exercises in class – possibly the best way of “marking” this work. Some of the identifications are fairly straightforward, some others will hopefully provide a worthy challenge for your brighter students.

$$\text{a) Amount of CO}_2 = \text{amount of C} = \frac{3.107}{44.01} = \mathbf{0.07060 \text{ mol}}$$

$$\text{Amount of H}_2\text{O} = \frac{1}{2} \text{ amount of H} = \frac{1.272}{18.02} = \mathbf{0.07059 \text{ mol}}$$

$$\text{Mass of C} = 12.01 \times 0.07060 = 0.8479 \text{ g}$$

$$\text{Mass of H} = 2 \times 1.01 \times 0.07059 = 0.1426 \text{ g}$$

$$\text{Mass of O} = 1.273 - 0.8479 - 0.1426 = 0.2825 \text{ g}$$

$$\text{Amount of O} = \frac{0.2825}{16.00} = \mathbf{0.01766 \text{ mol}}$$

$$\text{Ratio of C:H:O} = 0.07060:0.1412:0.01766 = 3.998:7.995:1$$

Empirical formula of A is  $\text{C}_4\text{H}_8\text{O}$

- b) The highest significant peak is at  $m/z = 72$ , hence the molar mass of the compound is probably  $72 \text{ g mol}^{-1}$ . The molecular formula is therefore the same as the empirical formula;  $\text{C}_4\text{H}_8\text{O}$ .
- c) As they are all isomers they have the same molecular formula and hence all have a molar mass of  $72 \text{ g mol}^{-1}$ . They should therefore all have molecular ion peaks at  $m/z = 72$ , but these are only noticeable for A, B, C, (D?) & G.
- d) This peak is never the largest peak and it is not even present in E and F. The reason for this is that the excess energy from the ionisation process frequently results in the breaking of a covalent bond, causing the molecule to fragment.
- e) i) *Why one greater than the molecular ion peak?* This is caused by the presence of a  $^{13}\text{C}$  atom (which comprises ~1% natural carbon) in the molecule.  
ii) *Why one greater than the molecular ion peak?* This is caused by the loss of a hydrogen atom as part of the fragmentation process
- f) i)  $m/z = 57$ : This corresponds to the loss of a methyl group ( $\text{CH}_3^-$ ).  
ii)  $m/z = 43$ : This could correspond to the loss of an ethyl group ( $\text{C}_2\text{H}_5^-$ ) or an aldehyde group ( $-\text{CHO}$ ).
- g) Yes, all of the mass spectra have peaks at  $m/z=15$  ( $\text{CH}_3^+$ ) and  $m/z=29$  ( $\text{C}_2\text{H}_5^+$  or  $\text{CHO}^+$ ).

- h)  $C_3H_8^+$ .
- i) A saturated  $C_4$  compound would have 10 ( $2 \times 4 + 2$ ) hydrogens. A has only 8 hydrogens (O does not affect the IHD) hence it has an IHD of 1.
- j) Compound A must either have one double bond ( $C=C$  or  $C=O$ ), or one ring in its structure.
- k)  $-OH$ :  $3200-3600\text{ cm}^{-1}$        $>C=O$ :  $1700-1750\text{ cm}^{-1}$

Containing  $-OH$ : D, E, F & G

Containing  $>C=O$ : A, B & C

- l) If  $-OH$  is present the  $>C=O$  group cannot account for the IHD, therefore to account for the IHD a  $>C=C<$  or a ring must be present.
- m) The  $>C=C<$  absorbs at  $1620-1680\text{ cm}^{-1}$ . There are absorptions in this region for B & D implying they contain  $>C=C<$ , but they are absent in E, F & G, hence these compounds must contain ring structures.
- n) The hydrogen in an aldehyde has a very distinctive, high field, peak at  $9.4-10.0\text{ ppm}$  in  $^1H$  and this is present in the spectra of A and B, which are presumably aldehydes. Assuming there is a hydrogen attached to a double bonded carbon of the  $>C=C<$  group then a peak at  $4.5-6.0$  will be present and this is the case in the spectra of D and G.
- o)

Compound	A	B	C	D	E	F	G
Group							
$-OH$				✓	✓	✓	✓
$>CO$	✓	✓	✓				
$-CO-H$	✓	✓					
$>C=C<$				✓			✓

C must be butanone ( $CH_3-CO-C_2H_5$ ) because it contains a carbonyl group but it is not an aldehyde and there is only one possible structure for this.

**Pair 1:** A & B      **Pair 2:** D & G      **Pair 3:** E & F

- p) **Pair 1:** Considering these two aldehydes, A has three different hydrogen environments (other than the  $-CHO$  hydrogen) in a ratio of 3:2:2 whereas B has only two hydrogen environments in a ratio of 6:1. Hence A must be butanal  $\{CH_3CH_2CH_2-CHO\}$  and B methylpropanal  $\{(CH_3)_2CH-CHO\}$ .

**Pair 2:** Considering these two alkenes, D has five different hydrogen environments in a ratio of 3:2:1:1:1 (the peaks between 5.0 and 5.3 can be considered as one (they are actually due to two to different E/Z configurations) and G also has five hydrogen environments in a ratio of 2:2:2:1:1 (in both cases one of the "1"s must be the  $-OH$ ). If the double bond is between the first two carbons in the chain there are two possible isomers ( $CH_2=CH-CH_2-CH_2OH$  &  $CH_2=CH-CH(OH)-CH_3$ , remembering that the  $-OH$  cannot be on the same C as the double bond, otherwise it would rearrange to the more stable carbonyl group) both of which would have five hydrogen environments, the former would have a ratio of 2:1:2:2:1 and the latter 2:1:1:1:3 (going from left to right, though the two  $CH_2=$  hydrogens will not be entirely equivalent owing to different E/Z configurations). If the double bond is between the middle two carbons in the chain there is only one possible structural isomer ( $CH_3-CH=CH-CH_2OH$ , though it could exist as two E/Z isomers) which would have five hydrogen environments with a ratio 3:1:1:2:1. The hydrocarbon chain could be branched and this again would give rise to only one possible structural isomer ( $CH_2=C(CH_3)-CH_2OH$ ) which would only have four hydrogen environments with the ratio being 2:3:2:1. Comparing these possibilities with the spectra then G must be  $CH_2=CH-CH_2-CH_2OH$  (but-1-en-4-ol) and D could be  $CH_2=CH-CH(OH)-CH_3$  or  $CH_3-CH=CH-CH_2OH$ .



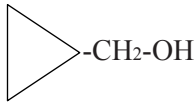
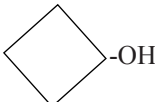
The former is more probable because one of the hydrogens (2.0 ppm) is not directly joined to a double bonded carbon and also the methyl group seems little influenced by the double bond, so D is  $\text{CH}_2=\text{CH}-\text{CH}(\text{OH})-\text{CH}_3$  (but-1-en-3-ol) HL students will also notice that the methyl group is a doublet, split by the  $-\text{CH}(\text{OH})-$  hydrogen.

**Pair 3:** There are three possible cycloalkane alcohols, cyclobutanol ( $\text{C}_4\text{H}_7-\text{OH}$ ), methylcyclopropanol ( $\text{CH}_3-\text{C}_3\text{H}_4-\text{OH}$ ) and cyclopropylmethanol ( $\text{C}_3\text{H}_5-\text{CH}_2-\text{OH}$ ). Cyclobutanol would have 4 different hydrogen environments in a ratio 4:2:1:1, methylcyclopropanol would have 5 different hydrogen environments in a ratio 3:2:1:1:1 and cyclopropylmethanol would also have 4 different hydrogen environments in a ratio 4:2:1:1 (again different E/Z configurations are being ignored). Neither E nor F has a 3:2:1:1:1 split and there is no sign of a methyl group so neither is methylcyclopropanol. Compound F shows the 4:2:1:1 split clearly and only one hydrogen (4.2 ppm) is significantly different to the others (the  $-\text{OH}$ ) and so this is likely to be cyclobutanol. Compound E has three hydrogens that are rather different to the rest (3.5 ppm & 3.3 ppm) and this is what might be expected for methylcyclopropanol (the  $-\text{CH}_2-\text{OH}$ ). The four hydrogens that might be thought to be equivalent in the cyclopropane ring would appear to be split (0.3 ppm & 0.6 ppm) depending on whether they are on the same side as the  $-\text{CH}_2-\text{OH}$ , or on the opposite side.

- r) There are strong absorptions in the  $600-800\text{ cm}^{-1}$  region in the spectra of compounds H to L.
- s) Any fragment containing chlorine would be expected to give two peaks at 2  $m/z$  units apart with the one at the higher value being  $1/3$  the height of the other owing to the presence of  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  in naturally occurring chlorine. In H this can be clearly seen in the 77 & 79 peaks and for L in both the 78 & 80 and the 65 & 67 peaks. When more than one chlorine is present the range of possible masses increases and the ratios become more complex.
- t) H, J and K all have peaks at  $m/z$  values  $>78$  ( $M_r$  of  $\text{C}_3\text{H}_7^{35}\text{Cl}$ ) so they contain more than one Cl, whereas I and L only have peaks below this and so are probably monochlorinated. The greatest  $m/z$  peaks in H and K are all in the region  $\sim 110-120$  ( $\text{C}_3\text{H}_6^{35}\text{Cl}_2$  has  $M_r = 112$ ) so they probably contain two Cl atoms, but probably not three or more as there are no peaks at values  $>120$ . J critically has two very small peaks at  $\sim 146$  so it probably contains three chlorines ( $\text{C}_3\text{H}_5^{35}\text{Cl}_3$  has  $M_r = 146$ ).

There are two isomers of  $\text{C}_3\text{H}_7\text{Cl}$  and, as the NMR spectrum of L is very simple (2 peaks with a 1:6 ratio) it would appear to be 2-chloropropane ( $\text{CH}_3-\text{CHCl}-\text{CH}_3$ ). The spectrum of I shows three peaks in a 2:2:3 ratio and so this would correspond to 1-chloropropane ( $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{Cl}$ ). There are 4 possible isomers of dichloropropane (1,1 2,2, 1,2 & 1,3). Compound H shows that there is only one hydrogen environment so this must be 2,2-dichloropropane ( $\text{CH}_3-\text{CCl}_2-\text{CH}_3$ ). 1,3-dichloropropane ( $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Cl}$ ) has two hydrogen environments (1:2 ratio), whereas 1,1-dichloropropane ( $\text{CHCl}_2-\text{CH}_2-\text{CH}_3$ ) and 1,2-dichloropropane ( $\text{Cl}-\text{CH}_2-\text{CHCl}-\text{CH}_3$ ) would both have 3 different environments with a ratio of 1:2:3. In 1,1-dichloropropane 5 of the 6 hydrogens are in an alkyl type environment so would be expected to give peaks  $\sim 1-2$  ppm, whereas in 1,2-dichloropropane only one is in an alkyl type environment and two are attached to the same carbon as a chlorine and so would absorb in the 3.5-4.4 ppm region. The NMR spectrum of compound K looks more similar to the latter and so it is probably 1,2-dichloropropane. Compound J has just two hydrogen environments with a 4:1 ratio and both of them are hydrogens attached to the same carbon as a chlorine, so this must be 1,2,3-trichloropropane ( $\text{Cl}-\text{CH}_2-\text{CHCl}-\text{CH}_2-\text{Cl}$ ).

- u) The IR spectra in the region  $900$  to  $1500\text{ cm}^{-1}$  differ tremendously, hence this region acts like a “fingerprint” of a particular compound so it can be used to identify a compound by comparing the spectrum obtained with a spectrum from a library of IR spectra.

Letter	Name	Formula
A	Butanal	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CO-H}$
B	Methylpropanal	$\text{CH}_3\text{-CH(CH}_3\text{)-CO-H}$
C	Butanone	$\text{CH}_3\text{-CH}_2\text{-CO-CH}_3$
D	But-1-en-3-ol	$\text{CH}_2\text{=CH-CH(OH)-CH}_3$
E	Cyclopropylmethanol	 -CH <sub>2</sub> -OH
F	Cyclobutanol	 -OH
G	But-1-en-4-ol	$\text{CH}_2\text{=CH-CH}_2\text{-CH}_2\text{OH}$
H	2,2-dichloropropane	$\text{CH}_3\text{-CCl}_2\text{-CH}_3$
I	1-chloropropane	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Cl}$
J	1,2,3-trichloropropane	$\text{Cl-CH}_2\text{-CHCl-CH}_2\text{-Cl}$
K	1,2-dichloropropane	$\text{Cl-CH}_2\text{-CHCl-CH}_3$
L	2-chloropropane	$\text{CH}_3\text{-CHCl-CH}_3$

## SYLLABUS RELEVANCE; TOPIC A3

Experiments could include investigating the decomposition of potassium sodium tartrate with cobalt chloride and the decomposition of hydrogen peroxide with manganese (IV) oxide.

## Apparatus (per group)

- 6 × boiling tubes
- 25 cm<sup>3</sup> measuring cylinder
- 4 × 100 cm<sup>3</sup> conical flask
- 0-110°C thermometer
- Top pan balance reading to 0.001 g (if possible connected to data logging software)

## Apparatus (generally available)

- Water bath at 70°C

## Chemicals required

- 1 mol dm<sup>-3</sup> hydrogen peroxide (100 cm<sup>3</sup> per group)
- Solid manganese(IV) oxide (manganese dioxide, ~5 g per group)
- Dilute hydrochloric acid (~50 cm<sup>3</sup> per group)
- 0.1 mol dm<sup>-3</sup> iron(II) sulfate (~10 cm<sup>3</sup> per group)
- 0.1 mol dm<sup>-3</sup> iron(III) sulfate (~10 cm<sup>3</sup> per group)
- 0.1 mol dm<sup>-3</sup> potassium iodide (~10 cm<sup>3</sup> per group)
- Hexane (~5 cm<sup>3</sup> per group)
- Solid sodium potassium tartrate (~5 g per group)
- Solid cobalt(II) chloride (~1 g per group)

## Notes

*Probable timing--~90 minutes*

This revises many of the basic concepts of catalysts, both heterogeneous and homogeneous – that they speed up reactions, that they are not consumed and that the catalysed reaction has a lower activation energy (and hence is less affected by temperature) than the equivalent uncatalysed reaction. Heterogeneous act by providing an active surface on which the reaction can take place, whereas homogeneous ones are actively involved in changing the reaction mechanism.

Again it provides a wonderful opportunity to do the “pink foam” demonstration as it is basically the same reaction as the first part of the Investigation:

Put a couple of spatulas full of “red lead” into the bottom of a 500 cm<sup>3</sup> conical flask and add a good squirt of detergent and about an equal volume of water, then swirl it around the inside of the flask. Support the flask on a tripod over a sink (for easy cleaning up!), tip in about 25 cm<sup>3</sup> of the 100-Volume hydrogen peroxide and stand back. You should get a pink foam serpent erupting out of the top of the flask. It does work with manganese(IV) oxide, but I prefer the pretty pink produced by the “red lead”.

**Warning:** *This involves 100-volume hydrogen peroxide, which is a very corrosive liquid, blistering the skin easily. Keep the students well back, do not allow them to touch the foam and wear gloves on your hands, especially when cleaning up. Note too that “red lead” (Pb<sub>3</sub>O<sub>4</sub>), like all lead compounds, is quite toxic.*



## Sample results

## Heterogeneous catalysis

Quantity	Room temperature		Heated water bath	
	Initial	Final	Initial	Final
Time; hh mm	12-38	16-05	15-02	16-07
Mass /g	94.21	94.11	98.03	97.66
Temperature /°C	21.5	22.5	69.0	75.0

3) &amp; 5)

Temp. /°C	Room temp.	Reduced temp.
	22.0	12.5
Time /s	System mass /g	
0	100.13	99.08
20	100.03	99.02
40	99.91	98.92
60	99.78	98.88
80	99.70	98.77
100	99.65	98.74
120	99.63	98.69
140	99.62	98.65
160	99.62	98.61
180	99.61	98.60

4)

Mass of weighing bottle & MnO <sub>2</sub>	5.77 g
Mass of weighing bottle after emptying	5.28 g
Mass of MnO <sub>2</sub> added	0.49 g
Mass of filter paper	1.07 g
Mass of filter paper & MnO <sub>2</sub> after drying	1.49 g
Mass of MnO <sub>2</sub> recovered	0.42 g

## Relevant qualitative observations

For the uncatalysed reaction there was little, if any sign of gas being evolved at either temperature, whereas for the catalysed reaction there was obvious effervescence and the temperature of the system increased substantially. The manganese(IV) oxide powder was black and very finely divided. Even after rinsing some remained in the reaction vessel and after filtering it was noticed that some had also passed through the filter paper.

### Homogeneous catalysis

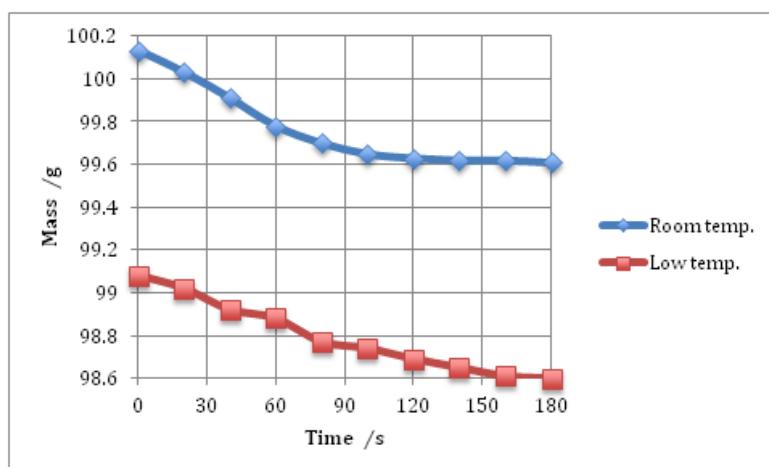
- 6) The very pale green solution turns to a yellow-orange colour and when sodium hydroxide is added a brown precipitate forms.
- 7) The solution becomes a darker shade of brown and the upper layer of hexane becomes a pink-purple colour.
- 8) The colourless reaction mixture very slowly becomes a yellow colour and the upper layer of hexane becomes a pink-purple colour.
- 9) The same colour change as in 8) occurs but much more rapidly and then a black precipitate forms.

### A more complex example of homogeneous catalysis

- 10) The hydrogen peroxide remains colourless as the white tartrate is dissolved in it. When the solution is heated on its own, it starts to bubble near the boiling point of the solution, making it a little difficult to distinguish gas formation from boiling. When the dark purple cobalt(II) chloride dissolves in the mixture it gives a pink solution. Gentle warming of the solution (still comfortable to hold, so  $\sim 50^\circ\text{C}$ ?) causes the colour to change through grey to a bright green colour. The solution then starts to effervesce very vigorously and it becomes very hot. Eventually the evolution of gas ceases leaving a green solution. This then, over about half a minute changes colour back to the original pink.

## Data Analysis

### Heterogeneous catalysis



System	Temperature	Rate /g s <sup>-1</sup>
H <sub>2</sub> O <sub>2</sub> at room temperature	22	$8.05 \times 10^{-6}$
H <sub>2</sub> O <sub>2</sub> in water bath	72	$9.49 \times 10^{-5}$
H <sub>2</sub> O <sub>2</sub> + MnO <sub>2</sub> at room temperature	22	$6.37 \times 10^{-3}$
H <sub>2</sub> O <sub>2</sub> + MnO <sub>2</sub> cooled	12.5	$4.00 \times 10^{-3}$

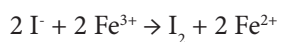
- b) The manganese(IV) oxide increased the rate of reaction tremendously.
- c) For the uncatalysed reaction a  $50^\circ\text{C}$  rise in temperature increased the rate by a factor of 11.8, corresponding to a factor of 0.236 per degree. For the catalysed reaction a  $9.5^\circ\text{C}$  rise in temperature increased the rate by a factor of 1.59, corresponding to a factor of 0.168 per degree. As the greater the activation energy the greater the effect of temperature on rate, this indicates that the activation energy is greater for the uncatalysed reaction. These data correspond to activation energies of  $42 \text{ kJ mol}^{-1}$  for the uncatalysed reaction and  $34 \text{ kJ mol}^{-1}$  for the catalysed reaction.
- d) 86% of the manganese(IV) oxide catalyst was recovered from the reaction mixture.

**Homogeneous catalysis**

- e) The hydrogen peroxide has oxidised the iron(II) to iron(III):



- f) The iron(III) has oxidised the iodide ions to iodine:



- g) The hydrogen peroxide has slowly oxidised the iodide ions to iodine:



- h) The iron(II) ions increased the rate of reaction between the hydrogen peroxide and the iodide ions. This occurred because the sum of the reactions in the first two reactions is the same as the third reaction, but the activation energy, and hence the rate of reaction, of the reactions involving iron ions is lower than the direct reaction. The black precipitate occurs because all of the iodide ions have been oxidised to iodine, so the iodine cannot remain dissolved as the tri-iodide ion ( $\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$ ).

**A more complex example of homogeneous catalysis**

- i) The cobalt(II) ions increased the rate of reaction between the hydrogen peroxide and the tartrate ions.
- j) The colour changes probably indicated that the oxidation state of cobalt was altering during the course of the reaction.
- k) The colour finally returned to its original pink colour showing that the cobalt(II) ions have not undergone any permanent change.
- l) The colour change to green occurred before any gas was evolved which seems to indicate that they are not products of the same reaction. Similarly the evolution of gas stops a significant time before the colour returns to its original pink.



## SYLLABUS RELEVANCE: TOPIC B2

Experiments could involve identification of amino acid mixtures by paper chromatography.

## Apparatus (per group)

- 3 × 250 cm<sup>3</sup> beakers
- 3 × thin layer chromatography plates (approx 5 cm x 10 cm)
- Pencil

## Apparatus (generally available)

- Melting point tubes
- Clear plastic kitchen wrap
- Oven at ~120°C

## Chemicals required

- 1% aqueous solutions of 4 amino acids (~10 cm<sup>3</sup> of each)  
(Arginine, glycine, leucine and valine work well, but probably others do too)

A mixture of 2 or 3 of these (~10 cm<sup>3</sup>)

- Eluent solutions (~10 cm<sup>3</sup> per group of each)
  - Neutral – a 5:1 (by volume) mixture of butan-1-ol and water
  - Acid – the neutral mixture with 10% glacial ethanoic acid added
  - Alkali – the neutral mixture with 10% saturated aqueous ammonia added
- Ninhydrin spray (containing ~10 cm<sup>3</sup> of a 0.02 mol dm<sup>-3</sup> solution in propanone)

**Warning:** Ninhydrin is highly toxic and can be absorbed through the respiratory tract, skin and eyes. Students need to wear gloves and goggles as well as working in a fume cupboard so as to avoid all contact. Seek immediate medical advice if exposure occurs.



## Notes

Probable timing – ~90 minutes

This provides students with a chance to carry out separation of an amino acid mix, such as result from the hydrolysis of a protein, in practice. It also gives students an opportunity to try to correlate the  $R_f$  values in the various solvents with the molecular structure of the amino acids.

## Sample results

Distance travelled from the starting line in cm:

Sample	Acid	Neutral	Alkaline
Eluent front	7.5	7.6	7.8
Arginine	-0.1 to +0.3	-0.3 to +0.4	0.1 to 0.8
Glutamic acid	-0.2 to +0.2	-0.2 to + 1.3	1.3 to 3.9
Glycine	-0.1 to +0.5	0.1 to 1.1	0.7 to 2.1
Leucine	1.7 to 2.3	1.6 to 3.0	3.6 to 4.3
Valine	0.9 to 1.6	1.4 to 2.2	2.5 to 3.5
Mixture	-0.2 to +0.3 0.9 to 1.5	-0.2 to +0.4 <0.5 to 0.8 1.5 to 2.3	0.0 to 0.7 1.3 to >2.5 2.5 to 3.6

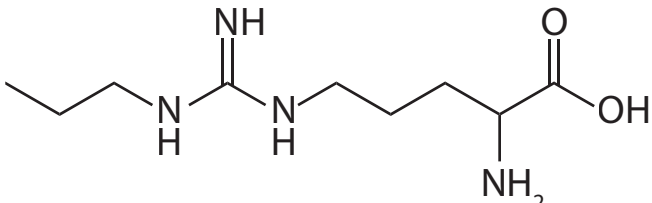
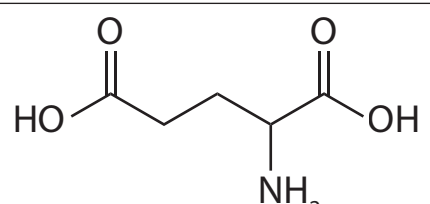
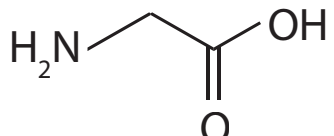
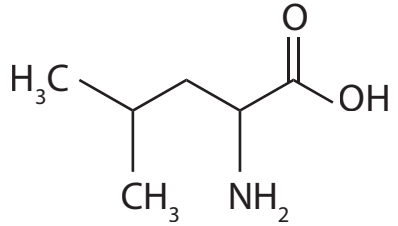
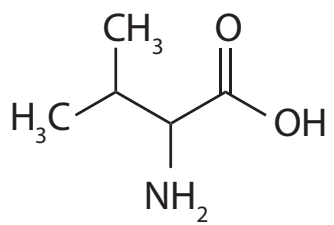
## Data Analysis

## Sample answers

a) Calculate the  $R_f$  value for each spot:

Sample	Acid	Neutral	Alkaline
Arginine	-0.01 to +0.04	-0.04 to +0.05	0.01 to 0.10
Glutamic acid	-0.03 to +0.03	-0.03 to 0.17	0.17 to 0.50
Glycine	-0.01 to +0.06	0.01 to 0.14	0.09 to 0.27
Leucine	0.23 to 0.31	0.21 to 0.39	0.46 to 0.55
Valine	0.12 to 0.22	0.18 to 0.29	0.32 to 0.45
Mixture	-0.03 to +0.04	-0.03 to +0.05	0 to 0.09
	0.12 to 0.20	0.07 to 0.11	0.17 to 0.32
		0.20 to 0.30	0.32 to 0.46

b)

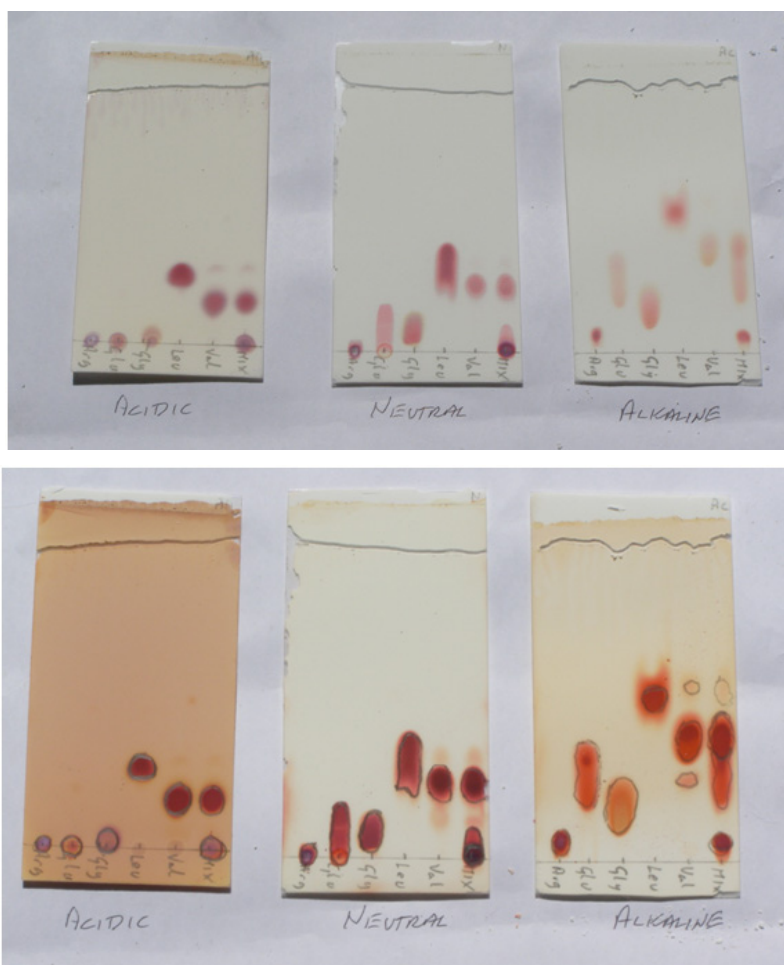
Arginine	
Glutamic acid	
Glycine	
Leucine	
Valine	

As can be seen from the structures above Arginine has lots of polar groups and hence can bond quite tightly to the polar stationary phase, so it has a very low  $R_f$  in all solvents. This is also true for glutamic acid in acidic and neutral media, but the acid groups cause it to be quite soluble in the alkaline eluent increasing the  $R_f$  significantly. Glycine is also quite polar, but appears to be slightly more mobile in neutral and alkaline solvents. Leucine and valine both have quite long hydrocarbon chains reducing their polarity and hence bonding to the solid phase. Both have reasonably large  $R_f$  values in all the solvents with leucine, the less polar of the two, always being slightly greater.

- c) As can be seen from the shading in a), it appears that the mixture comprised arginine, glutamic acid and valine, with very little doubt in the assignments.

## Evaluation

- d) The practical was actually quite successful at identifying the components of the mixture. That being said the spots on the chromatogram were rather spread out leading to a degree of uncertainty in the actual  $R_f$  values. This might be improved by using a smaller dropper so that the initial spots were not so diffuse. There were hardly any  $R_f$  values over 0.5 meaning that the spots were all compressed into the lower regions of the chromatogram, so maybe some experimentation with different media and eluents might result in more efficient separation. Using longer plates, and consequently waiting longer for them to elute, would also give clearer separation between the amino acids.



## SYLLABUS RELEVANCE; TOPIC C1

The energy density of different fuels could be investigated experimentally.

## Apparatus (per group)

- Copper calorimeter
- 100 cm<sup>3</sup> measuring cylinder
- 0–110°C thermometer

## Apparatus (generally available)

- Aluminium foil
- Balance capable of weighing to 0.01 g

## Chemicals required

Fuels in containers where they can be easily combusted, such as metal dishes with solid fuels (such as firelighters), spirit lamps filled with safe liquid fuels (such as ethanol and paraffin) and canister-fuelled gas burners.

## Notes

*Probable timing—~90 minutes*

This provides students with a chance to measure the enthalpy of combustion of various fuels and to use these data to calculate various quantities that they need to be familiar with in this Option.

## Sample Data

Fuel	Mass ± 0.005 g		Temperature ± 0.5 °C	
	Initial	Final	Initial	Final
Butane torch	244.70	244.16	21.0	47.0
Methylated spirit	225.08	224.42	22.0	44.0
Kerosene	216.55	216.08	22.0	45.5
Firelighter	46.42	45.15	22.0	47.5

Volume of water taken = 100 ± 0.5 cm<sup>3</sup>

## Qualitative observations

The butane torch gave quite a fierce, but almost colourless flame, that heated up the water very quickly. The flame from the meths burner was much less fierce, but it was quite clean, producing little smoke. The flame from the kerosene was yellow and quite smoky and the flame from the firelighter was even smokier and deposited more soot on the calorimeter.

## Data Analysis

a), b) &amp; c)

Fuel	Temperature change $\pm 1\text{ }^{\circ}\text{C}$	Heat evolved /kJ	Mass change $\pm 0.01\text{ g}$	Specific energy $\text{kJ g}^{-1}$	Density $\text{g dm}^{-3}$	Energy density $\text{MJ dm}^{-3}$
Butane torch	26.0	10.87	0.54	20.13	2.5 (g) 600 (l)	0.0500 12.1
Meths	22.0	9.20	0.66	13.93	790	11.0
Kerosene	23.5	9.82	0.47	20.90	810	16.9
Firelighter	25.5	10.66	1.27	8.39	640	5.37

$$\text{Approximate uncertainty of temperature change} = \frac{1}{25} \times 100 = \pm 4\%$$

$$\text{Approximate uncertainty of mass change} = \frac{0.01}{0.60} \times 100 = \pm 1.5\%$$

$$\text{Approximate uncertainty of water volume} = \frac{0.5}{100} \times 100 = \pm 0.5\%$$

$$\text{Approximate overall uncertainty} = \pm 6\%$$

d)

Fuel	Heat evolved /kJ	Mass change /g	Molar mass /g mol <sup>-1</sup>	Amount used /mol	$\Delta H_{\text{comb}}$ /kJ mol <sup>-1</sup>
Butane	10.87	0.54	58.14	0.00929	-1170
Ethanol (Meths)	9.20	0.66	46.08	0.0143	-642

## Evaluation

e)

Fuel	Experimental $\Delta H_{\text{comb}}$ /kJ mol <sup>-1</sup>	Literature value /kJ mol <sup>-1</sup>	Efficiency %
Butane	-1170	-2878	41
Ethanol (Meths)	-642	-1367	47

- f) The accuracy of the determination for those fuels for which enthalpies of combustion can be calculated is very poor, both below 50%. It is probable that the data for the other fuels was no better and probably worse because of less complete combustion. The precision of the determinations ( $\pm 6\%$ ) was not good, but was more than adequate taking into account the magnitude of the systematic errors.

In all cases one of the major sources of error would be heat loss from the uninsulated calorimeter. In addition the heat capacity of this was not taken into account. Incomplete combustion is also a probable source of error, especially as for both kerosene and the firelighter copious black smoke indicated that the combustion was far from complete. The experimental uncertainties appear to be an order of magnitude smaller than these systematic errors.

- g) Drawing the hot combustion gases through a heat exchange coil in an insulated calorimeter, as is found in a flame calorimeter, would reduce heat losses and using an electrical heater to calibrate this would reduce these even further as well as taking into account the heat capacity of the calorimeter. This would not affect the incomplete combustion, which could only be addressed by better mixing of the fuel with air, or even better oxygen. Carrying out the combustion in a bomb calorimeter with excess oxygen would probably be the best way to determine more accurate values.
- h) For a transport application that carries its own fuel, the energy density will be important because if this is too low the load will be bulky, and probably heavy, and large fuel tanks will be required. A high specific energy is also desirable for these applications to minimise the mass of the fuel itself.

Other factors that need to be taken into account for all applications are the availability and cost of the fuel. Other things that must be considered are rate of energy production (power) and safety and pollution issues, including the long-term consideration as to whether the source of the fuel is finite or renewable.



## SYLLABUS RELEVANCE: TOPIC D2

Experiments could include the synthesis of aspirin.

**Apparatus (per group)**

- 100 cm<sup>3</sup> Quickfit flask
- Condenser for flask
- 10 cm<sup>3</sup> measuring cylinder
- 25 cm<sup>3</sup> measuring cylinder
- 250 cm<sup>3</sup> beaker
- Suction filtration apparatus (Buchner funnel, flask & pump)
- Melting point apparatus
- 2 × boiling tubes

**Apparatus (generally available)**

- Top pan balance
- Filter paper for Buchner funnels
- Melting point tubes

**Chemicals required**

- Ethanoic (acetic) anhydride (~20 cm<sup>3</sup> per student)
- Concentrated phosphoric acid (~1 cm<sup>3</sup> per student)
- 2-hydroxybenzoic (salicylic) acid (~10 g per student)
- 2 mol dm<sup>-3</sup> aqueous sodium hydroxide (~5 cm<sup>3</sup> per student)
- 0.1 mol dm<sup>-3</sup> aqueous iron(III) chloride (~1 cm<sup>3</sup> per student)
- 50% aqueous ethanoic (acetic) acid (~40 cm<sup>3</sup> per student)

**Notes**

*Probable timing—~90 minutes and ~30 minutes in a later lesson to take measurements of the dry purified product.*

This provides students with a chance to produce a crystalline product – something that is always very satisfying! It also provides them with practice in the skills of recrystallization and the taking of melting points.

There are often problems getting the crude product to separate as a solid and having a few seed crystals of pure product available to seed this can be very helpful.

Note that the Investigation will work without ethanoic anhydride (difficult to obtain in some countries) but the yields are much lower. Its major function is to react with the water and hence shift the equilibrium (Le Chatelier's Principle), so increasing the amount of acid and increasing the heating time would compensate. (Maybe there is an Extended Essay in that for someone?)

The expected melting point of the purified product is 136°C.

### (Sample) Data Collection

Mass of salicylic acid	= 10.00 g
Mass of crude product	= 14.00 g
Mass of recrystallised product	= 8.75 g
Melting point range of the impure product	= 116 to 120 °C
Melting point range of the purified product	= 122 to 124 °C

### Relevant qualitative observations

Initially the white solid 2-hydroxybenzoic acid did not dissolve in the colourless ethanoic acid and acidification of the mixture cause more acid to separate. As the mixture was heated and the reaction proceeded, the solid dissolved to give a colourless liquid. Initially when the mixture was poured into the water an oil separated out, but cooling and scratching the bottom of the container caused a white solid to separate.

Warming with water

*The white solid was almost insoluble in water.*

Warming with aqueous sodium hydroxide

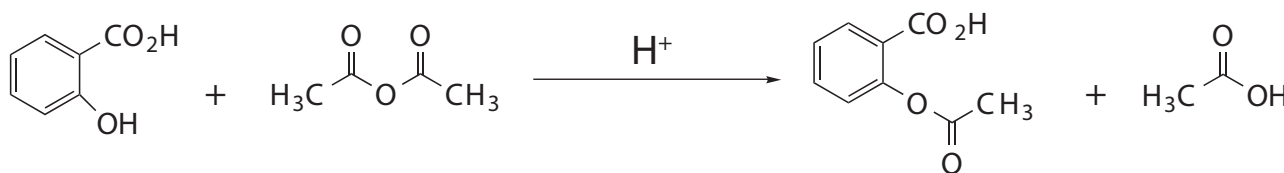
*The white powder dissolved readily to produce a colourless solution.*

Adding aqueous iron(III) chloride

*The colourless solution turned an intense purple colour when the pale yellow iron(III) chloride was added.*

### (Sample) Data Analysis

a)



b) Molar mass of 2-hydroxybenzoic acid = 138.13 g mol<sup>-1</sup>

Molar mass of acetylsalicylic acid = 180.16 g mol<sup>-1</sup>

Amount of 2-hydroxybenzoic acid =  $\frac{10.00}{138.13} = 0.0724 \text{ mol}$

Theoretical mass of acetylsalicylic acid =  $0.0724 \times 180.16 = 13.0 \text{ g}$

Percentage yield of crude product =  $\frac{14.0}{13.0} \times 100 = 108\%$

Percentage yield of recrystallised product =  $\frac{8.75}{13.0} \times 100 = 67.1\%$

- c) The melting point range of the crude material is at a lower temperature and is broader than that of the recrystallised material. This is what is expected as impurities always lower the melting point of materials and because they are not homogeneous the range is greater. In addition the crude product was not well dried, so some solvent would have remained and the iron(III) chloride test indicated unreacted salicylic acid as an impurity.
- d) The substance being purified is significantly more soluble in the hot recrystallization solvent than it is in the cold solvent. Some impurities may be less soluble in the solvent and hence these will not dissolve in the warm solvent and can be removed either by decanting or filtration. Other impurities will be more soluble and hence will remain in solution after the solid product recrystallises.
- e) The solubility test showed that, because it is an acid, acetylsalicylic acid is much more soluble in an alkali than it is in water. This property is made use of in soluble aspirin, the usual formulation of which comprises the calcium salt of acetylsalicylic acid.
- f) The crude product gave a strong purple colour when iron(III) chloride was added, indicating the presence of significant quantities of unreacted 2-hydroxybenzoic acid in the crude product because 2-hydroxybenzoic acid, unlike acetylsalicylic acid, is a phenol and forms a coloured complex ion with iron(III) ions.
- g) The yield of crude product is greater than 100% indicating that the solid was still quite wet. The yield of purified product is reasonable, though from a commercial point of view the loss of 33% would be significant. The high yield of crude product implies that significant loss of product probably occurred at the recrystallisation stage, remaining dissolved in the solvent filtered off. It is also likely that the acetylation reaction was not complete giving rise to some loss of crude product. There was also some minor loss of solid in the filter funnel and filter paper.

## Evaluation

- h) The sample of the crude product retained for melting point determination should have been better dried before determining its melting point. The yield may have been improved if less solvent had been used for recrystallisation, but this would probably have been at the expense of purity, similarly with regard to using less liquid for the initial precipitation of the solid product. Increasing the heating time would probably have also resulted in a slightly increased yield.
- i) i. Spectrum A is acetylsalicylic acid and Spectrum B is 2-hydroxybenzoic acid. The major difference is the presence of a second distinct carbonyl stretch in the acetylsalicylic acid ( $1700$  &  $1750\text{ cm}^{-1}$ ) and the broader and more intense -O-H absorption ( $3000 - 3400\text{ cm}^{-1}$ ) in the 2-hydroxybenzoic acid.
- ii. Both spectra clearly show carbonyl ( $>C=O$ ) absorptions at  $1700-1750\text{ cm}^{-1}$ , as well as C-H absorptions at  $2850-3090\text{ cm}^{-1}$ .
- iii. 2-hydroxybenzoic acid has a strong absorption at  $2930\text{ cm}^{-1}$ , a frequency at which acetylsalicylic acid has a much lower absorption, so this would probably be the best choice. The O-H absorption at  $\sim 3250\text{ cm}^{-1}$  would also work quite well.